Unexpected Formation of the Isopropylamine Complex [2,3,4,5-$Ph_4(\eta^4$-$C_4CO)](CO)_2Ru(H_2NCHMe_2)$ in the Attempted Synthesis of an Isopropyl Alcohol Complex

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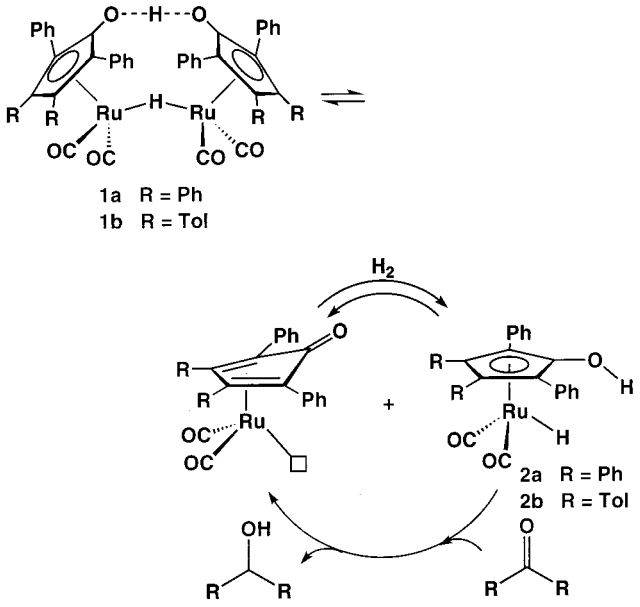
The reaction of [2,3,4,5-$Ph_4(\eta^4$-$C_4CO)]Ru(CO)_3$ (**5a**) with Na_2CO_3 in aqueous acetone followed by low-temperature treatment with NH_4Cl was reported to give the material **A**, which was formulated as the isopropyl alcohol complex [2,3,4,5-$Ph_4(\eta^4$-$C_4CO)](CO)_2Ru$-$(HOCHMe_2)$ (**3a**). Reinvestigation of this reaction indicates that **A** is instead the isopropylamine complex [2,3,4,5-$Ph_4(\eta^4$-$C_4CO)](CO)_2Ru(H_2NCHMe_2)$ (**4a**). The formation of **4a** is proposed to occur by formation of the imine of acetone followed by reduction of the imine by the (hydroxycyclopentadienyl)ruthenium hydride [2,3,4,5-$Ph_4(\eta^5$-$C_4COH)]Ru(CO)_2H$ (**2a**) formed in the reaction of **5a** with Na_2CO_3 in aqueous acetone and subsequent acidification with aqueous NH_4Cl.

Introduction

Shvo's diruthenium hydride complex {[2,3,4,5-$Ph_4(\eta^5$-$C_4CO)]_2H\}Ru_2(CO)_4(\mu$-H) (**1a**) is an efficient catalyst for the hydrogenation of aldehydes and ketones[1] and is also very useful in the transfer hydrogenation of ketones using alcohols as the reducing agent.[2] In the reduction of ketones to alcohols, the mononuclear [2,3,4,5-$Ph_4(\eta^5$-$C_4COH)]Ru(CO)_2H$ (**2a**) has been proposed to be the active reducing agent and has been shown to reduce aldehydes and ketones (Scheme 1).[1b,c]

Since the reduction of ketones could initially produce an alcohol complex, the role of alcohol complexes in these reduction systems needs to be considered, even though they have never been directly observed in the reaction mixtures. On the basis, in part, of the observation of related amine complexes, Shvo proposed that reduction of ketones by **2a** initially produced alcohol complexes (Scheme 2).[3] Bäckvall[2] and Shvo[1] have both proposed mechanisms for ketone reduction by **2a** that involve oxygen coordination to Ru followed by hydride migration to the ketone carbonyl carbon that results in the direct formation of an alcohol complex. For the microscopic reverse, Bäckvall proposes β-hydride elimination from the alcohol complex.

Scheme 1



Since β-hydride elimination normally requires a vacant coordination site at the metal and since the resulting ketone complex is formally a 20e system,

(1) (a) Shvo, Y.; Czarkie, D.; Rahamim, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7400. (b) Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885. (c) Menashe, N.; Salant, E.; Shvo, Y. *J. Organomet. Chem.* **1996**, *514*, 97.

