Electron-Rich, Bulky Ruthenium PNP-Type Complexes. Acceptorless Catalytic Alcohol Dehydrogenation

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Reaction of the electron-rich, bulky tridentate PNP ligand (2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine) with $Ru(PPh_3)_3Cl_2$ at 65 °C resulted in formation of a solution containing the dinitrogen monomeric Ru(II) complex **1a** and the N_2-bridged dinuclear Ru(II) complex **1b**, which can be interconverted. Passing argon through the solution results in formation of pure **1b**. The Ru(II) hydride dinitrogen complex **2** was obtained by the reaction of complex **1b** with 2 equiv of $NaBEt_3H$. Complex **1b** reacted with 4 equiv of $AgOCOCF_3$ to yield $[Ru(PNP)(CF_3COO)_2]$, **3**. The Ru(II) carbonyl hydride complex **4** was obtained by the reaction of PNP and $Ru_2(OAc)_4$ in methanol as a result of O−H activation and decarbonylation of methanol. Complexes **1b**, **2**, and **4** were structurally characterized by X-ray crystallography. Complexes **1b** and **2** catalyze the dehydrogenation of secondary alcohols to the corresponding ketones with good yields and high selectivity accompanied with the evolution of dihydrogen in a homogeneous system without a need for a hydrogen acceptor. The presumed intermediate Ru dihydride complex is generated in situ by reaction **1b** or **2** with a base (1 equiv for each Ru−Cl bond), and the reaction can proceed in the absence of excess base or acid.

Introduction

Transition metal complexes of bulky, electron-rich "pincer" ligands have found important applications in synthesis, bond activation, and catalysis.[1] The bulky, tridentate ligand can stabilize coordinatively unsaturated complexes, and when this ligand bears strong σ-donating groups, reactive unsaturated, electron-rich complexes can be obtained. While the neutral nitrogen−phosphorus tridentate ligand of the Ph-PNP type, in which the central pyridine-based ring donor contains diphenylphosphine substituents in the *ortho* positions, was already reported in 1971,[2] and several transition metal complexes (Rh, Ir, Pd, Pt, and Ru) based on it have been reported,[3−6] more electron-rich complexes of the PNP type containing alkyl substituents on phosphorus are very rare. Following our interest in the chemistry of electron-rich tridentate PCP,[7] PCN,[8] and PCO[9] systems, we synthesized the highly electron-donating t-Bu-PNP ligand (2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine) bearing *tert*-butyl-substituted phosphines[10] and reported its rhodium and iridium complexes in which the Ir−PNP system performed interesting vinylic C−H bond activation[10] and selective *ortho* C−H activation of haloarenes.[11] Hartwig reported that a palladium t-Bu-PNP system effectively catalyzed the addition of amines to acrylic acid derivatives.[12]

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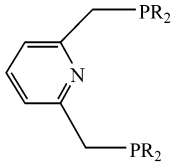
Burger[13] reported a square-planar iridium(I) complex with a bulky pyridine-diimine (N,N,N) ligand, which exhibited thermal intermolecular C−H bond activation.

Transition metal complexes have been widely investigated as catalysts for hydrogen-transfer reactions of alcohols to form the corresponding ketones. A typical characteristic of these reactions is the need for a hydrogen acceptor, such as another ketone, olefin, or halocarbon compound. Homogeneous systems capable of catalyzing dehydrogenation of alcohols without a hydrogen acceptor are rare. Rh(III)-$SnCl_2$/HCl,[14] Rh-$(OAc)_4$/PR_3,[15] and Ru $(OCOCF_3)_2(CO)(PR_3)_2$/CF_3COOH[16] catalyze the dehydrogenation of alcohols to the corresponding ketones without an external hydrogen acceptor, but they require an acid as a hydride ion acceptor. Lu et al.[17] reported that $IrH_5(i\text{-}Pr_3P)_2$ catalyzed dehydrogenation of alcohols in hexamethyldisiloxane solution, the maximum catalytic turnover number being 150. Saito et al.[18] reported that $RhCl(PPh_3)_3$ catalyzed the dehydrogenation of 2-propanol to acetone in the presence of excess triethylamine with the highest turnover number being 10. Photochemical catalytic dehydrogenation of alcohols was reported by Cole-Hamilton.[19] Here we report on t-Bu-PNP ruthenium complexes that catalyze the dehydrogenation of secondary alcohols to ketones in the absence of any hydrogen acceptor, resulting in very good yields and turnover numbers and exhibit excellent selectivity.

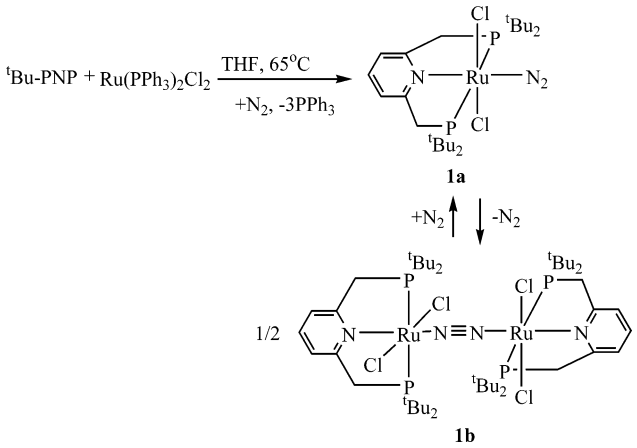


(Ph-PNP, R = Ph; t-Bu-PNP, R = t-Bu)

Results and Discussion

Synthesis and Characterization of $[(PNP)RuCl_2]_2$-(μ-N_2), 1b. Our attempts to synthesize ruthenium complexes bearing the t-Bu-PNP ligand (2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine) by alkene displacement from the Ru(II) complex $(NBD)RuCl_2$ (NBD = 2,5-norbornadiene) or from the Ru(0) complex Ru(COD)-(COT) (COD = 1,5-cyclooctadiene, COT = cyclooctatriene) were not successful. However, it was possible to prepare Ru(II) complexes by PPh_3 displacement. Thus, upon heating a THF solution of $Ru(PPh_3)_3Cl_2$ with 1 equiv of the t-Bu-PNP ligand at 65 °C for 3 h under a nitrogen atmosphere, quantitative conversion took place, and $^{31}P\{^1H\}$ NMR of the THF solution exhibited two

