Probing the Effect of the Ligand X on the Properties and Catalytic Activity of the Complexes RuHX(diamine)(PPh_3)$_2$ (X = OPh, 4-$SC_6H_4OCH_3$, $OPPh_2$, $OP(OEt)_2$, CCPh, NCCHCN, $CH(COOMe)_2$; diamine = 2,3-Diamino-2,3-dimethylbutane, (*R*,*R*)-1,2-Diaminocyclohexane)

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The reactivity of the ruthenium−amido bond in RuH($NH_2CMe_2CMe_2NH$)(PPh_3)$_2$ (**1**) toward weak acids HX and the influence of the X group on the catalytic activity of the resulting complex are explored here. Complex **1** reacts with the weak acids HX (X = OPh, 4-SC_6H_4OMe, $OPPh_2$, $OP(OEt)_2$, CCPh, NCCHCN, $CH(COOMe)_2$) to form complexes of the type RuHX(tmen)(PPh_3)$_2$ (tmen = 2,3-diamino-2,3-dimethylbutane). The complexes with X = PhOH···OPh, 4-SC_6H_4OMe, $OP(OEt)_2$, CCPh, $CH(COOMe)_2$ have been characterized by X-ray crystallography. The X group is situated trans to the hydride in all cases and is bonded to ruthenium via the donor atoms O, S, P, C, and O, respectively. The phenol in the phenoxide adduct RuH(PhOH···OPh)(tmen)(PPh_3)$_2$ bridges via hydrogen bonds between the alkoxide oxygen and an amino hydrogen to form a six-membered RuO···HO···HN ring. One carbonyl oxygen of the malonate bonds to the Ru, while the other accepts a hydrogen bond from an amino hydrogen. The analogous complexes RuHX(dach)(PPh_3)$_2$ (dach = (*R*,*R*)-1,2-diaminocyclohexane) were synthesized by the reaction of RuHCl(dach)(PPh_3)$_2$ (**2**) with an equimolar amount of potassium *tert*-butoxide and HX. For all of the complexes the Ru−H vibrational frequency and the ^{1}H NMR chemical shift of Ru−H correlate with the electronegativity of the trans atom X. The amido complex **1** and the complexes with X = $CH(COOMe)_2$ and OPh are active catalysts for the Michael addition of dimethyl malonate to 2-cyclohexen-1-one. RuH(NCCHCN)(tmen)(PPh_3)$_2$ reacts with the Michael acceptor 2-cyclohexen-1-one to give RuH(NCC(C_6H_9O)CN)(tmen)(PPh_3)$_2$, a trapped Michael adduct that has been characterized by X-ray crystallography. On the basis of these observations a catalytic cycle for the Michael addition reactions is proposed that involves the addition of the C−H bond of the Michael donor to the Ru−N bond followed by attack on the Michael acceptor and elimination of the Michael adduct, possibly by a 1,3-proton migration as observed for the malononitrile adduct. Only the complexes with X = H, CCPh are catalysts or precatalysts for the hydrogenation of neat acetophenone to 1-phenylethanol in the absence of added base under 10 atm of H_2 at 20 °C. Evidence is provided that the phenylacetylide complexes are precatalysts that are converted to the active *trans*-dihydride catalysts (X = H).

Introduction

Late-transition-metal amido complexes are of interest as catalysts for polar bond transfer hydrogenation and H_2 hydrogenation[1−3] and as intermediates in catalytic hydroamination and other C−N bond-forming reactions such as arylamine synthesis.[4] The amido hydrido complex RuH($NH_2CMe_2CMe_2NH$)(PPh_3)$_2$ (**1**)[3] is a catalyst for the H_2 hydrogenation of ketones to alcohols. Metal- and nitrogen-based reactivity are key to the catalyst's activity. In the catalytic cycle, dihydrogen, a very weak acid ($pK_\alpha^{THF}(H_2/H^-) > 44$,[5] $pK_a^{MeCN}(H_2/H^-) = 76/1.37 = 55$[6]), splits heterolytically across the ruthenium−amido bond to form the *trans*-dihydrido diamino complex *trans*-RuH_2(tmen)(PPh_3)$_2$. Complex **1** reacts reversibly with other weak acids, including acetophenone ($pK_a^{DMSO} = 24.7$),[7] to give the enolate complex RuH(OCPh=CH_2)(tmen)(PPh_3)$_2$ and with the alcohols ^{t}BuOH and ^{i}PrOH ($pK_a^{DMSO} = 30-32$) to give the alkoxide complexes RuH(OR)(tmen)(PPh_3)$_2$.[3] It reacts irreversibly with formic acid ($pK_a^{DMSO} \approx 11$) to give the formate complex RuH(OCH=O)(tmen)(PPh_3)$_2$.[3] These are reactions of a 16-electron complex with a dative[8] amido group.

Another class of ruthenium complexes with dative amido bonds that show metal−ligand bifunctional reactivity are the

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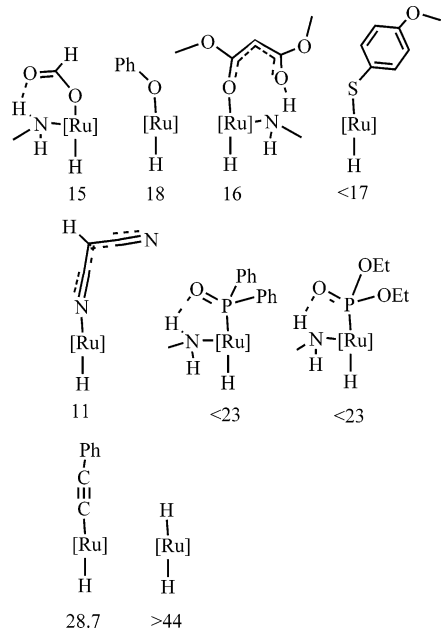
η^6-arene complexes Ru(arene)((*S*,*S*)-NHCHPhCHPhNTs).[1] These are catalysts for the asymmetric transfer hydrogenation of ketones and imines[9] and the Michael addition of malonates and β-keto esters to α,β-unsaturated ketones[10,11] and nitroalkenes.[12] In these reactions the C−H bond of the Michael donor is proposed to add across the Ru−amido bond, and in one case a carbon-bonded malonate complex, Ru[$CH(CO_2CH_3)_2$][(*R*,*R*)-Tsdpen](η^6-mesitylene), was structurally characterized.[10] Reaction of the η^6-cymene complex with an acidic alcohol produces the unstable alkoxide complexes Ru(cymene)(OCH_2CF_3)(((*S*,*S*)-NHCHPhCHPhNTs).[13] We show here that complex **1** and some of its derivatives are also catalysts for the Michael addition reaction, although they operate via an oxygen-bonded malonate route. In addition, a Michael adduct has been trapped at the metal in one case.

Fryzuk and co-workers[14,15] and Caulton and co-workers[16] have observed HX addition reactions, including intramolecular C−H addition across the Ru−amido bond in pincer ligand complexes of the type Ru($N(SiMe_2CH_2PPh_2)_2$)(PPh_3)Cl and Ru($N(SiMe_2CH_2P^tBu_2)_2$)OTf. There is also much recent chemistry concerning nondative amido complexes in 18-electron ruthenium complexes where the nitrogen is the site of reactivity, serving as a very strong base.[8,17−21] For example, the 18-electron ruthenium amido complex $RuH(NH_2)(dmpe)_2$[20] reacts with weak acids with a range of pK_a values: methanol (29.0 in DMSO), water (31.2 in DMSO), phenol (18 in DMSO), aniline (30.6 in DMSO), dihydrogen (>44 in THF[5]), phenylacetonitrile (22.3 in DMSO), fluorene (22.9 in THF), phenylacetylene (28.7 in DMSO), and triphenylmethane (31.5 in THF). These reactions are thought to proceed via protonation at nitrogen without coordination to the metal to produce an ion pair.

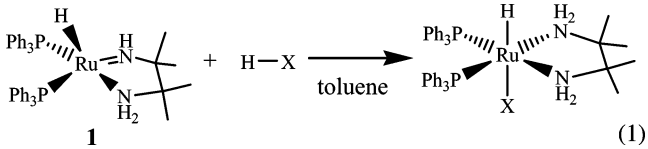
An objective of the current work is to determine the influence of the X group trans to hydride in the complexes RuHX(diamine)(PPh_3)$_2$ on catalytic activity toward H_2 hydrogenation of ketones and Michael addition reactions. It is known that X = H is an active catalyst, while X = Cl is inactive for the hydrogenation reaction in the absence of added base.[3,22,23] Similarly, in the related RuHX(diamine)(diphosphine) complexes X = H,[3] BH_4[24] are catalysts in the absence of base, while X = Cl is inactive. The complexes $RuH(BH_4)$(binap)(phosphine-amine)[25] and $RuH(BH_4)$(diamine)(diphosphinite)[26] allow the successive enantioselective Michael addition reactions of malonates with enones followed by enantioselective hydrogenation. Ruthenium−amido chemistry is suspected to be key to this reactivity.

Chart 1. Coordination Mode of the X Ligand in the Complex *trans*-RuHX(diamine)(PPh_3)$_2$ Arranged by the Group in the Periodic Table of the Atom Attached to Ruthenium and the pK_a^{DMSO} Values of the Weak Acid HX Used To Generate the Complex According to Eq 1 or 2



Results and Discussion

Preparation. The complexes RuHX(tmen)(PPh_3)$_2$ are synthesized by reacting **1** with the appropriate weak acid in toluene under argon, as shown in eq 1, where HX is HOCHO,[3] HOPh, $CH_2(COOMe)_2$, 4-HSC_6H_4OMe, $NCCH_2CN$, $OPHPh_2$, $OPH(OEt)_2$, H_2[3] or HCCPh.