(2) (a) Almeida, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J. E. *Chem. Eur. J.* **1996**, *2*, 1533. (b) Larsson, A. L. E.; Persson, B. A.; Bäckvall, J. E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1211. (c) Persson, B. A.; Larsson, A. L. E.; Le Ray, M.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 1645. (d) Persson, B. A.; Huerta, F. F.; Bäckvall, J. E. *J. Org. Chem.* **1999**, *64*, 5237. (e) Huerta, F. F.; Laxmi, Y. R. S.; Bäckvall, J. E. *Org. Lett.* **2000**, *2*, 1037. (f) Laxmi, Y. R. S.; Bäckvall, J. E. *Chem. Commun.* **2000**, 611.

(3) Abed, M.; Goldberg, I.; Stein, Z.; Shvo, Y. *Organometallics* **1988**, *7*, 2054.

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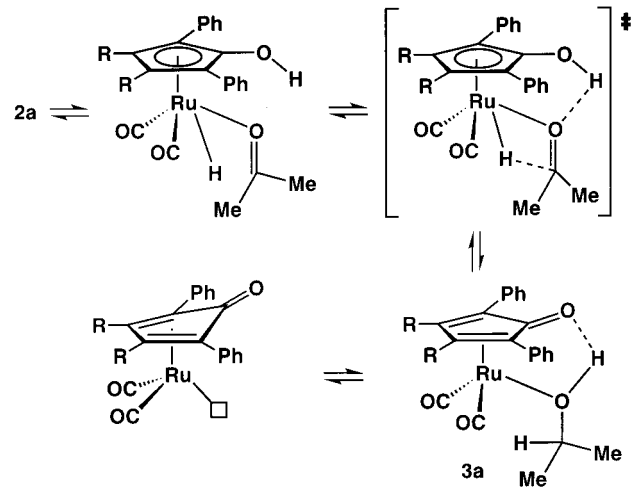
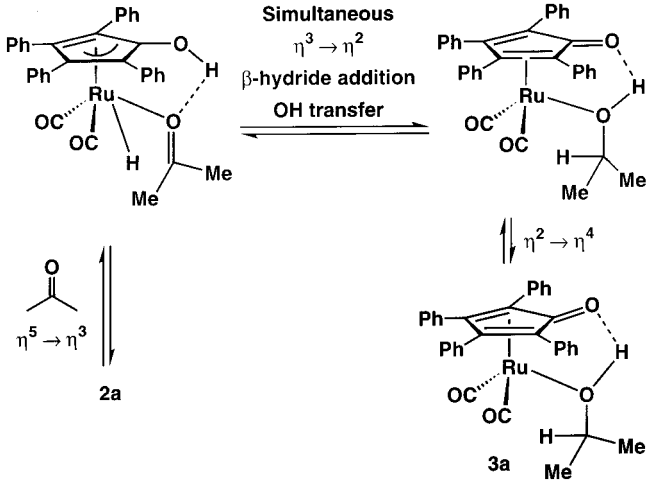
Scheme 2



Scheme 3



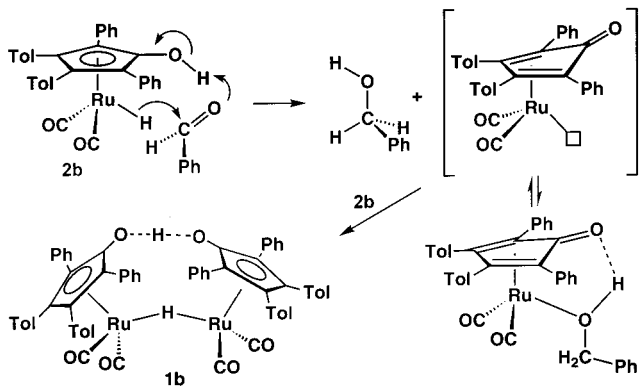
Bäckvall has suggested that η^5- to η^3-ring slippage may be involved in these reactions (Scheme 3).[4−5]

Casey has studied the kinetics of the reduction of benzaldehyde by the related tolyl complex [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru$(CO)_2$H (**2b**) and found deuterium isotope effects for both OD and RuD substitution that require simultaneous transfer of a proton from the OH group to the aldehyde oxygen and transfer of hydride from Ru to carbon.[6] Casey has proposed that benzaldehyde reduction occurs outside the coordination sphere of Ru (Scheme 4). The formation of an alcohol complex after the rate-determining step and its rapid reaction with excess RuH to give a diruthenium complex is a possibility.