Scheme 1



singlet peaks at 68.1 and 65.0 ppm in a ratio of 8:100, in addition to a singlet corresponding to free PPh_3. The singlet peaks indicate that the two phosphorus atoms of the PNP complexes are equivalent and that the complex is symmetric. The triphenylphosphine ligand is not coordinated to the ruthenium center, in contrast to the reported Ph-PNP-Ru(II) dichloride complex[3d] in which triphenylphosphine is coordinated to Ru (*trans* to the pyridine nitrogen), probably because of the steric bulk of the four *tert*-butyl groups of the PNP ligand. The major product was identified as the dinitrogen-bridged dimer complex **1b** (Scheme 1). It appears to exist in equilibrium with the monomer **1a**, in a ratio that depends on the concentration of the complex and the pressure of N_2. Thus, bubbling argon through the toluene-d_8 solution containing **1a** and **1b** (8:100, respectively) resulted in almost exclusive formation of the dimer **1b**. On the other hand pure **1a** could not be obtained by bubbling N_2 through the same toluene-d_8 solution, resulting in a ratio **1a**:**1b** = 10:100. Similar dimer−monomer equilibria were reported for various dinitrogen complexes.[20,21]

Orange prismatic crystals of **1b** suitable for X-ray analysis were grown from a benzene−pentane solution at room temperature. Only **1b** crystallized under these conditions. The crystal structure of **1b** (Figure 1) displays a distorted octahedral geometry around the metal center. The dinitrogen molecule is bound to the ruthenium center *trans* to the nitrogen atom of the PNP ligand and is bridging between the two square-planar PNP-Ru units, which are twisted around the RuNNRu axis with a dihedral angle of 86.1°, which can be compared with the reported complex of (μ-N_2)[$RuCl_2$-(NN′N)]$_2$[5d] (NN′N = 2,6-[bis(dimethylamino)methyl]-pyridine) (89.4°). Both PNP ligands are coordinated meridionally, resulting in *trans*-positioning of the chloride ligands. Moreover, the Ru1−N2−N3−Ru2 bonding is almost linear. The bridging N2−N3 distance of 1.119(4) Å is normal, similar to the two reported Ru dinitrogen complexes,[5d,22] and slightly longer than that of free N_2 (1.098 Å).

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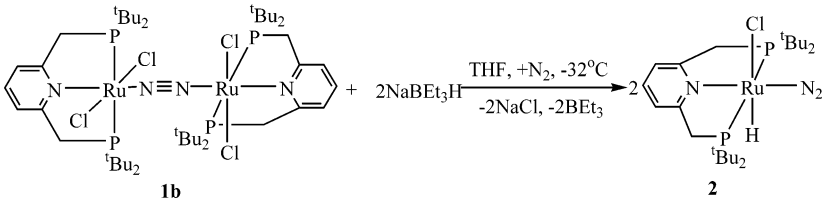
Scheme 2



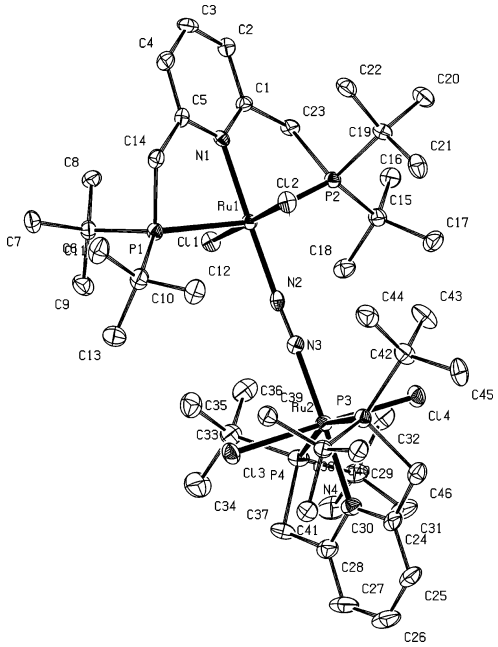


Figure 1. ORETP diagram of a molecule of complex **1b** with the thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 1b

Ru1−N2	1.965(4)	Ru2−N3	1.964(4)
Ru1−N1	2.069(3)	Ru2−N4	2.063(3)
Ru1−P1	2.437(1)	Ru2−P3	2.404(1)
Ru1−P2	2.416(1)	Ru2−P4	2.431(1)
Ru1−Cl2	2.407(2)	Ru2−Cl3	2.423(1)
Ru1−Cl1	2.420(1)	Ru2−Cl4	2.410(1)
N2−N3	1.119(4)		
N1−Ru1−N2	178.5(1)	N3−Ru2−N4	177.4(1)
N1−Ru1−P2	80.7(1)	N4−Ru2−P3	81.7(1)
P1−Ru1−P2	160.83(4)	P4−Ru2−N4	80.4(1)
N1−Ru1−Cl2	89.7(1)	P3−Ru2−P4	161.9(4)
N1−Ru1−Cl1	90.1(1)	N4−Ru2−Cl3	88.8(1)
Cl2−Ru1−Cl1	179.67(4)	N6−Ru2−Cl4	89.9(1)
P1−Ru1−N1	80.2(1)	Cl3−Ru2−Cl4	178.03(4)
N2−N3−Ru2	177.1(3)	N3−N2−Ru1	176.7(3)

Reaction of 1b with $NaBEt_3H$. Formation of the Ruthenium Hydrido Dinitrogen Complex (PNP)-Ru(H)Cl(N_2), 2. Reaction of complex **1b** with 2 equiv of $NaBEt_3H$ in THF at −32 °C resulted in formation of complex **2** in 75% yield (Scheme 2). The presence of the hydride coordinated to the Ru(II) center is confirmed by the ^{1}H NMR spectrum, which indicates a triplet peak at −14.59 ppm with J_{PH} = 19.3 Hz. The IR spectrum exhibits one absorption band at 1910 cm^{-1} for the Ru−H and another absorption band at 2111 cm^{-1}, which suggests the presence of a dinitrogen molecule coordinated to the Ru center. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 86.8 ppm, indicating that the two phosphorus atoms of the PNP ligand are equivalent. The