A variety of weak acids with a range of pK_a^{DMSO}(HX) values was employed to produce a range of structures with O, S, N, P, H, and C donor atoms, as listed in Chart 1. The weak acids aniline (pK_a^{DMSO} = 30.6), triphenylmethane (pK_a = 31.5), and triethoxysilane as reagents in eq 1 gave no reaction.

In the reaction of eq 1, the red solution of **1** in toluene quickly becomes yellow upon addition of the weak acid. The characteristically yellow products are precipitated with the addition of hexanes. Solutions were found to be very air sensitive, readily turning black upon exposure to air. Solid samples are less air sensitive, gradually darkening within minutes to hours.

The modes of coordination of the X ligands shown in Chart 1 were determined by a combination of NMR, IR, and X-ray crystallographic studies, as described below.

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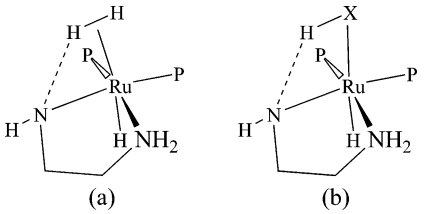
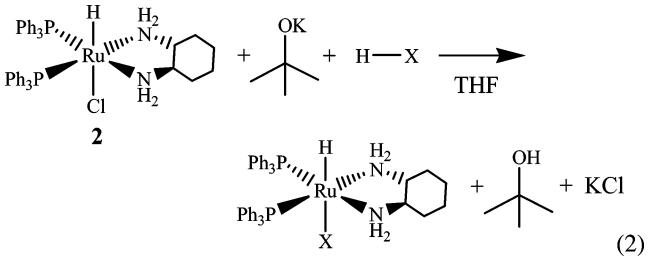


Figure 1. (a) Transition-state structure for dihydrogen splitting at RuH(NHCH$_2$CH$_2$NH$_2$)(PH$_3$)$_2$.[3] (b) Possible transition-state structure for H−X bond splitting.

The mechanism of the H−X addition reactions (eq 1) may be similar to that observed for complex **1** with dihydrogen,[3] where a weakly interacting η^2-dihydrogen ligand on ruthenium is deprotonated by the amido nitrogen (Figure 1a). In a similar fashion the H−X bonds could be activated and cleaved heterolytically (Figure 1b). If the metal has a coordination site as in complex **1**, then a weak interaction of HX with Ru would increase the acidity of HX. With HX coordinated, the amido nitrogen can no longer act as a π-donor to ruthenium and thus becomes more basic. This metal−ligand bifunctional effect allows the cleavage of unactivated bonds. An alternative mechanism involving the addition of weak acids to ruthenium(0) by oxidative addition, a mechanism known for 50 years,[27,28] is much less likely. For example, the complex RuH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$} is thought to add phenylacetylene to give RuH(CCPh){P(CH$_2$CH$_2$PPh$_2$)$_3$} by a reductive elimination/oxidative addition route.[29] The reductive elimination of one end of the tmen ligand to give a transient ruthenium(0) intermediate, Ru(PPh$_3$)$_2$(tmen), has not been observed.

The yellow complexes RuHX(dach)(PPh$_3$)$_2$ containing the diamine (*R*,*R*)-1,2-diaminocyclohexane are synthesized in a metathesis route by reacting RuHX(dach)(PPh$_3$)$_2$ (**2**) with potassium *tert*-butoxide and the appropriate weak acid in THF under nitrogen (eq 2). This route gives significantly improved yields

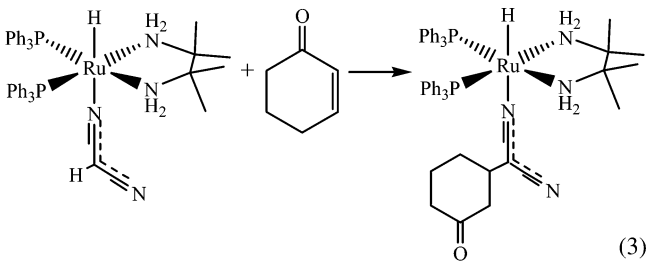


(2)

relative to a two-step procedure where a solution of the unstable red hydrido amido complex RuH(NHC$_6$H$_{10}$NH$_2$)(PPh$_3$)$_2$[23] is first generated by reaction of **2** with base and then reacted with the weak acid HX. The structures of the complexes all have X trans to hydride except for the phenoxide complex, where cis isomers are also observed in minor amounts (see below).

A short-lived red color due to the amido intermediate is observed when adding the reactants together with stirring. The dach-containing complexes are more soluble than the tmen complexes and are readily soluble in THF. The sensitivity of these complexes to air was found to be similar to that for the tmen analogues.

An additional complex was prepared by the Michael addition reaction of RuH(NCCHCN)(tmen)(PPh$_3$)$_2$ with 2-cyclohexen-1-one in toluene to give RuH(NCC(C$_6$H$_9$O)CN)(tmen)(PPh$_3$)$_2$ according to eq 3. This is an unusual case where the Michael



(3)

adduct is trapped on the metal. Usually the adduct falls off in the reaction of coordinated anions derived from nitriles with electrophiles.[30] However, Hayashi and co-workers have observed, by use of NMR, a Michael adduct intermediate in the asymmetric 1,4-addition of organoboronic acids to enones catalyzed by [Rh(binap)(OH)]$_2$.[31] In addition, Michael adducts are retained in the metal complex resulting from the addition of Michael acceptors to η^2-arene complexes, a powerful method for regio- and stereospecific C−C bond formation.[32−34]

X-ray Crystallography. Complexes containing the tmen ligand crystallized much more readily than those containing the dach ligand. Seven pseudo-octahedral tmen-containing complexes, those with X = OCHO,[3] PhOH···OPh, 4-SC$_6$H$_4$OMe, PO(OEt)$_2$, CCPh, OC(OMe)CHCOOMe, NCC(C$_6$H$_9$O)CN), have been characterized by X-ray crystallography (Figures 2−7; all but the ipso phenyl carbons of the PPh$_3$ ligands have been removed for clarity). The structure of the distorted square pyramid defined by the fragment RuHN$_2$P$_2$ to which the X ligand is attached varies only slightly from complex to complex. The P−Ru−P angles vary between 96 and 100° and the diamine bite angles between 73 and 76°.

The complex RuH(OPh)(tmen)(PPh$_3$)$_2$ crystallizes when an extra 1 equiv of phenol is present in solution (Figure 2a). This phenol is hydrogen-bonded in a six-membered Ru−O···H−O(Ph)···H−N− ring in the resulting pseudo-octahedral complex (Figure 2b). The ruthenium−oxygen bond length of 2.364(2) Å is much longer than previously observed Ru−alkoxide distances (e.g. 2.239(2) Å in trans-RuH(4-O-C$_6$H$_4$Me)(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$)[35] and longer than the Ru−O distance of 2.29 Å in the related formate complex RuH(OCHO)(tmen)(PPh$_3$)$_2$.[3] The complex has considerable [RuH(diamine)(PPh$_3$)$_2$]$^+$[PhO···HOPh]$^-$ ion pair character, with a weakly interacting biphenoxide ligand analogous to a bifluoride ligand, as in [RuH(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$]$^+$[FHF]$^-$ with Ru−F = 2.284(5) Å.[36,37] The hydrogen-bonded ring structure is related to those of the alcohol-assisted splitting of dihydrogen on ruthenium catalysts, as proposed by Ito et al.,[38] Sandoval et al.,[24] Casey et al.,[39] and Hedberg et

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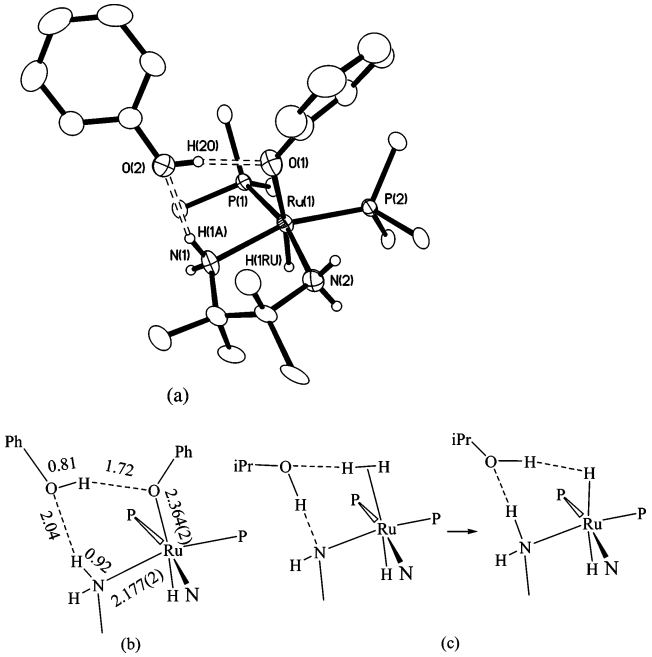

Figure 2. (a) Molecular structure of RuH(OPh)(tmen)$(PPh_3)_2$·HOPh. Selected bond distances (Å) and angles (deg): Ru(1)−O(1) = 2.364(2), Ru(1)−H(1RU) = 1.53(3), Ru(1)−N(1) = 2.177(2), Ru(1)−N(2) = 2.179(2), Ru(1)−P(2) = 2.2690(7), Ru(1)−P(1) = 2.2697(8); H(1RU)−Ru(1)−N(1) = 88(1), N(1)−Ru(1)−N(2) = 75.20(9), N(1)−Ru(1)−P(2) = 163.57(7), N(2)−Ru(1)−P(2) = 92.01(7), N(1)−Ru(1)−P(1) = 93.13(7), N(2)−Ru(1)−P(1) = 167.31(7), P(2)−Ru(1)−P(1) = 98.49(3), N(1)−Ru(1)−O(1) = 83.83(8), N(2)−Ru(1)−O(1) = 80.87(9), P(2)−Ru(1)−O(1) = 104.62(5), P(1)−Ru(1)−O(1) = 103.14(6). (b) The six-membered ring. (c) Related ring structures proposed for the alcohol-assisted splitting of dihydrogen.

al.,[40] where the phenoxide ligand takes the place of the hydride (Figure 2c).