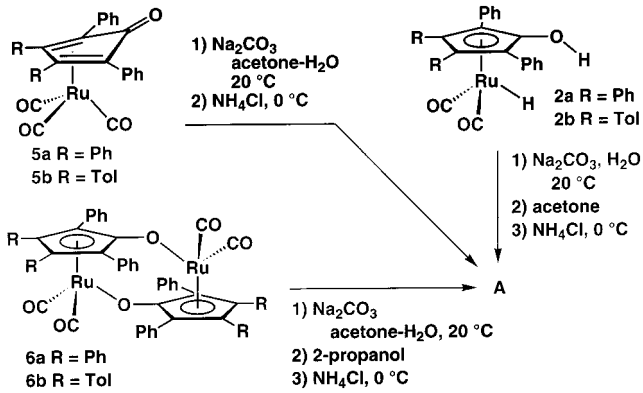
Recently, Park reported the synthesis of the ruthenium complex **A** by several routes, all of which involved acetone and a ruthenium complex and low-temperature protonation of supposed intermediates with NH_4Cl (Scheme 5).[7] Elemental analysis, X-ray crystallography,

(4) Csjernyik, G.; Éll, A. H.; Fadini, L.; Pugin, B.; Bäckvall, J. E. *J. Org. Chem.* **2002**, *67*, 1657.
(5) Shvo proposed that the hydrogenation of alkenes and alkynes proceeds through a ring-slip mechanism: Shvo, Y.; Goldberg, I.; Czerkie, D.; Reshef, D.; Stein, Z. *Organometallics* **1997**, *16*, 133.
(6) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090.
(7) Jung, H. M.; Shin, S. T.; Kim, Y. H.; Kim, M.-J.; Park, J. *Organometallics* **2001**, *20*, 3370.

Scheme 4



Scheme 5



MS, ^{1}H and ^{13}C NMR, and IR spectroscopy data of Park's complex **A** were said to support the proposed formulation as the isopropyl alcohol complex [2,3,4,5-Ph_4(η^4-C_4CO)]$(CO)_2$Ru$(HOCHMe_2)$ (**3a**).

Because of the importance of alcohol complexes in the mechanism of carbonyl reductions by RuH, the groups of Casey and Bäckvall decided to collaborate on studies of Park's "alcohol complex" **A**. The Stockholm group synthesized the material **A**, and the Wisconsin group synthesized the related compound **A*** with *p*-tolyl groups to aid in NMR spectroscopy studies.

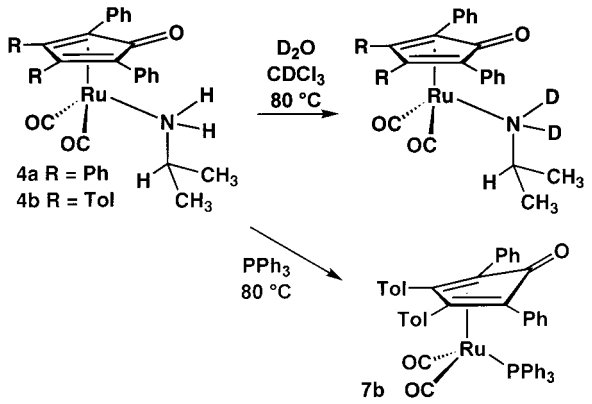
Here we report that Park's "alcohol complex" **A** is actually the isopropylamine complex [2,3,4,5-Ph_4(η^4-C_4-CO)]$(CO)_2$Ru(H_2NCHMe_2) (**4a**). Park's group has reinterpreted their data and are in agreement that **A** is the isopropylamine complex **4a**.

Results

Of Park's three routes to **A**, the highest purity and yield came from reaction of dienone complex **5a** with Na_2CO_3 in acetone−water followed by treatment with NH_4Cl at 0 °C. The Stockholm group reproduced the Park procedure and obtained material **A** in 44% yield. The Wisconsin group followed a related procedure, starting with the tolyl-substituted dienone complex **5b**, and obtained a 32% yield of the tolyl analogue **A***, which had properties similar to those reported by Park for **A**.