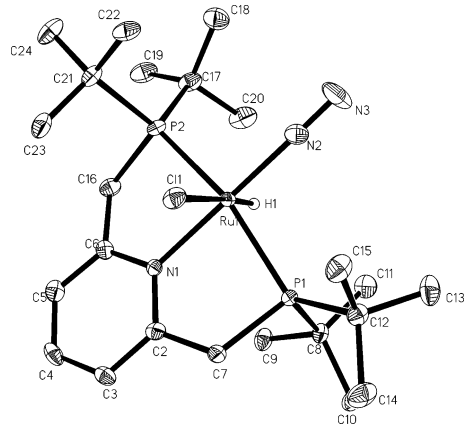


Figure 2. ORETP diagram of a molecule of complex **2** with the thermal ellipsoids at the 50% probability level. Hydrogen atoms except for the hydride ligand are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 2

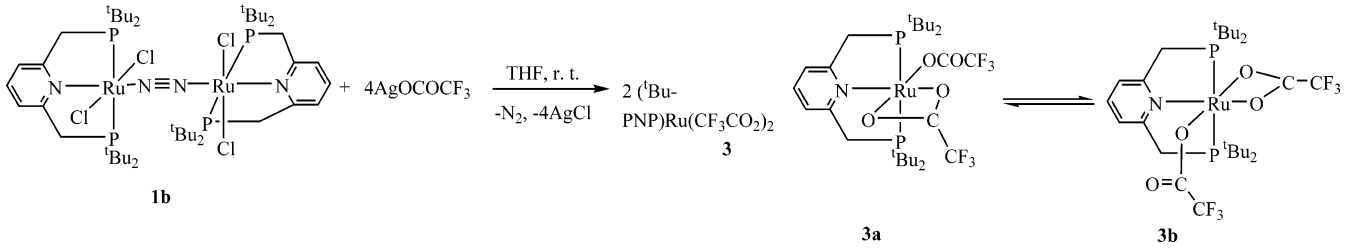
Ru1−N2	1.925(3)	Ru1−N1	2.087(2)
Ru1−P2	2.344(1)	Ru1−Cl1	2.588(1)
Ru1−P1	2.337(1)	Ru1−H1	1.59(3)
N2−N3	1.107(4)		
N1−Ru1−N2	179.2(1)	P1−Ru1−N1	81.6(1)
N1−Ru1−P2	83.1(1)	Cl1−Ru1−H1	176.6(11)
N1−Ru1−Cl1	86.4(1)	N3−N2−Ru1	179.2(3)
N1−Ru1−H1	90.5(11)		

^{1}H NMR exhibits two triplet peaks at 1.25 and 1.64 ppm for the *tert*-butyl protons and two groups of double triplet peaks at 2.90 and 3.87 ppm for the methylene protons, indicating lack of a symmetry plane involving the P, N, P atoms. Complex **2** is soluble in common solvents and slightly soluble in pentane.

Yellow prismatic crystals of **2** suitable for X-ray analysis were obtained by slow diffusion of pentane into a THF solution of complex **2**. The crystal structure of **2** (Figure 2) shows that the ruthenium center adopts a distorted octahedral coordination geometry including the PNP, hydride, dinitrogen, and chloride ligands. The dinitrogen molecule is bound to the Ru(II) center in a η^1 mode and is located *trans* to the pyridine nitrogen, while the hydride is *trans* to the chloride ligand. Because of the meridional coordination geometry of the PNP framework and the lack of a plane of symmetry involving the P, N, P atoms, the protons of the four *tert*-butyl and two methylene groups are inequivalent. The N−N bond distance of the dinitrogen ligand of **2** (1.107(4) Å) is slightly shorter than that observed for complex **1** (1.119(4) Å) and that of the reported complex [(η^1-N_2)RuH(2,6-(CH_2P-t-Bu_2)$_2$$C_6H_3$)] (1.117(5) Å).[15b]

Synthesis and Characterization of (PNP)Ru-($OCOCF_3$)$_2$, 3. Reaction of complex **1b** with 4 equiv of $AgOCOCF_3$ in THF resulted in formation of the yellow

Scheme 3



complex **3** in good yield (90%) (Scheme 3). The IR spectrum of **3** exhibits an intense absorption at 1691 cm^{-1} assignable to the coordinated carboxylate group. $^{31}P\{^1H\}$ NMR of **3** shows a singlet peak at 68.8 ppm. The ^1H NMR at room temperature exhibits the *tert*-butyl groups as a broad singlet at 1.05 ppm with an integration corresponding to 36 protons and the methylene groups as a broad singlet at 3.51 ppm with an integration of four protons, suggesting fluxional behavior of **3** in solution (Scheme 3). Upon cooling to 203 K, ^1H NMR measurements of complex **3** in toluene-d_8 exhibit the PNP ligand as two doublet peaks at 3.47 and 2.77 ppm with $^1J_{HH} = 16$ Hz for two inequivalent sets of PCH_2 protons, while the *tert*-butyl protons give rise to a triplet with $^3J_{PH} = 8$ Hz and three singlets, indicating that the coordination plane defined by the PNP and Ru(II) center is asymmetric (the three singlets probably a result of hindered rotation). Moreover, the ^{19}F NMR spectrum of **3** exhibits two peaks at −75.65 and −75.67 ppm at 203 K, corresponding to bidentate and monodentate coordination modes of the two trifluoroacetate anions, respectively (Scheme 3). The four methyl signals in the ^1H NMR spectra at 203 K give rise to two broad singlet peaks when warmed to 243 K, while the two doublet signals of the methylene group at 203 K become broad and form two broad singlets. At 263 K, the ^1H NMR spectrum of **3** exhibits one very broad peak at 1.12 ppm for the *tert*-butyl protons and one broad signal at 3.30 ppm for the methylene protons. Upon raising the temperature, the two singlet peaks of the *tert*-butyl and methylene groups become sharper, and at 333 K, one triplet is observed with $J_{PH} = 6$ Hz, corresponding to the *tert*-butyl groups with 36 protons. Due to decomposition of the complex above 343 K in toluene-d_8, we could not observe full coalescence of the methylene protons (Figure 3). The ^{19}F NMR of complex **3** exhibits one singlet above 263 K. The variable-temperature $^{31}P\{^1H\}$ NMR spectrum of **3** does not provide additional information about the structural changes since the chemical shifts of **3** in toluene-d_8 at 203 K (67.9 ppm) and at 333 K (69.2 ppm) were not very different from the value at 283 K (68.8 ppm). The ^1H NMR and ^{19}F NMR spectra indicate that the two trifluoroacetate ligands are coordinated to the Ru(II) center in a different mode and undergo fast exchange between the chelating and monodentate coordination modes at room temperature (Scheme 3, **3a** and **3b**).