The molecular structure of the thiolate complex RuH(4-SC_6H_4OMe)(tmen)$(PPh_3)_2$ shows a pseudo-octahedral structure with the thiolato ligand trans to hydride (Figure 3). The Ru−S distance of 2.5274(9) Å is similar to the 2.526(1) Å Ru−S distance in the complex *trans*-RuH(SPh)$(PPh_2CH_2CH_2PPh_2)_2$, with thiolate trans to hydride.[41]

The crystal structure of RuH$(OP(OEt)_2)$(tmen)$(PPh_3)_2$ has an intramolecular electrostatic interaction between O(3) on diethyl phosphonate and H(2A) on a nitrogen of the tmen ligand, as indicated by the short distance of 2.1 Å (Figure 4). The O3···H2A−N(2) angle is ∼139°. There are no other structurally characterized ruthenium phosphonate complexes for comparison. However, there is an iron phosphonate complex, $Fe(CO)_2$(HN−N−C)$(PO(OMe)_2)$, that has a similar intramolecular NH···OP hydrogen bond with H···O = 2.3 Å.[42]

The phenylacetylido complex RuH(CCPh)(tmen)$(PPh_3)_2$ displays a similar pseudo-octahedral geometry with hydride trans to phenylacetylide, as shown in Figure 5. The Ru−C bond at 2.071(3) Å is the same as the Ru−C distance of 2.079 Å in the other hydrido phenylacetylido complex that has been structurally characterized, cis-RuH(CCPh){$P(CH_2CH_2PPh_2)_3$}.[29]

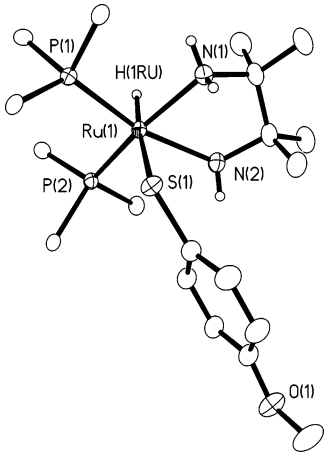

Figure 3. Molecular structure of RuH(4-$SC_6H_4OCH_3$)(tmen)-$(PPh_3)_2$. Selected bond distances (Å) and angles (deg): Ru(1)−H(1RU) = 1.57(3), Ru(1)−N(1) = 2.181(2) Ru(1)−N(2) = 2.205(2), Ru(1)−P(1) = 2.2695(8), Ru(1)−P(2) = 2.2715(9), Ru-(1)−S(1) = 2.5274(9); N(1)−Ru(1)−N(2) = 73.54(9), N(1)−Ru-(1)−P(1) = 92.05(7), N(2)−Ru(1)−P(1) = 165.54(7) N(1)−Ru(1)−P(2) = 163.66(7), N(2)−Ru(1)−P(2) = 94.46(7), P(1)−Ru(1)−P(2) = 99.46(3), N(1)−Ru(1)−S(1) = 84.12(7), N(2)−Ru(1)−S(1) = 88.24(7), P(1)−Ru(1)−S(1) = 91.41(3), P(2)−Ru(1)−S(1) = 106.99(3).

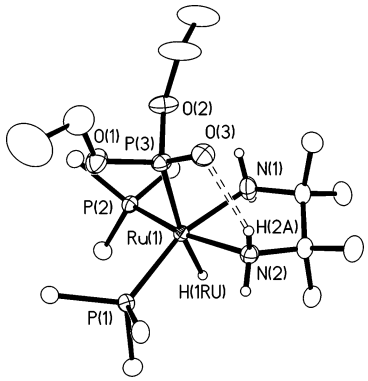

Figure 4. Molecular structure of RuH$(OP(OEt)_2)$(tmen)$(PPh_3)_2$. Selected bond distances (Å) and angles (deg): Ru(1)−H(1RU) = 1.63(3), Ru(1)−N(1) = 2.166(2), Ru(1)−N(2) = 2.181(2), Ru(1)−P(1) = 2.2772(5) Ru(1)−P(2) = 2.2872(5), Ru(1)−P(3) = 2.3486-(5); H(1RU)−Ru(1)−N(1) = 82.0(9), H(1RU)−Ru(1)−N(2) = 91.6(9), N(1)−Ru(1)−N(2) = 75.19(7), H(1RU)−Ru(1)−P(1) = 86.4(9), N(1)−Ru(1)−P(1) = 163.52(5), N(2)−Ru(1)−P(1) = 93.50(5), H(1RU)−Ru(1)−P(2) = 85.0(9), N(1)−Ru(1)−P(2) = 92.27(5), N(2)−Ru(1)−P(2) = 167.37(5), P(1)−Ru(1)−P(2) = 98.42(2), H(1RU)−Ru(1)−P(3) = 171.7(9), N(1)−Ru(1)−P(3) = 90.03(6), N(2)−Ru(1)−P(3) = 83.79(5), P(1)−Ru(1)−P(3) = 100.79(2), P(2)−Ru(1)−P(3) = 97.98(2).

The reaction of **1** with dimethyl malonate produced a complex with a rare monodentate oxygen-bonded ligand (Figure 6). In most instances this ligand acts as a bidentate ligand in metal complexes. In this case, only one carbonyl oxygen, O(1), binds to the metal, while the other carbonyl oxygen, O(2), is hydrogen-bonded to one of the protons on N(1). The planar O(1)−C(7)−C(8)−C(9)−O(2) chain and short, similar O═C (1.239(4), 1.225(4) Å) and C−C distances (1.404(5), 1.413(5) Å) signal the presence of π delocalization. Wang et al. have reported the observation by NMR of a ruthenium methyl acetoacetonate complex where both oxygen- and carbon-bonded ligands are thought to be present.[11] There has been one structural characterization of a carbon-bonded malonate on ruthenium in the complex Ru$[CH(CO_2CH_3)_2]$[(*R*,*R*)-Tsdpen](η^6-mesitylene).[10]

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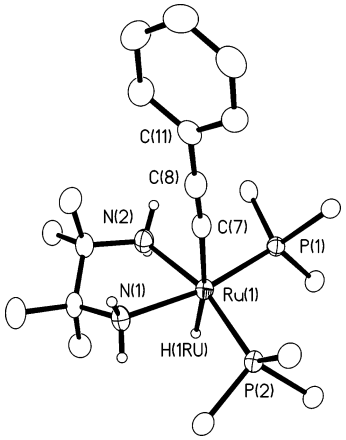

Figure 5. Molecular structure of RuH(CCPh)(tmen)(PPh$_3$)$_2$. Selected bond distances (Å) and angles (deg): Ru(1)−H(1RU) = 1.68(3), Ru(1)−C(7) = 2.071(3), Ru(1)−N(1) = 2.198(3), Ru(1)−N(2) = 2.208(3), Ru(1)−P(1) = 2.2550(9), Ru(1)−P(2) = 2.2599(9); C(7)−Ru(1)−N(1) = 86.9(1), C(7)−Ru(1)−N(2) = 87.1(1), N(1)−Ru(1)−N(2) = 74.6(1), C(7)−Ru(1)−P(1) = 89.8(1), N(1)−Ru(1)−P(1) = 167.83(8), N(2)−Ru(1)−P(1) = 93.51(8), C(7)−Ru(1)−P(2) = 102.4(1), N(1)−Ru(1)−P(2) = 93.75(8), N(2)−Ru(1)−P(2) = 164.68(9), P(1)−Ru(1)−P(2) = 98.40(3).

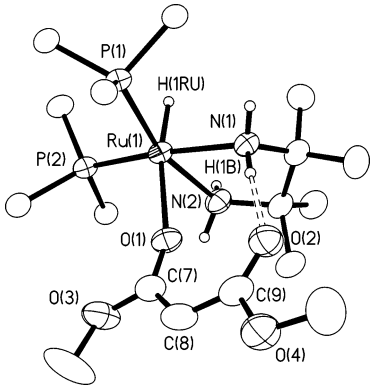

Figure 6. Molecular structure of RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$. Selected bond distances (Å) and angles (deg): Ru(1)−H(1RU) = 1.50, Ru(1)−N(1) = 2.154(3), Ru(1)−N(2) = 2.180(3), Ru(1)−P(2) = 2.2392(9), Ru(1)−P(1) = 2.2494(8), Ru(1)−O(1) = 2.265(2); N(1)−Ru(1)−N(2) = 75.6(1), N(1)−Ru(1)−P(2) = 170.26(7), N(2)−Ru(1)−P(2) = 94.72(8), N(1)−Ru(1)−P(1) = 91.85(7), N(2)−Ru(1)−P(1) = 163.82(8), P(2)−Ru(1)−P(1) = 97.35(3), N(1)−Ru(1)−O(1) = 77.3(1), N(2)−Ru(1)−O(1) = 78.9(1), P(2)−Ru(1)−O(1) = 102.61(7), P(1)−Ru(1)−O(1) = 108.70(7).