Problems with the "CHOH" ^{1}H NMR Resonances of A. The ^{1}H NMR spectra obtained were very similar to those reported by Park, with a major exception. Both groups noted that the resonance that had been assigned to the OH proton (δ 2.44, br s, 1H) was integrated for about 2H and appeared as a broad split peak with peak

Scheme 6



separation of about 5 Hz. In an attempt to remove water that might have been responsible for the high integration and the observation of two peaks, the NMR solvents and ruthenium complexes were rigorously dried; however, the spectra were unchanged. ^{1}H NMR spectra were taken at both 300 and 500 MHz to determine whether the two peaks at δ 2.44 were due to two chemical shifts or to coupling. The peak separation remained at about 5 Hz, indicative of coupling, not a chemical shift difference. 2D COSY ^{1}H NMR spectra of **A** demonstrated that the 2H resonance at δ 2.44 was coupled to the 1H "septet" at δ 2.87. When the "septet" resonance for the $CHMe_2$ group at δ 2.87 was blown up, the resonance was found to be a nonet (nine lines). The intensities of the seven inner lines of the δ 2.87 resonance were much closer to those expected for a nonet (inner seven lines 1:3.5:7:8.75:7:3.5:1) than for a true septet (1:6:15:20:15:6:1).[8] Moreover, when the δ 2.44 signal in the ^{1}H NMR spectrum was selectively irradiated, the coupling pattern and peak intensities of the signal at δ 2.87 were indeed changed to the feature expected for a true septet.

Problems with Exchange Reactions of A. Before the additional NMR spectroscopy data detailed above were obtained and on operating with the presumption (in scientific method terminology, "working hypothesis") that **A** and **A*** were alcohol complexes, both the Wisconsin and Stockholm groups began studies of the reactivity of **A** and **A***. These studies were at variance with the expected properties of alcohol complexes and led to questioning of the structures of **A** and **A*** and to a more careful examination of ^{1}H NMR spectroscopy data as described above.

Alcohol complexes would be expected to rapidly exchange their OH proton with D_2O. However, when D_2O was added to a solution of either **A** or the tolyl analogue **A***, the 2H resonance at δ 2.44 assigned to an "OH" group was not washed out until the solutions were heated at 80 °C (Scheme 6). This slow exchange is unexpected for an OH group.

Alcohol complexes would be expected to undergo exchange of the alcohol ligand. (Park mentioned the "Unexpected Stability of the Alcohol Complex" in the title of his paper.) The Wisconsin group also found **A*** to be very unreactive toward substitution. In an attempt to observe "exchange" with isopropyl alcohol, **A*** was heated at 80 °C in the presence of $(CD_3)_2CDOD$, but no changes in spectra were observed. Similarly, no reaction of **A*** with benzyl alcohol was seen up to 80 °C. In the mechanism for ketone reduction proposed by Casey (Scheme 4), the formation of an alcohol complex after the rate-determining step was considered as a possibility only if it reacted rapidly with excess ruthenium hydride **2b** to give the diruthenium hydride **1b**. However, no reaction of **A*** with hydride complex **2b** was seen below 80 °C, and no formation of diruthenium bridging hydride **1b** was observed. PPh_3 reacted with **A*** slowly at 80 °C to form the known phosphine complex [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$(CO)_2RuPPh_3$ (**7b**) (Scheme 6).

In Bäckvall's mechanism for alcohol oxidation (Scheme 3), an isopropyl alcohol complex would be expected to undergo rapid and reversible conversion to acetone and a (dienone)$Ru(CO)_2$ intermediate. However, when the Park material **A** was heated in acetone-d_6 at 70 °C in a sealed NMR tube, no incorporation of coordinated deuterated isopropyl alcohol or evolution of nondeuterated acetone was observed.