Synthesis and Characterization of [RuH(PNP)-(CO)(OAc), 4. Heating a solution of $Ru_2(OAc)_4$ with 2 equiv of the PNP ligand in methanol at 65 °C for 4 h resulted in formation of [Ru(PNP)H(CO)(OAc) (**4**) in 65% yield (Scheme 4). The IR spectrum of **4** exhibits a strong absorption at 1921 cm^{-1} assignable to coordinated CO. Decarbonylation of primary alcohols by ruthenium(II)

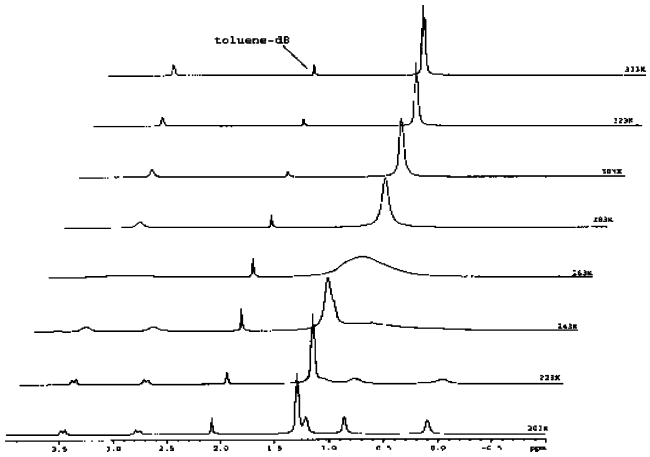
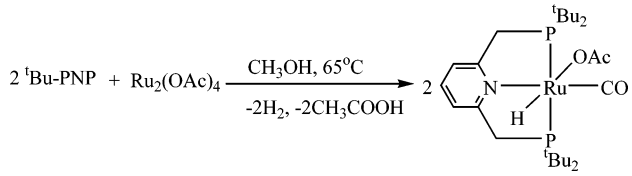


Figure 3. Variable-temperature ^1H NMR spectrum of complex **3** in the *tert*-butyl and methylene groups region.

Scheme 4



complexes to form Ru carbonyl complexes has been reported.[23] The ^{31}P NMR of **4** in C_6D_6 exhibits one peak at 87.1 ppm for the two phosphorus atoms of PNP. The ^1H NMR of **4** exhibits the hydride ligand as a triplet at −16.49 ppm with $J_{PH} = 19.3$ Hz, the *tert*-butyl protons as two virtual triplets at 1.22 and 1.88 ppm, and the methylene protons as two doublets of triplets at 3.05 and 3.98 ppm. The ^1H NMR data are consistent with a structure in which the PNP ligand is meridionally coordinated to the ruthenium center and the PNP−Ru coordination plane is asymmetric, similar to the structure of complex **2**. The chemical shift (−16.34 ppm) of the hydride ligand indicates that the hydride is located *trans* to the chloride ligand or to the pyridine nitrogen atom rather than to CO. In comparison, the signal of the hydride *trans* to CO appears at −5.15 ppm in the case of $RuHCl(CO)_2(P(i\text{-}Pr)_3)_2$[24] and at −3.68 to −7.15 ppm for $[RuH(CO)(PP)_2]^+$ (PP = dppm, dppe).[25] The signal of the hydride *trans* to the pyridinic nitrogen appears at −11.3 ppm in the case of $[RuH(CO)(bpy)_2]^+$ [26] and at −12.1 ppm for $[RuH(CO)(py)_2(PPh_3)_2]ClO_4$.[27] The

(23) (a) Pierantozzi, R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 1821. (b) Geoffroy, G. L.; Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054.
(24) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.
(25) Santos, A.; Lopez, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren, A. M. *Organometallics* **1994**, *13*, 3605.

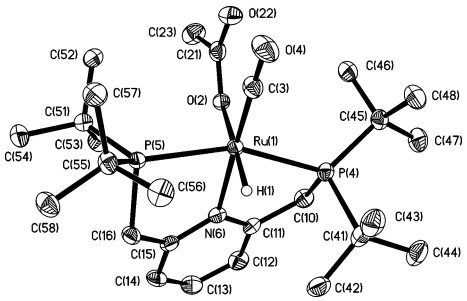


Figure 4. ORETP diagram of a molecule of complex **4** with the thermal ellipsoids at the 50% probability level. Hydrogen atoms except for the hydride ligand are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 4

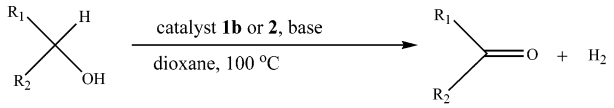
Ru1−N6	2.146(2)	Ru1−P4	2.334(1)
Ru1−P5	2.344(1)	Ru1−C3	1.835(3)
Ru1−O2	2.248(2)	Ru1−H1	1.55(3)
O4−C3	1.166(3)	O2−C21	1.266(3)
O22−C21	1.238(3)		
P4−Ru1−P5	158.05(3)	N6−Ru1−C3	176.2(1)
N6−Ru1−O2	81.5(1)	C3−Ru1−O2	102.4(1)
O2−Ru1−P4	92.3(1)	C3−Ru1−P4	99.3(1)
C3−Ru1−P5	97.9(1)	Ru1−C3−O4	175.7(2)
C3−Ru1−H1	85.7(10)	N6−Ru1−H1	90.4(10)
O2−Ru1−H1	171.6(10)	P4−Ru1−H1	84.0(10)

signal of the hydride ligand *trans* to Cl was reported at −13.5 to −15.4 ppm for $RuH(CO)(PPh_3)(PP)$ (PP = dppm, dppp).[25] A singlet at 2.30 ppm with an integration of three protons is assigned to the acetate protons.