The Michael adduct formed in eq 3 retains a Ru−N bond, as shown in Figure 7. The Ru(1)−N(3) bond distance of 2.137(5) Å is similar to that of the Ru−N bond (2.16(2) Å) for the nitrile trans to hydride in the related complex RuH(PPh$_3$)$_3$(NCCH$_2$CO$_2$Et)(NCCHCO$_2$Et)[30] and the Os−N bond (2.116(3) Å) to the malononitrile anion trans to hydride in OsH(NCCHCN)(PPh$_3$)$_2$(tmen).[43] The new C−C bond created in eq 3 is between trigonal-planar C(8) and tetrahedral C(10). There is a delocalized π system over N(3)−C(7)−C(8)−C(9)−N(4) with N−C distances of 1.170(7) and 1.149(8) Å and C−C distances of 1.389(8) and 1.397(9) Å.

NMR Characterization. There are several features of the NMR spectra of the tmen-containing complexes that are common to all. There are only two amine proton resonances

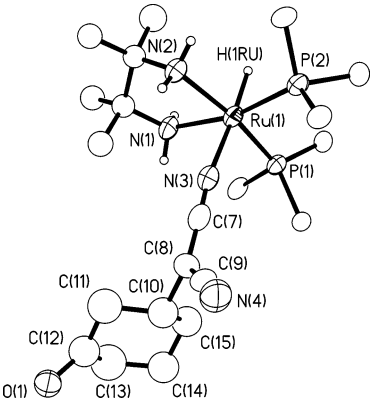

Figure 7. Molecular structure of RuH(NCC(C$_6$H$_9$O)CN)(tmen)(PPh$_3$)$_2$. Selected bond distances (Å) and angles (deg): Ru(1)−H(1RU) = 1.63, Ru(1)−N(3) = 2.137(5), Ru(1)−N(1) = 2.190(4), Ru(1)−N(2) = 2.199(5), Ru(1)−P(1) = 2.259(1), Ru(1)−P(2) = 2.267(1); N(3)−Ru(1)−N(1) = 86.3(2), N(3)−Ru(1)−N(2) = 86.7(2) N(1)−Ru(1)−N(2) = 76.1(2), N(3)−Ru(1)−P(1) = 92.2(1), N(1)−Ru(1)−P(1) = 92.7(1), N(2)−Ru(1)−P(1) = 168.8(1), N(3)−Ru(1)−P(2) = 101.3(1), N(1)−Ru(1)−P(2) = 166.4(1), N(2)−Ru(1)−P(2) = 93.0(1), P(1)−Ru(1)−P(2) = 98.08(5).

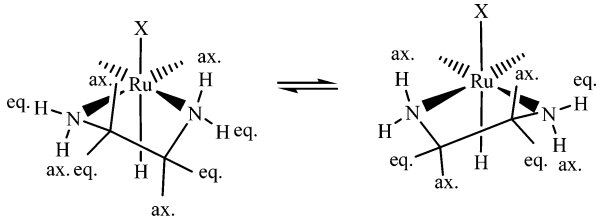

Figure 8. Exchange of groups by the ring flip of the 2,3-diamino-2,3-dimethylbutane ligand.

(AX or AB spin system) and two methyl resonances in the ^{1}H NMR spectra. Due to the lack of symmetry caused by the *trans*-HRuX system, four of each of these resonances might have been expected for axial or equatorial groups syn to the X or H sides of the molecules. The rapid flipping of the five-membered Ru−tmen ring causes an exchange of groups and averaging of chemical shifts of pairs of these groups that are syn to X and syn to H, respectively (Figure 8). In the cases where the X groups (OCHO, POPh$_2$, PO(OEt)$_2$, OC(OMe)CHCOOMe) form NH···O hydrogen bonds (or electrostatic attractions) with the NH groups (see Chart 1 and Figures 4 and 6), there must also be exchange between hydrogen bond partners to achieve the averaging of the signals. The presence of these hydrogen bonds in solution is manifested by a downfield shift by about 2 ppm of one of the averaged NH signals (syn to the X ligand).

The triplet for the hydride in the ^{1}H NMR spectrum is in keeping with the hydride trans to X geometry observed in the X-ray crystal structures. The chemical shift of the hydride varies systematically with a change in the electronegativity of the atom of the X ligand trans to the hydride (Figure 9). A rough correlation is observed showing an upfield hydride shift as the electronegativity of the atom trans to the hydride increases. This correlation provides support for the bonding modes proposed in Chart 1 for the ambidentate ligands. As expected from the correlation in Figure 9, the hydride peak for the dimethyl malonate complex is found upfield at −21.8 ppm for oxygen trans to hydride, not downfield for carbon trans to hydride. The chemical shift of the hydride in the malononitrile anion complex RuH(NCCHCN)(tmen)(PPh$_3$)$_2$ is −15.4 ppm: more consistent, according to Figure 9, with nitrogen coordination instead of carbon coordination. Indeed, the structure of the analogous osmium complex shows that it is monodentate and bonded via

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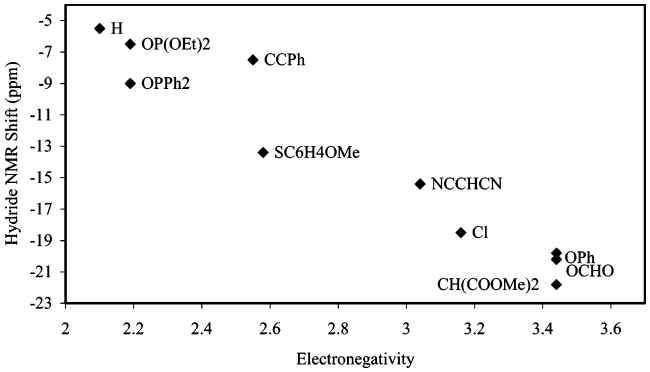


Figure 9. Correlation between hydride ^{1}H NMR shifts and the electronegativity of the atom trans to hydride in the complexes RuHX(tmen)(PPh_3)$_2$.

nitrogen,[43] and the structurally characterized Michael adduct (Figure 7) has a similar chemical shift of −15.3 ppm.

When X is OP(OEt)$_2$ and $OPPh_2$, the usual hydride triplet pattern is split into a doublet of triplets. As expected, the trans coupling to the phosphorus of the diethyl phosphonyl and diphenylphosphinyl ligands is large with respect to the cis coupling to the triphenylphosphine ligands and shows that these X ligands are bonded to ruthenium via phosphorus.

The complex RuH(NCC(C_6H_9O)CN)(tmen)(PPh_3)$_2$ has unique NMR spectra compared to those of the other tmen complexes, due to the chiral carbon C(10) (Figure 7). The phosphine ligands are diastereotopic, and so the ^{31}P{^{1}H} NMR spectrum displays an AB pattern. Although the NH peaks are masked by the cyclohexanoyl multiplet, four distinct methyl peaks are observed for the tmen ligand.

The chirality of the dach ligand results in more complex NMR spectra for its complexes. The diastereotopic phosphine ligands produce an AB pattern in the ^{31}P{^{1}H} NMR spectra, except in the case of RuH(4-SC_6H_4OMe)(dach)(PPh_3)$_2$, where a coincidental overlapping of peaks produces a singlet. The similarity of the environments of the phosphine ligands still produces a triplet pattern for the hydride peaks in the ^{1}H NMR spectra. The hydride chemical shifts for the dach complexes follow the same electronegativity correlation found with the tmen complexes in Figure 9. The phosphorus NMR spectra for the diethyl phosphonyl (Figure 10) and diphenylphosphinyl complexes are interesting because of the ABX patterns produced.

The NMR spectra of RuH(OPh)(dach)(PPh_3)$_2$ provide evidence for one major and two minor isomers. The major hydride resonance is a triplet at −24.4 ppm. The relative peak intensities indicate that this pattern corresponds with an AB pattern in the ^{31}P{^{1}H} NMR spectrum with δ_A 69.0 and δ_B 65.9 ppm. The similarity to the spectra of the other dach complexes suggests that the major isomer is the usual hydride trans to X isomer. The minor hydride patterns consist of a triplet at −13.4 ppm and a doublet of doublets at −13.7 ppm. These peaks correspond with two doublets at 82.0 and 67.7 ppm and two doublets at 80.0 and 67.4 ppm, respectively, in the ^{31}P{^{1}H} NMR. Cis isomers of this type have been characterized for the complexes RuH_2(dach)(PPh_3)$_2$ and RuH_2(en)(PPh_3)$_2$.[23] The isomers that have a hydride trans to a phosphine give a J_{HP} coupling constant close to 100 Hz. All J_{HP} constants for the minor isomers of RuH(OPh)(dach)(PPh_3)$_2$ are significantly smaller, suggesting that the hydride is always trans to an amine ligand. The three isomers are shown in Figure 11.

Infrared Characterization. The ruthenium hydride stretches found in the IR spectra of the tmen and dach complexes follow a rough correlation with the electronegativity of the atom trans

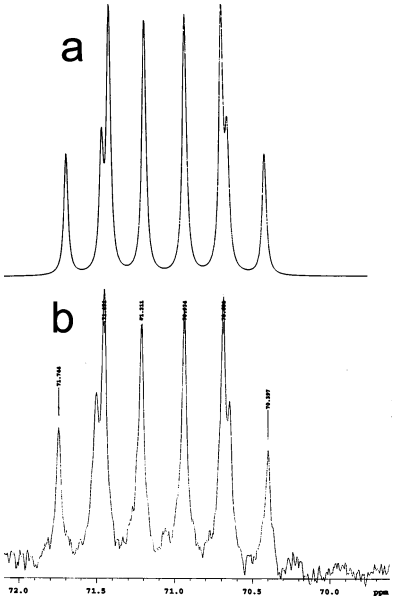


Figure 10. PPh_3 peaks in the ^{31}P{^{1}H} NMR spectrum at 300 MHz of RuH(OP(OEt)$_2$)(dach)(PPh_3)$_2$: (a) simulated; (b) experiment.