Reinterpretation of A and A* as Isopropylamine Complexes. The ^{1}H NMR spectra and the much lower than expected reactivity of **A** and **A*** are inconsistent with the formulation of **A** as the isopropyl alcohol complex **3a**. We are now convinced that the compounds are in fact isopropylamine complexes **4a**,**b**. The nonet at δ 2.87 for the C*H*Me_2 resonance of **A** is now explained by equal coupling to two NH_2 hydrogens and six methyl hydrogens; the chemical shift is in better agreement with a hydrogen α to nitrogen rather than to oxygen. The 2H integration of the δ 2.44 resonance is now attributed to the NH_2 group. The spectral properties of **A** and **A*** are similar to those of Shvo's diethylamine complex [2,3,4,5-Ph_4(η^4-C_4CO)]$Ru(CO)_2(NHEt_2)$ (**8**)[3,9] and Casey's benzyl(methyl)amine complex [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]$Ru(CO)_2NH(CH_3)(CH_2Ph)$ (**9**).[10] In the ^{1}H NMR spectrum of **8** in C_6D_6, the chemical shift of the CH_2N resonance is δ 2.35 and the couplings of the NH hydrogen to the diastereotopic CH_2 hydrogens are 5.0 and 5.8 Hz. In the ^{1}H NMR spectrum of benzyl(methyl)-amine complex **9** in CD_2Cl_2, the chemical shift of the NH resonance is δ 1.66, the couplings of the NH hydrogen to the diastereotopic benzyl CH_2 hydrogens are 11.3 and 2.4 Hz, and that to the methyl hydrogens is 5.8 Hz. Shvo reported that the NH resonance of **8** persisted in D_2O but was washed out upon addition of DCl.

Independent Synthesis of Isopropylamine Complexes. The structural assignment of **A** and **A*** as isopropylamine complexes **4a** and **4b** was confirmed by independent synthesis. Compound **4a** was prepared in 73% yield from **5a** and isopropylamine analogously to Shvo's synthesis of the diethylamine complex [2,3,4,5-Ph_4(η^4-C_4CO)]$Ru(CO)_2(NHEt_2)$ (**8**)[3] (Scheme 7). Reaction of isopropylamine with the dienone diruthenium com-

(8) Park's ^{1}H NMR spectra of **A** also showed integration for 2H for the two peaks at δ 2.44 and approximately 1:3.5:7:8.75:7:3.5:1 intensity for the seven inner lines of the δ 2.87 resonance. These discrepancies were initially attributed to the presence of water as an impurity.

(9) Shvo, Y.; Abed, M.; Blum, Y.; Laine, R. M. *Isr. J. Chem.* **1986**, *27*, 267.

(10) Selected resonances from ^{1}H NMR of **9** (CD_2Cl_2, 250 MHz): δ 1.66 (br m, NH), 2.40 (d, ^3J = 5.8 Hz, NCH_3), 3.58 (ABX, $^3J_{AB}$ = 13.1 Hz, $^3J_{AX}$ = 11.3 Hz, NC*H*H), 3.77 (ABX, $^3J_{AB}$ = 13.1 Hz, $^3J_{BX}$ = 2.4 Hz, NCH*H*).[6]

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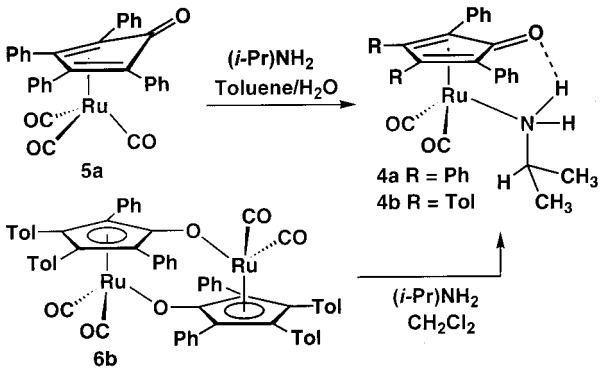
Scheme 7



plex **6b** gave a high yield of the isopropylamine complex **4b**. The properties of **4a**,**b** were identical with those of **A** and **A***.

Reinterpretation of X-ray, Mass Spectrometry, and Elemental Analysis Data of A. The X-ray structure data for **A** reported by Park included a 50:50 disorder for the OH hydrogen, with half-occupancy of a site intramolecularly hydrogen bonded to the dienone oxygen and half-occupancy of a site intermolecularly hydrogen bonded. The alcohol formulation **3a** and amine complex **4a** have the same total number of electrons. When the structure of **A** was modeled with the two hydrogen-bonded sites fully occupied (an additional half-electron each) and nitrogen in place of oxygen (one electron less), the values of R1 = 0.0298, wR2 = 0.0837, and goodness of fit on F^2 of 1.123 improved slightly to R1 = 0.0286, wR2 = 0.0813, and goodness of fit on F^2 of 1.054.[11] The bond distances to the heteroatom did not change significantly: Ru−O = 2.189(2) Å changed to Ru−N = 2.1882(18) Å, and O−C = 1.497(4) Å changed to N−C = 1.497(3) Å (Figure 1).