Yellow prismatic crystals of **4** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated benzene solution of **4**. The X-ray crystal structure of **4** (Figure 4) shows that the Ru(II) center adopts a distorted octahedral coordination geometry including PNP, hydride, CO, and monodentate acetate anion ligands (one each). The CO is bound to the Ru center *trans* to the N atom, while the hydride is located *trans* to the acetate and *cis* to CO (the angles of H1−Ru1−O2 and H1−Ru1−C3 are 171.6° and 85.7°, respectively). The C−O bond length (1.166 Å) is slightly longer than that of $RuCl(CO)[CH(C_2H_4P\text{-}t\text{-}Bu_2)_2]_2$[28] (1.150 Å) and of $RuH(CO)(CH(C_2H_4P\text{-}t\text{-}Bu_2)_2)_2$[28] (1.092 Å) and shorter than that of $RuCl(CO)(2,6\text{-}(CH_2P\text{-}t\text{-}Bu_2)_2)_2C_6H_3$[29] (1.183 Å).

Ruthenium-Catalyzed Dehydrogenation of Secondary Alcohols to Ketones. Heating secondary alcohols and 0.2 mol % of **1b** or 0.4 mol % of **2** with sodium isopropoxide (4 equiv to the dinuclear **1b**; 1 equiv to **2**, i.e., an equivalent of base for every Ru−Cl bond) in dioxane at 100 °C under argon for several hours (Scheme 5) resulted in the evolution of dihydrogen and formation of up to 91% yield of the corresponding ketones. The results of the dehydrogenation of various alcohols are shown in Table 4. Investigating the effect of the amount of base, a solution containing the dinuclear complex **1b** in neat 2-propanol with different amounts of KOH was refluxed for 24 h. The results are shown in Table 5. When 4 equiv of KOH was used for the dehydrogenation, the yield of acetone was equal to the conversion of the alcohol, obtaining excellent selectivity. Using 6 equiv of base resulted in higher yield and slightly lower selectivity to acetone, probably as a result of aldol condensation of acetone. Interestingly, further increase in the amount of base to a ratio of KOH:**1b** = 10 did not result in a significant change in conversion and yield, while a still higher concentration (KOH:**1b** = 40) was detrimental. No catalysis was observed at a ratio of KOH:**1b** = 2, suggesting the involvement of a Ru dihydride complex as a catalytic intermediate. Similarly, the hydrido chloride complex **2** did not catalyze the reaction in the absence of 1 equiv of base. Since use of KOH produces water, which might influence the reaction, sodium isopropoxide and KOH were compared. Solutions of 0.1 mol % of **2** and 0.05 mol % of **1b** and base (4 equiv for **1b**; 1 equiv for **2**) were refluxed in neat alcohols for several hours. The results are listed in Table 6. When complex **1b** and NaO-i-Pr were refluxed in 2-propanol for 24 h, 23.5% of acetone was formed, slightly higher than in the analogous reaction using KOH (21%). Similarly, the systems with complex **2** and NaO-i-Pr also result in higher yields than the corresponding catalysts with KOH. The RuHCl complex **2** was slightly more active than the $RuCl_2$ complex **1b**. Unfortunately, dehydrogenation of primary alcohols (methanol and 1-hexanol, for example) to the corresponding aldehydes was unsuccessful in our catalytic system (Table 6, entries 8 and 9), probably because

Scheme 5



(R_1, R_2= alkyl, aryl)

Table 4. Dehydrogenation of Alcohols by Complexes 1b and 2[a]

entry	substrate	cat.	base/ cat.	time (h)	conversion (%)	yield (%)	TON
1	2-propanol	**1b**	4	70	60	57.4	144
2	2-propanol	**2**	1	70	94	91	228
3	1-phenyl-1-ethanol	**2**	1	100	64.4	64.4	161
4	1-cyclohexanol	**2**	1	100	45.2	45.2	113
5	2-butanol	**2**	1	100	86.1	86.0	215

[a] Reaction conditions: catalyst 0.02 mmol of **2**, 0.01 mmol of the dinuclear **1b**; base = $NaO(CH(CH_3)_2$; alcohol 5 mmol; dioxane 2 mL; heated at 100 °C for the specified time under argon in an open system.

Table 5. Effect of Base/Catalyst Ratio on 2-Propanol Dehydrogenation[a]

cat.	KOH/cat. mol/mol	conversion (%)	yield (%)	TON
1b	40	19.7	18.3	183
1b	10	24	23	230
1b	6	22.5	22.2	222
1b	4	21	21	210
1b	2	0	0	0
2	0	0	0	0

[a] Reaction conditions: 0.005 mmol of the Ru dinuclear complex and 0.76 mL (10 mmol) of 2-propanol were refluxed at 83 °C under argon for 24 h in an open system.

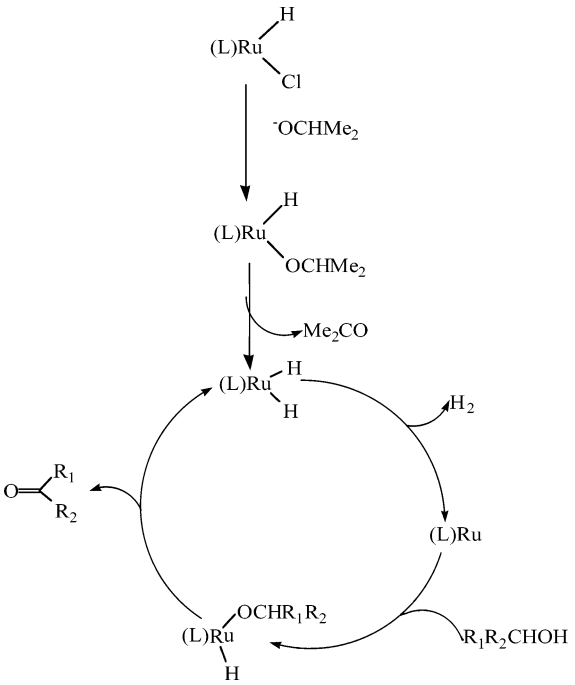
(26) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. *Organometallics* **1984**, *3*, 1241.
(27) Remero, A.; Vegas, A.; Santos, A.; Martinez-Ripoll, M. *J. Organomet. Chem*. **1987**, *319*, 103.
(28) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 5091.
(29) Gusev, D. G.; Madott, M.; Dolgushin, F.; Lyssenko, K. A.; Antipin, M. Yu. *Organometallics* **2000**, *19*, 1734.