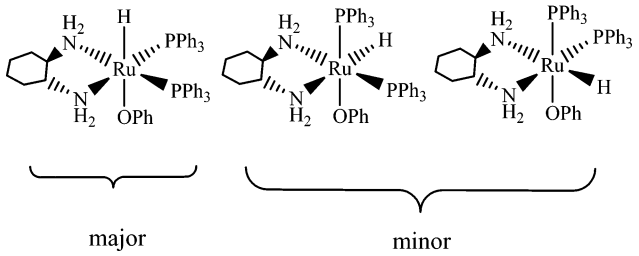


Figure 11. Major and minor isomers of RuH(OPh)(dach)(PPh_3)$_2$.

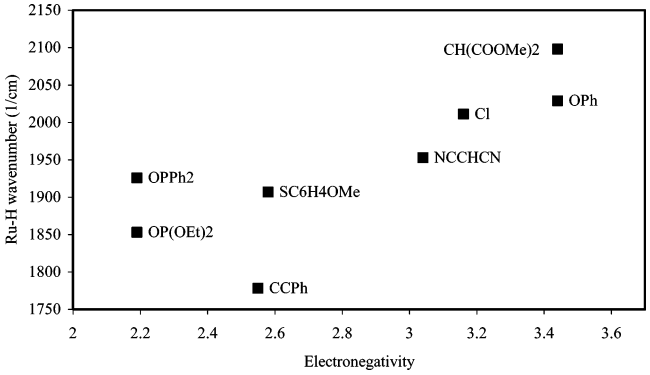


Figure 12. Correlation between the Ru−H stretching frequency and trans-atom electronegativity.

to the hydride, much like that found for the hydride NMR shifts. The metal hydride stretches occur between 1770 and 2100 cm^{-1}. The more electronegative atoms trans to the hydride tend to increase the stretching frequency, as shown in Figure 12.

The CN stretching wavenumber from the IR spectrum of RuH(NCCHCN)(diamine)(PPh_3)$_2$, diamine = tmen (2127 cm^{-1}), dach (2124 cm^{-1}), was useful in determining the coordination mode of the dicyanomethyl ligand. This ligand can coordinate through the deprotonated carbon or through one of the nitrile nitrogens. The CN stretches between 2120 and 2130 cm^{-1} are indicative of a nitrogen-bound ligand. Carbon-bound ligands would be expected to give a stretching wavenumber above 2200 cm^{-1}.[44,45] The X-ray crystal structure of the analogous osmium complex, OsH(NCCHCN)(tmen)(PPh_3)$_2$, has been reported to have a nitrogen-bound dicyanomethyl ligand and a CN stretch

Table 1. Catalysts for the Michael Addition of Dimethyl Malonate to 2-Cyclohexen-1-one in THF at 20 °C[a]

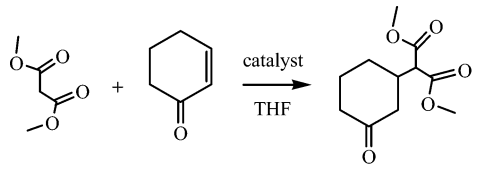
cat.	[cat.], mM	[sub], M	sub:cat.	time, h	conversn, %	TOF, h^{-1}
1	2.5	0.23	104	18	98	5.7
RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$	3.1	0.33	108	18	100	≥6.0
RuH(OPh)(tmen)(PPh$_3$)$_2$	2.0	0.20	101	24	94	4.0
RuHCl(tmen)(PPh$_3$)$_2$	3.0	0.33	110	18	0	0.0

[a] A 3 mL amount of solvent was used. Abbreviations: cat., catalyst; sub, substrate.

of 2126 cm^{-1}.[43] A similar CN stretch at 2102 cm^{-1} for the trapped Michael adduct suggests that this coordination mode is maintained when 2-cyclohexen-1-one is added to the dicyanomethyl ligand, as indicated by the X-ray crystal structure (Figure 7).

The CO and CC stretching absorptions at 1632 and 1538 cm^{-1} in the spectrum of RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$ are similar to those of the acac ligand and suggest that an electron-delocalized enolate form of the ligand is coordinated. This is consistent with an oxygen-bonded, as opposed to carbon-bonded, malonate ligand.

Michael Addition. The amido complex **1** and the complexes RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$ and RuH(OPh)(tmen)(PPh$_3$)$_2$ all catalyze the Michael addition of dimethyl malonate to 2-cyclohexen-1-one to produce 3-[bis(methoxycarbonyl)methyl]-cyclohexanone in THF at room temperature (eq 4 and Table 1).

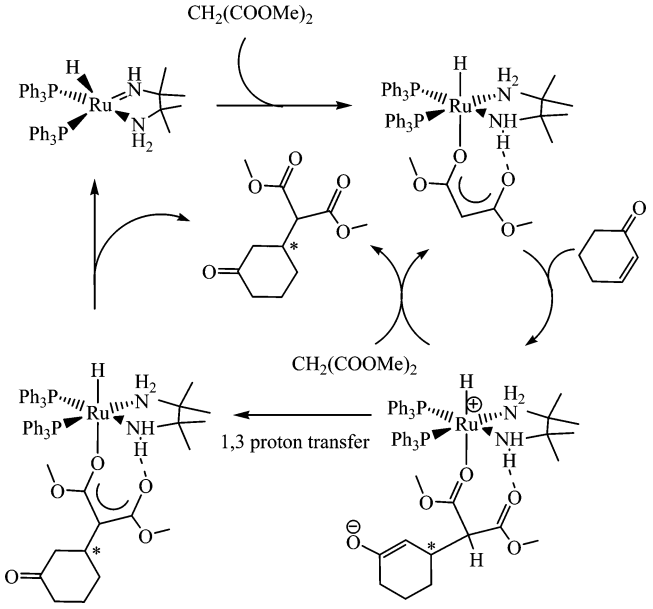


(4)

The amido and malonate complexes have similar activities, possibly suggesting that the addition of the C−H bond of dimethyl malonate to the amido complex is a step in the catalytic cycle. Their activity is more than 10 times that of the complexes RuH(BH$_4$)(S-binap)((*R,R*)-PPh$_2$CHPhCCHMeNH$_2$) (TOF 0.4 h^{-1} at 20 °C),[25] Ru(C$_6$Me$_6$)(NHCHPhCHPhNTs) (TOF 0.6 h^{-1} at 30 °C),[10] and La(O^{i}Pr)$_3$)/*S,S*-linked binol (TOF 0.13 h^{-1} at 20 °C),[46] although these other catalysts are highly enantioselective in the reaction. Tetrahydrofuran was chosen as the solvent, because it was found to be optimum for our borohydride catalysts.[25,26] The chloro complex RuHCl(tmen)(PPh$_3$)$_2$ and the malononitrile complex are not catalysts under these conditions.

While the malononitrile complex can be used as a Michael donor to 2-cyclohexen-1-one in a stoichiometric reaction (eq 3), the malonate complex may not react in this way. NMR spectra of a mixture of RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$ and the enone in C$_6$D$_6$ did not provide direct evidence for a reaction. At the moment we propose two possible mechanisms of catalysis (Scheme 1). Starting with the amido complex **1**, the Michael donor is first deprotonated by the amido nitrogen and then coordinated to the metal. The Michael acceptor is attacked at its electrophilic carbon to form a ruthenium-coordinated adduct. This attack might be promoted by hydrogen bonding of the

Scheme 1. Proposed Mechanisms of the Michael Addition Reactions Catalyzed by Complex 1 and RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$



enone carbonyl group with an amino N−H group, but this would need to be probed in a future, more detailed study. The adduct complex might quickly react with more malonate and release the Michael adduct. Alternatively, there may be a proton shift from the Michael donor to the α-carbon of the Michael acceptor in a fashion analogous to eq 3. Deprotonation of the amine ligand and release of the Michael product would complete the catalytic cycle.

The mechanism in Scheme 1 is slightly different from that proposed by Ikariya and co-workers,[10] where a malonate that is carbon-bonded to the metal attacks an enone that is positioned by an N(amine)−H−O(carbonyl) hydrogen bond.

The complex RuH(OPh)(tmen)(PPh$_3$)$_2$ also catalyzes this Michael addition reaction (Table 1). This is explained by the fact that the phenoxide complex rapidly reacts with an equimolar amount of dimethyl malonate to give a rapidly equilibrating mixture of the phenoxide complex and the complex RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$. The ^{1}H and ^{31}P{^{1}H} NMR spectra of this reaction show hydride and phosphorus peak positions with chemical shifts that are at an average of the positions found for the individual malonate and phenoxide complexes. A broadening of some peaks is also observed. Under catalytic conditions, the large excess of dimethyl malonate would result in a large concentration of the malonate complex, which would then catalyze the reaction.