The molecular weight of alcohol formulation **3a** is 1 greater than that of the amine complex **4a**. Park's low-resolution mass spectrum of **A** was obtained using the FAB method with 3-nitrobenzyl alcohol as the matrix material. The most intense peak in the isotopic cluster in the molecular ion region was found at *m/z* 602.16 and was assigned to the M^+ ion of **3a**. The *m/z* 602 peak is now assigned to the $(M + H)^+$ peak for the protonated amine complex;[12] FAB spectra typically give $(M + H)^+$ peaks when basic sites are available. The Stockholm group performed a MALDI-TOF MS on **A** with 2,5-dihydroxybenzoic acid as matrix, which gave the $(M + H)^+$ peak at *m/z* 602.1 (calcd for $C_{34}H_{30}NO_3{}^{102}Ru$, *m/z* 602.13) accompanied by an isotope pattern in good agreement with a simulated spectrum based on isotope distribution. For the tolyl derivative **4b**, the high-resolution electrospray mass spectrum obtained using a $CHCl_3$/MeOH solution (measured *m/z* 630.1568) allowed a clear distinction between $(M + H)^+$ of the amine complex **4b** (calcd for $C_{36}H_{34}NO_3{}^{102}Ru$ *m/z* 630.1592) and M^+ of alcohol complex **3b** (calcd for $C_{36}H_{32}O_4{}^{102}Ru$ *m/z* 630.1354).

While the ritual burning of compounds to obtain elemental analyses is often cited as a method for establishing composition and purity, the C,H analyses expected for alcohol complex **3a** (C, 67.87; H, 4.69) and for amine complex **4a** (C, 67.98; H, 4.87) are not experimentally distinguishable. Only O or N analysis would have distinguished **3a** from **4a**, and O analyses are rarely performed and N analysis is normally done only for compounds thought to contain nitrogen. Nitrogen analyses of **A**[13] and **A*** have now been performed and are consistent with their formulation as isopropylamine complexes **4a** and **4b**.

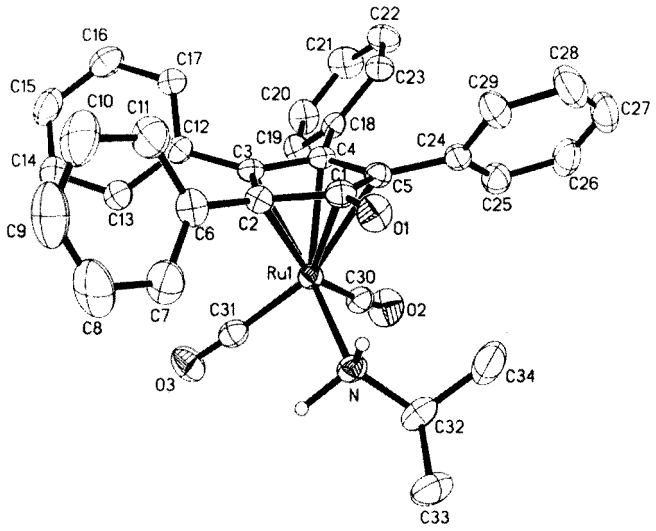
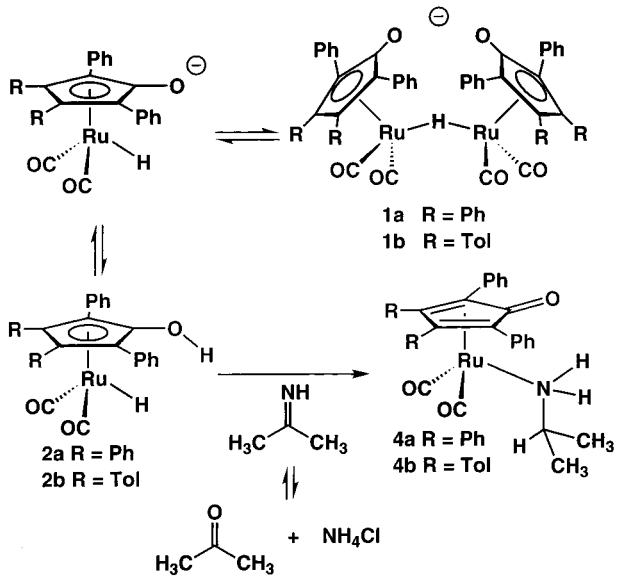


Figure 1. X-ray structure of isopropylamine complex **4a**.