Table 6. Comparison of Bases in Catalytic Alcohol Dehydrogenation

entry[a]	cat.	base	alcohol	temp (°C)	time (h)	conversion (%)	yield (%)	TON
1	**1b**	KOH	2-propanol	83	24	21	21	210
2	**2**	KOH	2-propanol	83	24	25	23	230
3	**1b**	NaO-i-Pr	2-propanol	83	24	24	23.5	235
4	**2**	NaO-i-Pr	2-propanol	83	24	27	26.5	265
5[b]	**2**	NaO-i-Pr	2-propanol	83	70	26.7	23.5	924
6	**2**	NaO-i-Pr	1-phenyl-1-ethanol	83	70	19.5	19	190
7[c]	**3**	NaO-i-Pr	2-propanol	83	24	12.6	10.6	383
8	**1b**	NaO-i-Pr	methanol	64	24	0	0	0
9	**1b**	NaO-i-Pr	1-hexanol	157	24	0	0	0

[a] Reaction conditions: catalyst 0.01 mmol of **2**, 0.005 mmol of **1b**; 2-propanol 0.76 mL (10 mmol); 4 equiv of base for **1b**; 1 equiv of base for **2**. [b] **2** 0.02 mmol; NaO-i-Pr 0.04 mmol; 6 mL of 2-propanol (78.5 mmol). [c] **3** 0.01 mmol; NaO-i-Pr 0.05 mmol; 5.5 mL (72.37 mmol) of 2-propanol.

Scheme 6



of the decarbonylation of the product aldehydes, resulting in an inactive ruthenium carbonyl, as was demonstrated by Geoffroy and Pierantozzi.[30] With secondary alcohols no catalyst deactivation was observed, and using lower catalyst concentrations resulted in higher turnover numbers.

Comparing our system with that of the Robinson catalyst, $Ru(OCOCF_3)_2(CO)(PPh_3)_2$,[16] which requires the presence of excess acid, we checked the catalytic behavior of our catalyst under acidic conditions. Refluxing a solution of complex **1b** with 500 equiv of 2-propanol in toluene in the presence of 24 equiv of CF_3COOH for 48 h resulted in no acetone formation, and the alcohol remained unchanged. Moreover, upon refluxing the acetate complex **3** with 250 equiv of 2-propanol and 12 equiv of CF_3COOH, or in the absence of acid in toluene for 24 h, no acetone or its condensation products were formed. Interestingly, upon refluxing complex **3** with 5 equiv of NaO-i-Pr in a large amount of 2-propanol (Table 6, entry 7), acetone was formed with a relatively high turnover number. These results clearly indicate that the mechanism of our catalytic system and that of the Robinson catalyst are entirely different.

(30) (a) Pierantozzi, R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 1821. (b) Geoffroy, G. L. Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054.

When the dinuclear complex **1b** was used as a catalyst for the dehydrogenation of alcohols, 4 equiv of base was needed, while with complex **2**, only 1 equiv of base was required. In other words, in both cases an equivalent of base is required for every Ru−Cl bond present. This strongly suggests that a very likely intermediate in the catalytic procedure is a Ru dihydride complex or a Ru(0) complex formed from it. A likely mechanistic scenario for the catalytic reaction is presented in Scheme 6. The notable features of this cycle are (a) it involves a Ru(0)/Ru(II) sequence, based on alcohol oxidative addition, β-H elimination, and dihydrogen reductive elimination and (b) it can operate under neutral conditions, the equivalent of base being required just to generate the active catalyst (Scheme 6). This is a significant point, when compared with other catalytic alcohol dehydrogenation systems which require excess base or acid.

Summary

New ruthenium dinitrogen and hydride complexes bearing an electron-rich, bulky t-Bu-PNP ligand were synthesized and fully characterized. The dinitrogen-bridged dinuclear complex **1b** prevails over the terminal nitrogen complex **1a**. The dinitrogen molecule is coordinated to the Ru(II) center in a η^1 mode in the hydrido complex **2**. The fluxional behavior of the bis-trifluoroacetate complex **3** in toluene, investigated by NMR, is a result of fast exchange between the bidentate and monodentate coordination modes of the two trifluoroacetate ligands. The Ru(II)-PNP acetate complex undergoes O−H activation and decarbonylation of methanol, resulting in a stable hydrido carbonyl complex **4.** Complexes **1b** and **2** are effective catalyst precursors for the dehydrogenation of secondary alcohols to ketones in the absence of a hydrogen acceptor in a homogeneous system. No catalyst deactivation with secondary alcohols was observed and turnover numbers as high as 900 were demonstrated for dehydrogenation of 2-propanol. The catalytic cycle very likely involves Ru dihydride and Ru(0) intermediates, which, once generated, can operate in the absence of added base (or acid). Further investigations of the catalytic activity of these new complexes and the relationship between their structure and reactivity are in progress.

Experimental Section

General Procedures. All experiments with metal complexes and phosphine ligands 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 argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. The ligand 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine (PNP),[11] $Ru(PPh_3)_3Cl_2$,[32] and $Ru_2(OAc)_4.2THF$ [33] were prepared according to literature procedures.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 250 or 400, 100, and 162 MHz, respectively, using Bruker AMX-250 and AMX-400 NMR spectrometers. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{31}P NMR chemical shifts are reported in parts per million downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Abbreviations used in the NMR follow-up experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, v, virtual. Elemental analyses were performed at Kolbe Laboratorium, Mulheim, Germany.

Synthesis of $[(PNP)RuCl_2]_2(\mu\text{-}N_2)$ 1b. To a suspension of $Ru(PPh_3)_3Cl_2$ (96 mg, 0.1 mmol) in THF (5 mL) was added PNP (40 mg, 0.1 mmol), and the mixture was heated at 65 °C for 2 h. $^{31}P\{^1H\}$ NMR of the resulting dark yellow solution indicated that it contained an equilibrium mixture of the monomeric **1a** and the μ-N_2 complex **1b** in a 8:100 ratio, respectively. The solution was cooled and concentrated under vacuum to 2 mL. Addition of 15 mL of pentane resulted in precipitation of a yellow solid, which was washed with diethyl ether (3 × 2 mL) and dried under vacuum overnight. Complex **1b** was obtained as a yellow solid (54 mg, 93% yield).