Hydrogenation of Acetophenone. The *trans*-dihydride complexes RuH$_2$(diamine)(PPh$_3$)$_2$, diamine = tmen,[3], dach,[23] are known to be extremely active ketone hydrogenation catalysts. The dihydride RuH$_2$(tmen)(PPh$_3$)$_2$ is generated by reacting complex **1** with dihydrogen, while the unstable *trans*-dihydride RuH$_2$(dach)(PPh$_3$)$_2$ can be accessed by reaction of the precursor RuHCl(dach)(PPh$_3$)$_2$ with KO^{t}Bu under dihydrogen. The only other complexes of the X trans to hydride series that are active for the hydrogenation of acetophenone to 1-phenylethanol without base at 20 °C are the phenylacetylide complexes RuH(CCPh)(tmen)(PPh$_3$)$_2$ and RuH(CCPh)(dach)(PPh$_3$)$_2$ (eq 5 and Table 2).

The turnover frequencies of the phenylacetylide complexes RuH(CCPh)(diamine)(PPh$_3$)$_2$ for the hydrogenations in neat acetophenone are less than those of the corresponding complexes **1**

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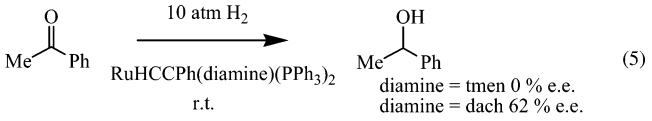
Table 2. Comparison of the Activity and Enantioselectivity of the Catalysts RuHX(diamine)$(PPh_3)_2$ in Neat Ketone or Benzene Solution at 20 °C

cat.	[cat.], mM	[ketone], M	H_2 pressure, atm	time, h	conversn, %	ee, %[a]	TOF, h^{-1}
			In Neat Acetophenone				
1	5.5	8.6	10	1	100	0	>1559
RuHCl(dach)$(PPh_3)_2$/base	1.8	8.6	3	< 8	100	62	>625
RuH(CCPh)(tmen)$(PPh_3)_2$	14	8.6	10	3.3	2	0	4
	14	8.6	10	24	100	0	>26
RuH(CCPh)(dach)$(PPh_3)_2$	9	8.6	10	3.5	100	62	>288
			In Benzene				
1			1			0	1070[b]
RuHCl(dach)$(PPh_3)_2$/base			5			55	715[c]
RuH(CCPh)(dach)$(PPh_3)_2$	1.0	0.017	5	0.33	1	62	0.5
	1.0	0.017	5	1.7	3	47	0.1
	1.0	0.017	5	21	6	33	0.05

[a] (*S*)-Phenylethanol. [b] Maximum rate = (112 M^{-1} s^{-1})[Ru][H_2].[3] [c] Rate = (14 M^{-1} s^{-1})[Ru][H_2].[23]

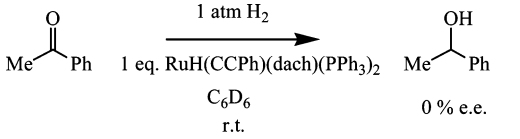


(5)

and the RuHCl(dach)$(PPh_3)_2$ complex when activated by KO^{t}Bu, especially at low conversion. The enantiopure complex RuH(CCPh)(dach)$(PPh_3)_2$ produces 1-phenylethanol from neat acetophenone in 62% ee(*S*), which is exactly the same optical purity as is observed for hydrogenations using the dihydride complex RuH_2(dach)$(PPh_3)_2$ (as a mixture of isomers).[23]

When benzene is used as a solvent, the TOF values for the phenylacetylide complexes are much less than those for the dihydride precursors. For the dach complex, the ee of the 1-phenylethanol starts off at 62% but degrades over time.

A stoichiometric mixture of RuH(CCPh)(dach)$(PPh_3)_2$ and acetophenone in benzene-d_6 under Ar does not react after 3 h. When the solution is placed under 1 atm of hydrogen and is left for 24 h, a 27% conversion to racemic 1-phenylethanol is observed (eq 6). Apparently the degradation of ee at these high ruthenium concentrations is even more serious.



(6)

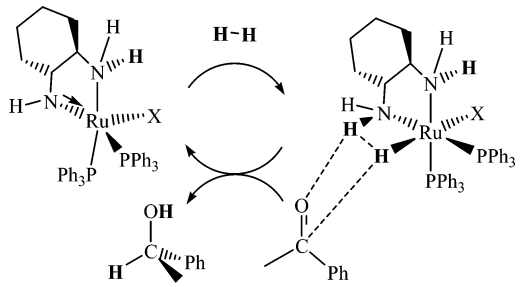
The mechanism of action of the phenylacetylide complexes (X = CCPh) does not appear to follow the cycle established for the dihydrides (X = H) (Scheme 2). When X = H, the dihydride transfers H^-/H^+ equivalents rapidly to the ketone to produce the hydridoamido complex. In contrast, this step is not observed for the phenylacetylide complexes. Even though this carbon-donor ligand has a low electronegativity and hence a high trans influence, it does not make the hydride trans to CCPh hydridic enough for the transfer reaction to acetophenone under comparable conditions.

These results are best explained by the conversion of the phenylacetylide complexes to the active dihydrides, which are the actual catalysts (eq 7). This reaction must be faster in neat

$$\text{RuH(CCPh)(diamine)}(PPh_3)_2 + H_2 \rightarrow \text{RuH}_2\text{(diamine)}(PPh_3)_2 + \text{HCCPh} + \text{unidentified products} \quad (7)$$

acetophenone than in benzene solution, because the TOF values are much larger under the former conditions (Table 2). A peak for free phenylacetylene is observed by gas chromatography for reactions performed both in neat acetophenone and in benzene. Catalysis is proposed to occur via Scheme 2 with X = H only. Side products in the reaction appear to catalyze the racemization of the alcohol that is produced, thus explaining the degradation in ee during prolonged reaction times.

Scheme 2. Hypothetical Cycle for the Hydrogenation of Acetophenone Catalyzed by the Complexes RuHX(dach)$(PPh_3)_2$ with X Trans to H[a]



[a] The cycle has been established for X = H.

Conclusions

A variety of potential catalyst precursors RuHX(diamine)$(PPh_3)_2$ with X trans to hydride are generated by the reaction of weak acids HX with the amido complex RuH$(NHCMe_2CMe_2NH_2)(PPh_3)_2$. Similar complexes with the dach ligand are produced by reaction of the KO^{t}Bu/HX with RuHCl(dach)$(PPh_3)_2$. Acids with a range of strengths can be used, but aniline with pK_a^{DMSO} = 30.6 does not react. The X ligands with hydrogen-bond acceptors, including O_2CH, $OPPh_2$, $OP(OEt)_2$, and $CH(COOMe)_2$, form O···HN hydrogen bonds with a cis amino group. The ambidentate ligands NCCHCN and $CH(COOMe)_2$ bond to ruthenium via a N or O donor, respectively, instead of the more hindered carbon centers. The mode of coordination is signaled by distinctive chemical shifts of the hydride resonance in the ^{1}H NMR spectrum and characteristic wavenumber values for the Ru−H stretch that vary with the electronegativity of the donor atom on X. The amido complex RuH$(NHCMe_2CMe_2NH_2)(PPh_3)_2$ and the related malonate and phenoxide complexes are active catalysts or precursors to catalysts for the Michael addition reaction. The activation of O−H, P−H, and S−H bonds at the ruthenium−nitrogen bond has been demonstrated and opens the possibility of new catalytic processes involving these elements.

Only the complexes with X = H, CCPh have activity as catalysts for acetophenone hydrogenation at room temperature. The phenylacetylide complexes RuH(CCPh)(diamine)$(PPh_3)_2$ are likely converted to the dihydrides under the conditions of the hydrogenation reaction, and so only the X = H complexes,

out of all of the X complexes tested, are true ketone hydrogenation catalysts.

Experimental Section

General Considerations. All preparations and manipulations were carried out under an argon, nitrogen, or hydrogen atmosphere using standard Schlenk, vacuum-line, and glovebox techniques. Dry, oxygen-free solvents were always used. Hexanes, tetrahydrofuran, and diethyl ether were dried and distilled under argon from sodium benzophenone ketyl. Toluene was dried and distilled under argon from molten sodium. Deuterated solvents were degassed and dried over activated molecular sieves. NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer (300 MHz for ^{1}H and 121.5 MHz for ^{31}P). All ^{31}P chemical shifts are reported relative to 85% H_2PO_4 as an external reference. All ^{1}H chemical shifts are reported relative to TMS but referenced to partially deuterated solvent signals. All infrared spectra were recorded on a Nicolet 550 Magna-IR spectrometer. Elemental analyses were done in the Chemistry Department on samples handled under argon. The complexes containing the dach ligand were spectroscopically pure and free of potassium salts, and yet they were reproducibly analyzed with low carbon (about 2% below the calculated values, even when oxidants were added).

Synthesis of *trans*-RuHX(tmen)(PPh$_3$)$_2$. All syntheses involving the addition of a weak acid, HX, to **1** were performed in the following manner: HX and **1** were added to a flask under argon and dissolved in toluene (1 mL). The orange solution quickly became yellow when stirred. The solution was stirred for 30 min. Hexanes (3 mL) was added to precipitate the product. The yellow solid was filtered, washed with hexanes, and dried under vacuum.

RuH(OPh)(tmen)(PPh$_3$)$_2$. Phenol (46 mg, 0.489 mmol) and **1** (300 mg, 0.404 mmol) were used. Crystals of quality sufficient for X-ray crystallography were grown by slow diffusion of hexanes into a concentrated solution of RuH(OPh)(tmen)(PPh$_3$)$_2$ with an extra 1 equiv of phenol in benzene. Yield: 260 mg (77%). ^{1}H NMR (C_6D_6, δ): 6.6−8.2 (m, phenyl, 35 H), 3.4 (d, NH, 2 H, J_{HH} = 10.0 Hz), 2.0 (d, NH, 2 H, J_{HH} = 10.0 Hz), 0.72 (s, CH_3, 6 H), 0.65 (s, CH_3, 6 H), −20.2 (t, RuH, 1 H, J_{HP} = 27.1 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 67.7 (s, PPh_3, 2 P). IR (Nujol, cm^{-1}): 3319 (ν(NH)), 2029 (ν(RuH)). Anal. Calcd for $RuP_2ON_2C_{48}H_{52}$: C, 68.96; H, 6.27; N, 3.35. Found: C, 68.36; H, 6.18; N, 2.99.