Scheme 8



Probable Mode of Formation of Isopropylamine Complex. It is proposed that amine complexes **4a** and **4b** are formed by reaction of the imine of acetone with the (hydroxycyclopentadienyl)ruthenium hydrides **2a**,**b** (Scheme 8). In all of the syntheses, the reaction mixtures contained acetone and NH_4Cl, which in the presence of Na_2CO_3 would be in equilibrium with the corresponding imine or iminium compound. Earlier, Casey reported that imines are exceedingly reactive

(11) The revised crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 176947).

(12) Isotope pattern for $(M + H)^+$ of **4a**: *m/z* (calcd, obsd) 605 (19, 22), 604 (54, 59), 603 (34, 47), 602 (100, 100), 601 (58, 62), 600 (45, 68).

(13) The Park group has obtained the following C,H,N analysis for **A** that is consistent with its formulation as the amine complex **4a**. Anal. Calcd for $C_{34}H_{29}NO_3Ru$: C, 67.99; H, 4.87; N, 2.33. Found: C, 67.97; H, 4.74; N, 2.40.

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toward (hydroxycyclopentadienyl)ruthenium hydride **2b** and produce amine complexes.[6] We suggest that the (hydroxycyclopentadienyl)ruthenium hydrides **2a**,**b** are formed by protonation of an anionic hydride intermediate formed in reactions of **2** with base, of **5** with base, and of **6** with base followed by isopropyl alcohol. Previously, Shvo reported that protonation of similar reaction mixtures at room temperature leads to the formation of the diruthenium hydride complex **1a** as the major product.[1] In separate experiments that involved the concentration of the reaction mixture before acidification or the extension of reaction time, Park showed that the anionic diruthenium hydride complex [2,3,4,5-$Ph_4(\eta^5\text{-}C_4CO)]_2Ru_2(CO)_4(\mu\text{-}H)^-$ was formed quantitatively and that the acidification of the acetone solution of the anionic diruthenium hydride complex with aqueous NH_4Cl led to the formation of diruthenium hydride complex **1a** exclusively.

Conclusion. Be wary when all data does not fit a preconceived formulation! The importance of alcohol complexes remains, and all three groups will continue to search for routes to such intermediates to test their role in the mechanism of reduction.

Experimental Section

[2,3,4,5-$Ph_4(\eta^4\text{-}C_4CO)](CO)_2Ru(H_2NCHMe_2)$ (4a). Procedure A. A saturated aqueous solution of Na_2CO_3 (15 mL) was added to a solution of **5a** (205 mg, 0.36 mmol) in acetone (15 mL) at ambient temperature. After it was stirred for 1 h, the reaction mixture was cooled to 0 °C and acidified by addition of a saturated aqueous solution of NH_4Cl (25 mL). After concentration under vacuum, the residue was extracted with CH_2Cl_2 and chromatographed on silica gel (6:1 CH_2Cl_2/ethyl acetate) to give **4a** as a pale yellow powder (95 mg, 44%). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.98 (d, ^3J = 6.3 Hz, 6H, isopropyl CH_3), 2.44 (br d, $^3J \approx 5$ Hz, 2H, NH_2), 2.87 (nonet, ^3J = 6.3 Hz, 1H, $CHMe_2$), 7.04−7.20 (m, 16H, phenyl), 7.56 (d, ^3J = 8.2 Hz, 4H, phenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 24.7 (isopropyl CH_3), 51.6 ($CHMe_2$), 83.4 (2C of Cp), 103.7 (2C of Cp), 126.5 (2C, aromatic), 127.8 (4C, aromatic), 127.8 (2C, aromatic), 127.9 (4C, aromatic), 130.2 (4C, aromatic), 131.8 (2C, aromatic), 132.3 (4C, aromatic), 132.8 (2C, aromatic), 163.0 (1C of Cp), 201.1 (CO). IR (KBr): 2006 (s), 1949 (s) cm^{-1}. MS (MALDI-TOF, matrix: 2,5-dihydroxybenzoic acid): m/z $(M + H)^+$ calcd for $C_{34}H_{30}NO_3{}^{102}Ru$ 602.13, found 602.1. Isotope pattern for $(M + H)^+$ of **4a**: m/z (calcd, obsd) 605 (19, 13), 604 (54, 58), 603 (35, 48), 602 (100, 100), 601 (59, 86), 600 (45, 65), 599 (34, 62). Anal. Calcd for $C_{34}H_{29}NO_3Ru$: C, 67.99; H, 4.87; N, 2.33. Found: C, 68.17; H, 4.87; N, 2.18.