$^{31}P\{^1H\}$ (THF-d_8): 65.0 (s). ^1H (THF-d_8): 1.67 (b s, 36H, 2×P(C(CH_3)$_3$)$_2$), 3.58 (bd, J_{HH} = 14.1 Hz, 2H, CH_2P), 4.64 (bd, J_{HH} = 14.1 Hz 2H, $-CH_2P$), 7.30 (d, J_{HH} = 7.7 Hz, 2H, pyridine-H3, 5), 7.49 (t, J_{HH} = 7.7 Hz, 1H, pyridine-H4). $^{13}C\{^1H\}$ NMR (THF-d_8): 29.44 (s, P(C(CH_3)$_3$)$_2$), 30.57 (d, J_{PC} = 14.9 Hz, P(*C*(CH$_3$)$_3$)$_2$), 36.93 (s, CH_2P), 118.26 (s, Py-C3,5), 134.05 (s, Py-C4), 165.80 (s, py-C2,6). Anal. Calcd for $C_{46}H_{86}N_4P_4Cl_4Ru_2 \cdot 2(C_6H_6)$: C, 52.80; H, 7.49. Found: C, 52.68; H, 7.42.

Synthesis of $Ru(PNP)(H)Cl(N_2)$, 2. To a solution of **1b** (29 mg, 0.025 mmol) in THF (5 mL) were added 50 μL of a 1 M toluene solution of $NaBEt_3H$ (0.05 mmol) at −32 °C. The solution was stirred at −32 °C for 0.5 h and then was allowed to warm to room temperature and stirred for another 0.5 h. The red solution was concentrated to 1 mL, and 5 mL pentane was added slowly to precipitate a yellow solid, which was dried under vacuum overnight. Complex **2** was obtained as a yellow solid (21 mg, 75% yield).

IR (KBr, pellet): 2111.2 (ν_{NN}), 1910 (ν_{Ru-H}) cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): 86.81 (s). ^1H NMR (C_6D_6): −14.59(t, J_{PH} = 19.3 Hz, 1H, Ru-H), 1.25 (vt, J_{PH} = 6.1 Hz, 18H, P(C(CH_3)$_3$)$_2$), 1.64 (vt, J_{PH} = 6.5 Hz, 18H, P(C(CH_3)$_3$)$_2$), 2.90 (vdt, J_{HH} = 15.8 Hz, J_{PH} = 3.6 Hz, 2H, −CH*H*-P),), 3.87 (vdt, J_{HH} = 15.8 Hz, J_{PH} = 3.1 Hz, 2H, −C*H*H−P), 6.48 (d, J_{HH} = 7.6 Hz, 2H, pyridine-H3, 5), 6.77 (t, J_{HH} = 7.6 Hz, 1H, pyridine-H4). $^{13}C\{^1H\}$NMR (THF-d_8): 27.64(s, P(C(*C*H$_3$)$_3$)$_2$), 28.31 (s, P(*C*(CH$_3$)$_3$)$_2$), 35.17 (s $-CH_2P$), 117.42 (s, Py-C3,5), 133.50 (s, Py-C4), 163.18 (s, py-C2,6). Anal. Calcd for C23$H_{44}N_3P_2ClRu$: C, 49.23; H, 7.91. Found: C, 49.34; H, 8.08.

Synthesis of $Ru(PNP)(OCOCF_3)_2$, 3. To a solution of **1b** (29 mg, 0.025 mmol) in THF (5 mL) was added $AgOCOCF_3$ (22 mg, 0.1 mmol). The mixture was stirred at room temperature for 0.5 h in the dark and then filtered through a Celite pad. The light yellow filtrate was evaporated under vacuum. The yellow residue was recrystallized from benzene, giving 33 mg of **3** as yellow crystals (90% yield).

IR (KBr, pellet): 1691 cm^{-1}. $^{31}P\{^1H\}$ MNR (toluene-d_8, 283 K): 68.8 (s). $^{31}P\{^1H\}$ NMR (toluene-d_8, 203 K): 67.9 (s). $^{19}F\{^1H\}$ NMR (toluene-d_8, 283 K): −74.78 (s). $^{19}F\{^1H\}$ NMR (toluene-d_8, 203 K): −75.65 (s), −75.67 (s). ^1H NMR (toluene-d_8, 283 K): 1.15 (s br, 36H, P(C(CH_3)$_3$)$_2$), 3.30 (s br, 4H, $-CH_2$-P), 6.33 (d, J_{HH} = 8.0 Hz, 2H, pyridine-H3, 5), 6.54 (t, J_{HH} = 8.0 Hz, 1H, pyridine-H4). ^1H NMR (toluene-d_8, 203 K): 0.07 (s br, 6H, P(C(CH_3)$_3$)$_2$), 0.81 (s br, 6H, P(C(CH_3)$_3$)$_2$), 1.18 (s br, 6H, P(C(CH_3)$_3$)$_2$), 1.19 (s br, 18H, P(C(CH_3)$_3$)$_2$), 2.77 (d, J_{HH} = 16 Hz, 2H, −C*H*H-P), 3.47 (d, J_{HH} = 16 Hz, 2H, −CH*H*-P), 6.14 (d, J_{HH} = 8.0 Hz, 2H, pyridine-H3,5), 6.47 (t, J_{HH} = 8.0 Hz, 1H, pyridine-H4). $^{13}C\{^1H\}$ NMR (toluene-d_8, 283 K): 30.18 (s, P(C(*C*H$_3$)$_3$)$_2$), 34.60 (s, P(*C*(CH$_3$)$_3$)$_2$), 36.65 (s $-CH_2P$), 115.28 (s, CF_3-), 119.59 (s, Py-C3,5), 134.17 (s, Py-C4), 167.93 (s, CF3*C*OO), 169.44 (s, py-C2,6). Anal. Calcd for $C_{27}H_{43}NO_4F_6P_2Ru$: C, 44.87; H, 6.00. Found: C, 44.73; H, 6.09.