RuH(OPh-*d*$_5$)(tmen)(PPh$_3$)$_2$. ^{1}H NMR (C_6D_6, δ): 6.0−8.5 (m, phenyl, 30 H), 3.5 (br s, NH, 2 H), 2.0 (br s, NH, 2 H), 0.7 (s, CH_3, 12 H), −20.7 (t, RuH, 1 H, J_{HP} = 27.4 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 67.2 (s).

RuH(4-SC$_6$H$_4$OCH$_3$)(tmen)(PPh$_3$)$_2$. 4-Methoxybenzenethiol (24 mg, 0.171 mmol) and **1** (100 mg, 0.135 mmol) were used. Yield: 85 mg (71%). ^{1}H NMR (C_6D_6, δ): 6.6−8.1 (m, phenyl, 34 H), 3.4 (s, OCH_3, 3 H), 3.2 (d, NH, 2 H, J_{HH} = 10.3 Hz), 1.9 (d, NH, 2 H, J_{HH} = 10.3 Hz), 0.7 (s, CH_3, 6 H), 0.5 (s, CH_3, 6 H), −13.4 (t, RuH, 1 H, J_{HP} = 24.6 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 67.7 (s, PPh_3, 2 P). IR (Nujol, cm^{-1}): 3340 (ν(NH)), 3321 (ν(NH)), 3270 (ν(NH)), 3217 (ν(NH)), 1907 (ν(RuH)). Anal. Calcd for $RuSP_2ON_2C_{49}H_{54}\cdot 0.25C_7H_8$: C, 67.35; H, 6.24; N, 3.10. Found: C, 67.39; H, 6.31; N, 3.12.

RuH(OPPh$_2$)(tmen)(PPh$_3$)$_2$. Diphenylphosphine oxide (34 mg, 0.164 mmol) and **1** (122 mg, 0.168 mmol) were used. Yield: 102 mg (66%). ^{1}H NMR (C_6D_6, δ): 6.6−8.3 (m, phenyl, 40 H), 5.4 (s br, NH, 2 H), 2.0 (d, NH, 2 H, J_{HH} = 9.3 Hz), 0.9 (s, CH_3, 6 H), 0.8 (s, CH_3, 6 H), −9.0 (dt, RuH, 1 H, J_{HP1} = 99.9 Hz, J_{HP2} = 24.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 80.1 (t, $OPPh_2$, 1 P, J_{PP} = 17.5 Hz), 65.7 (d, PPh_3, 2 P). IR (Nujol, cm^{-1}): 3342 (ν(NH)), 1926 (ν(RuH)). Anal. Calcd for $RuP_3ON_2C_{54}H_{57}\cdot 2C_7H_8$: C, 70.71; H, 6.32; N, 2.70. Found: C, 70.01; H, 6.29; N, 2.70.

RuH(OP(OEt)$_2$)(tmen)(PPh$_3$)$_2$. Diethyl phosphite (67 mg, 0.485 mmol) and **1** (300 mg, 0.404 mmol) were used. Yield: 250 mg (70%). ^{1}H NMR (C_6D_6, δ): 6.8−8.0 (m, phenyl, 30 H), 4.1−4.5 (m, NH and CH_2, 6 H), 1.8 (d, NH, 2 H, J_{HH} = 10.2 Hz), 1.2 (t, CH_3, 6 H, J_{HH} = 7.0 Hz), 1.0 (s, CH_3, 6 H), 0.9 (s, CH_3, 6 H), −6.5 (dt, RuH, 1 H, J_{HP1} = 146.1 Hz, J_{HP2} = 22.3 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 121.3 (t, $OP(OEt)_2$, 1 P, J_{PP} = 30.4 Hz), 70.4 (d, PPh_3, 2 P). IR (Nujol, cm^{-1}): 3347 (ν(NH)), 1853 (ν(RuH)). Anal. Calcd for $RuP_3O_3N_2C_{46}H_{57}\cdot 0.25C_7H_8$: C, 63.51; H, 6.59; N, 3.10. Found: C, 63.48; H, 6.43; N, 3.01.

RuH(CCPh)(tmen)(PPh$_3$)$_2$. Phenylacetylene (18 mg, 0.176 mmol), **1** (100 mg, 0.135 mmol). Yield: 55 mg (48%). ^{1}H NMR (C_6D_6, δ): 6.9−8.2 (m, phenyl, 35 H), 2.6 (d, NH, 2 H, J_{HH} = 10.6 Hz), 2.0 (d, NH, 2 H, J_{HH} = 10.6 Hz), 0.9 (s, CH_3, 6 H), 0.7 (s, CH_3, 6 H), −7.5 (t, RuH, 1 H, J_{HP} = 22.2 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 73.9 (s, PPh_3, 2 P). IR (Nujol, cm^{-1}): 3347 (ν(NH)), 3323 (ν(NH)), 3285 (ν(NH)), 3264 (ν(NH)), 2053 (ν(CC)), 1778 (ν(RuH)). Anal. Calcd for $RuP_2N_2C_{50}H_{52}$: C, 71.16; H, 6.21; N, 3.32. Found: C, 71.21; H, 6.34; N, 3.46.

RuH(NCCHCN)(tmen)(PPh$_3$)$_2$. Malononitrile (15 mg, 0.227 mmol) and **1** (150 mg, 0.202 mmol) were used. Yield: 151 mg (93%). ^{1}H NMR (C_6D_6, δ): 6.7−7.8 (m, phenyl, 30 H), AB pattern 2.0 (A, NH, 2 H, J_{AB} = 10.9 Hz) and 1.9 (B, NH, 2 H), 0.6 (s, CH_3, 6 H), 0.5 (s, CH_3, 6 H), −15.4 (t, RuH, 1 H, J_{HP} = 25.2 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 70.3 (s, PPh_3, 2 P). IR (Nujol, cm^{-1}): 3318 (ν(NH)), 3221 (ν(NH)), 3155 (ν(NH)), 2127 (ν(CN)), 1953 (ν(RuH)). Anal. Calcd for $RuP_2N_4C_{45}H_{48}$: C, 66.90; H, 5.99; N, 6.93. Found: C, 66.40; H, 6.02; N, 6.45.

RuH(CH(COOMe)$_2$)(tmen)(PPh$_3$)$_2$. Dimethyl malonate (27 mg, 0.2044 mmol) and **1** (120 mg, 0.1618 mmol) were used. Yield: 95 mg (67%). ^{1}H NMR (C_6D_6, δ): 6.8−7.8 (m, phenyl, 30 H), 4.6 (s, CH, 1 H), 4.3 (d, NH, 2 H, J_{HH} = 10.6 Hz), 3.5 (s, OCH_3, 6 H), 2.1 (d, NH, 2 H, J_{HH} = 10.6 Hz), 1.0 (s, CH_3, 6 H), 0.7 (s, CH_3, 6 H), −21.8 (t, RuH, 1 H, J_{HP} = 27.1 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): 69.4 (s, PPh_3, 2 P). IR (Nujol, cm^{-1}): 3349 (ν(NH)), 3302 (ν(NH)), 3112 (ν(NH)), 3057 (ν(NH)), 2098 (ν(RuH)), 1682 (ν(CO)), 1538 (ν(CC)). Anal. Calcd for $RuP_2O_4N_2C_{47}H_{50}$: C, 64.59; H, 6.23; N, 3.21. Found: C, 64.0; H, 6.41; N, 3.11.

RuH(NCC(C$_6$H$_9$O)CN)(tmen)(PPh$_3$)$_2$. 2-Cyclohexen-1-one (9 mg, 0.0936 mmol) and RuH(NCCHCN)(tmen)(PPh3)$_2$ (32 mg, 0.396 mmol) were added to a flask under argon and dissolved in toluene (1 mL). The yellow solution was stirred for 3 h. Hexanes was added to precipitate the product. The yellow solid was filtered, washed with hexanes, and dried under vacuum. Yield: 34 mg (95%). ^{1}H NMR (C_6D_6, δ): 6.8−7.8 (m, phenyl, 30 H), 1.1−2.7 (m, cyclohexanoyl, NH, 13 H), 0.64 (s, CH_3, 3 H), 0.63 (s, CH_3, 3 H), 0.57 (s, CH_3, 3 H), 0.48 (s, CH_3, 3 H), −15.3 (t, RuH, 1 H, J_{HP} = 24.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6, δ): AB pattern, 70.6 (A, PPh_3, 1 P, J_{AB} = 37.8 Hz), 69.7 (B, PPh_3, 1 P). IR (Nujol, cm^{-1}): 3401 (ν(NH)), 3321 (ν(NH)), 3154 (ν(NH)), 3051 (ν(NH)), 2102 (ν(CN)), 1959 (ν(RuH)), 1704 (ν(CO)). Anal. Calcd for $RuP_2ON_4C_{51}H_{56}\cdot 0.25C_6H_6$: C, 68.28; H, 6.28; N, 6.07. Found: C, 68.38; H, 6.16; N, 6.04.