Procedure B. Isopropylamine (63 μL, 0.73 mmol) was added to a solution of **5a** (209 mg, 0.37 mmol) in toluene (15 mL) and H_2O (2 mL). The reaction mixture was stirred for 2 h, after which a workup procedure similar to that described in procedure A gave **4a** in 73% yield.

[2,5-Ph_2-3,4-$Tol_2(\eta^4\text{-}C_4CO)](CO)_2Ru(H_2NCHMe_2)$ (4b). Procedure A. A saturated aqueous solution of Na_2CO_3 (25 mL) was added to a solution of **6** (630 mg, 0.55 mmol) in acetone (25 mL) at room temperature. After the mixture was stirred for 30 min, isopropyl alcohol (25 mL) was added and stirring was continued for another 30 min. The reaction mixture was acidified by addition of a saturated aqueous NH_4Cl solution (50 mL) at room temperature and concentrated under vacuum. The residue was extracted with CH_2Cl_2 and chromatographed on silica gel with 6:1 CH_2Cl_2/ethyl acetate to give **4b**. Recrystallization of **4b** from 3:1 hexane/CH_2Cl_2 at −10 °C gave air-stable pale yellow crystals of **4b** (220 mg, 32%). ^1H NMR ($CDCl_3$, 500 MHz): δ 0.97 (d, ^3J = 6.5 Hz, 6H, isopropyl CH_3), 2.22 (s, 6H, tolyl CH_3), 2.41 (br d, $^3J \approx 5$ Hz, 2H, NH_2), 2.86 (nonet, ^3J = 6.5 Hz, 1H, $CHMe_2$), 6.89 (d, ^3J = 8.5 Hz, 4H, tolyl), 7.04 (d, ^3J = 8.0 Hz, 4H, tolyl), 7.09−7.17 (m, 6H, phenyl), 7.56 (d, ^3J = 7.5 Hz, 4H, phenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 21.1 (tolyl CH_3), 24.5 (isopropyl CH_3), 51.3 ($CHMe_2$), 83.3 (2C of Cp), 103.2 (2C of Cp), 126.2 (2 C, aromatic), 127.6 (4C, aromatic), 128.3 (4C, aromatic), 128.5 (2C, aromatic), 130.1 (4C, aromatic), 131.9 (4C, aromatic), 132.8 (2C, aromatic), 137.2 (2C, aromatic), 162.8 (1C of Cp), 201.0 (CO). IR (CD_2Cl_2): 2012 (s), 1934 (s) cm^{-1}. MS (electrospray ionization, $CHCl_3$, MeOH): m/z $(M + H)^+$ calcd for $C_{36}H_{34}NO_3{}^{102}Ru$ 630.1592; calcd for $C_{36}H_{32}O_4{}^{102}Ru$ 630.1354, found 630.1568. Isotope pattern for $(M + H)^+$ of **4b**: m/z (calcd, obsd) 633 (12, 14), 632 (54, 38), 631 (37, 28), 630 (100, 100), 629 (58, 45), 628 (45, 43), 627 (34, 28). Anal. Calcd for $C_{36}H_{33}NO_3Ru$: C, 68.77; H, 5.29; N, 2.23. Found: C, 68.79; H, 5.30; N, 1.92.

Procedure B. Isopropylamine (5 μL, 0.06 mmol) was added via syringe to a CD_2Cl_2 suspension of **6b** (33 mg, 0.03 mmol), and the mixture was stirred for 30 min, until all the material dissolved. Solvent was removed under vacuum to afford **4b** (30 mg, 80%).

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