Synthesis of Ru(PNP)H(CO)(OAc), 4. $Ru_2(OAc)_4 \cdot 2THF$ (29.1 mg, 0.5 mmol) and PNP (39.6 mg, 0.1 mmol) were dissolved in methanol (5 mL). The solution was heated at 65 °C for 6 h. After cooling to room temperature, the yellow solution was evaporated under vacuum to dryness, and the residue was dissolved in THF and precipitated with diethyl ether (1:4 v/v). Complex **4** was obtained as a yellow solid (38 mg, 65% yield).

IR (KBr, pellet): 1921 cm^{-1}(ν_{CO}). $^{31}P\{^1H\}$ NMR (C_6D_6): 87.7 (s). ^1H NMR (C_6D_6): −16.34 (t, J_{PH} = 19.3 Hz, 1H, Ru-H), 1.22 (vt, J_{PH} = 6.3 Hz, 18H, P(C(CH_3)(CH$_3$)), 1.48 (vt, J_{PH} = 6.6 Hz, 18H, P(C(CH$_3$)(CH_3)), 2.30 (s, 3H, OAc), 3.05 (vt, J_{PH} = 3.3 Hz, J_{HH} = 16.1 Hz, 2H, −CH*H*-P), 3.98 (dt, J_{PH} = 3.2 Hz, J_{HH} = 16.1 Hz, 2H, −C*H*H-P), 6.61 (d, J_{HH} = 7.7 Hz, 2H, pyridine-H3, 5), 6.92 (t, J_{HH} = 7.7 Hz, 1H, pyridine-H4). $^{13}C\{^1H\}$ NMR (C_6D_6): 29.82 (s, P(C(*C*H$_3$)(CH$_3$)$_2$), 30.62 (s, P(C(CH$_3$)(*C*H$_3$)$_2$), 30.84 (s, P(*C*(CH$_3$)$_3$)$_2$), 35.73 (s, $-CH_2P$), 36.82 (s OCO*C*H$_3$), 38.16 (s, $-CH_2P$), 120.28 (s, Py-C3,5), 137.83 (s, Py-C4), 164.93 (s, py-C2,6), 175.40 (s, O*C*OCH$_3$), 209.72 (s, CO). Anal. Calcd for $C_{26}H_{47}NO_3P_2Ru$: C, 53.41; H, 8.11. Found: C, 53.34; H, 8.19.

Typical Procedure for the Catalytic Dehydrogenation of Alcohols. (a) The Ru complexes (0.01 mmol **2**, 0.005 mmol **1b**), $NaO(CH(CH_3)_2)$ (0.04 mmol for **1b**, 0.01 mmol for **2**), and alcohol (2.5 mmol) were dissolved in dioxane (2 mL), and the solution was heated at 100 °C for several hours (see Table 4) under argon atmosphere in an open system. After cooling, the ketone products were analyzed by GC with mesitylene as an internal standard using a Carboxen 1000 column on a HP 690 series GC system. (b) The Ru complexes (0.01 mmol **2**, 0.005 mmol **1b**) and various amounts of base (as specified in Tables 5 and 6) in the specified alcohols (10 mmol) were heated at 83 °C (or other specified temperature) for several hours. After cooling, the ketones were determined by GC with mesitylene as internal standard using a Carboxen 1000 column on a HP 690 series GC system.

X-ray Crystal Structure Determination of 1b, 2, 4, and 5b. The crystals were mounted on a nylon loop and flash frozen in a nitrogen stream at 120 K. Data were collected on a Nonius Kappa CCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The four structures were solved using direct methods with SHELXS-97 based on F^2.

Complex 1b: $C_{46}H_{86}N_4P_4Cl_4Ru_2+2(C_6H_6)$, orange prisms, 0.15 × 0.05 × 0.03 mm^3, monoclinic, $P2(1)/c$, a = 12.498(3) Å, b = 21.564(4) Å, c = 23.683(5) Å, β = 96.35(3)°, V = 6344(2) $Å^3$, Z = 4, fw = 1319.2, $F(000)$ = 2760, D_c = 1.381 Mg/m^3, μ = 0.784 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.037 for data with $I > 2\sigma(I)$ and R = 0.063 for all data (9103 reflections) with a goodness-of-fit of 1.020. Idealized hydrogen atoms were placed and refined in the riding mode.

(31) Although attempts in our laboratory to prepare a t-Bu-PNP-Ru dihydride or a t-Bu-PNP Ru(0) complex have not led so far to isolable complexes, a complex assignable as the dihydride was observed in solution upon reaction of **1b** with 2 equiv of $NaEt_3BH$ (^1H NMR in THF −5.06, t, 2H; ^{31}P NMR 102.7(s)). Solvent removal at room temperature resulted in decomposition.

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Complex 2: $C_{23}H_{44}N_3P_2ClRu$, yellow prisms, 0.10 × 0.10 × 0.10 mm^3, triclinic, $P\bar{1}$ (No.2), a = 8.7040(3) Å, b = 10.6320(3) Å, c = 15.5630(5) Å, α = 105.908(2)°, β = 93.965(2)°, γ = 98.136(2)°, V = 1362.3(1) Å^3, Z = 2, fw = 561.1, $F(000)$ = 588, D_c = 1.368 Mg/m^3, μ = 0.806 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.043 for data with $I > 2\sigma(I)$ and R = 0.064 for all data (6569 reflections) with a goodness-of-fit of 1.013. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H1 (Ru−H), which was located in the difference map and refined independently.

Complex 4: $C_{26}H_{47}NO_3P_2Ru$, yellow prisms, 0.10 × 0.10 × 0.10 mm^3, monoclinic, $P2(1)/c$, a = 14.785(3) Å, b = 12.146(2) Å, c = 16.231(3) Å, β = 91.32(3)°, V = 2914(1) Å^3, Z = 4, fw = 584.7, $F(000)$ = 1232, D_c = 1.333 Mg/m^3, μ = 0.673 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.032 for data with $I > 2\sigma(I)$ and R = 0.044 for all data (5308 reflections) with a goodness-of-fit of 1.020. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H1 (Ru−H), which was located in the difference map and refined independently.

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Note Added in Proof. Hydrido- and hydroxo-Ru carbonyl complexes of the t-Bu-PNP ligand have been reported very recently: Gibson, D. H.; Pariya, C.; Mashuta, M. S. *Organometallics* **2004**, *23*, 2510.

Supporting Information Available: Tables giving X-ray crystallographic data for complexes **1b**, **2**, and **4** and the corresponding CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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