Synthesis of *trans*-RuHX(dach)(PPh$_3$)$_2$. All of the syntheses involving the substitution of HCl for HX in **2** were performed as follows: HX, potassium *tert*-butoxide, and **2** were added to a flask under nitrogen and dissolved in THF (1 mL). A small amount of red-orange solution was formed when the solvent was added, but the solution became yellow upon stirring. The yellow solution was stirred for 15 min and then filtered through Celite. The filtrate was reduced to dryness, the residue was stirred in 2:1 hexanes−ether (3 mL), this mixture was filtered, and the solid was washed with hexanes and dried under vacuum.

RuH(OPh)(dach)(PPh$_3$)$_2$. Phenol (19 mg, 0.202 mmol), potassium *tert*-butoxide (20 mg, 0.178 mmol), and **2** (127 mg, 0.164 mmol) were used. Yield: 45 mg (33%). ^{1}H NMR (C_6D_6, δ): 6.5−8.1 (m, phenyl, 35 H), 0.0−3.8 (m, diamine, 14 H), −20.4 (t, RuH major isomer, J_{HP} = 26.1 Hz), −13.4 (t, RuH minor isomer 1, J_{HP} = 27.7 Hz), −13.7 (dd, RuH minor isomer 2, J_{HP1} = 33.8 Hz, J_{HP2}

= 24.4 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): major isomer, AB pattern, 69.0 (A, PPh_3, J_{AB} = 38.9 Hz) and 65.9 (B, PPh_3); minor isomer 1, 82.0 (d, J_{PP} = 36.5 Hz), 67.7 (d); minor isomer 2, 80.0 (d, J_{PP} = 37.2 Hz), 67.4 (d). IR (Nujol, cm^{-1}): 3319 (ν(NH)), 2028 (ν(RuH)).

RuH(4-$SC_6H_4OCH_3$)(dach)(PPh_3)$_2$. 4-Methoxybenzenethiol (30 mg, 0.214 mmol), potassium *tert*-butoxide (22 mg, 0.196 mmol), and **2** (140 mg, 0.180 mmol) were used. Yield: 135 mg (85%). ^1H NMR (C_6D_6, δ): 6.5−8.3 (m, phenyl, 34 H), 3.3 (s, OCH_3, 3 H), 0.0−2.8 (m, cyclohexyl, 14 H), −13.8 (t, RuH, 1 H, J_{HP} = 23.7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 69.2 (s, PPh_3). IR (Nujol, cm^{-1}): 3340 (ν(NH)), 3322 (ν(NH)), 1907 (ν(RuH)).

RuH($OPPh_2$)(dach)(PPh_3)$_2$. Diphenylphosphine oxide (31 mg, 0.153 mmol), potassium *tert*-butoxide (17 mg, 0.151 mmol), and **2** (110 mg, 0.142 mmol) were used. Yield: 70 mg (52%). ^1H NMR (C_6D_6, δ): 6.5−8.5 (m, phenyl, 40 H), 0.0−3.3 (m, diamine, 14 H), −9.0 (dt, RuH, 1 H, J_{HP1} = 98.7 Hz, J_{HP2} = 23.5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): ABX pattern, 80.8 (X, $OPPh_2$, 1 P), 66.7 (A, PPh_3, 1 P, J_{AX} = 16.2 Hz, J_{AB} = 33.7 Hz), 66.1 (B, PPh_3, 1 P, J_{BX} = 18.8 Hz). IR (Nujol, cm^{-1}): 3328 (ν(NH)), 3271 (ν(NH)), 1877 (ν(RuH)).

RuH($OP(OEt)_2$)(dach)(PPh_3)$_2$. Diethyl phosphite (24 mg, 0.148 mmol), potassium *tert*-butoxide (17 mg, 0.151 mmol), and **2** (104 mg, 0.134) were used. Yield: 20 mg (17%). ^1H NMR (C_6D_6, δ): 6.8−8.2 (m, phenyl, 30 H), 4.5 (dq, CH_2, 4 H, J_{HP} = 3.3 Hz, J_{HH} = 7.0 Hz), 0.0−4.3 (m, diamine, 14 H), 1.1 (t, CH_3, 6 H), −6.6 (dt, RuH, 1 H, J_{HP1} = 142.5 Hz, J_{HP2} = 20.8 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): ABX pattern, 118.8 (X, $OP(OEt)_2$, 1 P), 71.4 (A, PPh_3, 1 P, J_{AX} = 29.2 Hz, J_{AB} = 35.2 Hz), 70.7 (B, PPh_3, 1 P, J_{BX} = 30.4 Hz). IR (Nujol, cm^{-1}): 3337 (ν(NH)), 3279 (ν(NH)), 3232 (ν(NH)), 1791 (ν(RuH)), 1575 (ν(OP)).

RuH(CCPh)(dach)(PPh_3)$_2$. Phenylacetylene (23 mg, 0.225 mmol), potassium *tert*-butoxide (22 mg, 0.196), and **2** (140 mg, 0.180 mmol) were used. Yield: 40 mg (26%). ^1H NMR (C_6D_6, δ): 6.6−8.4 (m, phenyl, 35 H), 0.0−3.4 (m, diamine, 14 H), −7.5 (t, RuH, 1 H, J_{HP} = 21.6 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): AB pattern, 74.9 (A, PPh_3, 1 P, J_{AB} = 42.8 Hz), 74.5 (B, PPh_3, 1 P). IR (Nujol, cm^{-1}): 3323 (ν(NH)), 2053 (ν(CC)), 1778 (ν(RuH)).

RuH(NCCHCN)(dach)(PPh_3)$_2$. Malononitrile (10 mg, 0.151 mmol), potassium *tert*-butoxide (17 mg, 0.151 mmol), and **2** (107 mg, 0.138 mmol) were used. Yield: 61 mg (55%). ^1H NMR (C_6D_6, δ): 6.7−8.1 (m, phenyl, 30 H), 0.0−3.6 (m, diamine, 14 H), −15.8 (t, RuH, 1 H, J_{HP} = 25.0 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): AB pattern, 71.2 (A, PPh_3, 1 P, J_{AB} = 38.3 Hz) and 70.4 (B, PPh_3, 1 P). IR (Nujol, cm^{-1}): 3324 (ν(NH)), 2124 (ν(CN)), 1959 (ν(RuH)).

Hydrogenation of Neat Acetophenone. Under an argon atmosphere, RuH(CCPh)(tmen)(PPh_3)$_2$ (11 mg, 0.0130 mmol) was dissolved in acetophenone (999 mg, 8.315 mmol) (S:C = 638:1). The solution was transferred by syringe to a reactor under hydrogen and the reactor pressurized with 10 atm of hydrogen gas. Aliquots were collected at 3.25 and 24 h. Analysis by GC showed 2% and 100% conversion to 1-phenylethanol, respectively.

The above procedure was used with RuH(CCPh)(dach)(PPh_3)$_2$ (7 mg, 0.00832 mmol) and acetophenone (1.008 g, 8.3895 mmol) (S:C = 1008:1). An aliquot was taken at 3.5 h and analyzed by chiral GC. The chromatogram showed 100% conversion and 62% ee.

Hydrogenation of Acetophenone in Benzene. A solution of RuH(CCPh)(dach)(PPh_3)$_2$ was prepared in benzene with a concentration of 3.33×10^{-3} M. A 1.5 mL portion of this stock solution was diluted in 2 mL of benzene. The solution was drawn into a syringe. A solution of acetophenone (10 mg) was prepared in benzene (3 mL). This was drawn into a syringe. Both solutions were injected into a reactor under 5 atm of hydrogen gas, giving a total sample volume of 5 mL and catalyst and substrate concentrations of 1.00×10^{-3} and 0.0167 M, respectively. Aliquots were taken at 1200, 2400, 3600, 4800, 6000, and 77 100 s and analyzed by chiral GC for conversion and ee. Conversion (%)/ee (%) values for the above aliquots were 1/62, 1.5/57, 2/54, 2.5/52, 3/47, and 6/33, respectively.

Stoichiometric Reaction. RuH(CCPh)(dach)(PPh_3)$_2$ (10 mg, 0.0119 mmol) and acetophenone (2 mg, 0.0166 mmol) were reacted in C_6D_6 in an NMR tube with a gas adaptor. After 3 h no reaction was observed by ^1H and ^{31}P NMR spectroscopy. The sample was placed under 1 atm of hydrogen gas. At this point, 1-phenylethanol was observed in the ^1H NMR. The sample was left under hydrogen for 24 h and then analyzed by GC. The chromatogram showed 27% conversion and 1% ee.

Michael Addition. 2-Cyclohexen-1-one, dimethyl malonate, and a catalyst were dissolved in THF (ca. 3 mL) under argon and stirred. An aliquot was taken and exposed to oxygen to kill the catalyst. The sample was analyzed by chiral GC to determine conversion to the Michael product. Specific conditions and conversions are shown in Table 1.

Reaction of RuH(OPh)(tmen)(PPh_3)$_2$ with Dimethyl Malonate. RuH(OPh)(tmen)(PPh_3)$_2$ (54 mg, 0.0646 mmol) and dimethyl malonate (12 mg, 0.09083 mmol) were dissolved in C_6D_6 under argon. Equilibrium was observed by ^1H and $^{31}P\{^1H\}$ NMR. ^1H NMR (C_6D_6, δ): 6.5−7.9 (m, phenyl), 3.4 (s br, NH), 3.2 (s, OCH_3), 2.9 (s br, NH), 1.9 (s br, NH), 0.7 (s br, CH_3), −20.7 (t, RuH, J_{HP} = 27.9 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 68.4 (s).

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Supporting Information Available: X-ray crystallographic data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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