Sequences analogous to (3)-(6) have now been proposed for the reductions of carboxylate-bound chromium(V) by five anionic reducing agents (Table III). In comparing the selectivities toward Cr(V) and Cr(IV) (k_1/k_3) for these five reductants and for the radical intermediates derived from them (k_2/k_4), we see that marked autocatalysis and clocklike kinetic profiles related to the consumption of Cr(IV) are associated with dramatic turnarounds (10^3-fold) in $k_{Cr(V)}/k_{Cr(IV)}$ ratios in a given system. With hypophosphite (for which reversal in these selectivites is less striking) and with nitrite (for which both rate ratios exceed unity), autocatalytic behavior is subdued, and no clocklike pattern is evident. Despite elaborate arguments to the contrary,[6] such a reversal is not a requirement for autocatalysis, but without it a preponderant portion of the overall reaction proceeds along a noncatalytic path.

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Ruthenium(II)-Assisted Borohydride Reduction of Acetonitrile

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The sodium borohydride reduction of $[Ru(MeCN)_3(triars)](CF_3SO_3)_2$ (triars = $MeC(CH_2AsPh_2)_3$) in methanol yields the bis(amine) hydride $[RuH(NH_2CH_2Me)_2(triars)](CF_3SO_3)$. The amine and methylene protons are inequivalent on the NMR time scale up to +80 °C. Deuterium substitution studies support the intermediacy of a metal-imine complex in the reduction. By contrast, reaction of $NaBH_4$ and $[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (triphos = $MeC(CH_2PPh_2)_3$) gives the hydride borohydride complex $[RuH(BH_4)(triphos)]$. NMR and GC measurements prove that MeCN is not reduced to amine in this case. The difference in reactivity is attributed to the difference in trans effects of the phosphorus and arsenic donors.

Introduction

The efficacy of sodium borohydride as a reducing agent in organic synthesis is apparent in the extant chemical literature. Substrates such as aldehydes and ketones are smoothly reduced by $NaBH_4$.[1] However, nitriles are more difficult to reduce, usually requiring a much more powerful reductant (e.g., $LiAlH_4$) or conversion to alkylnitrilium salts before addition of borohydride.[2] Alternatively, the transformation of nitriles to amines can be affected by $NaBH_4$ in the presence of $CoCl_2$[3] or of Raney nickel[4] in alcohols.

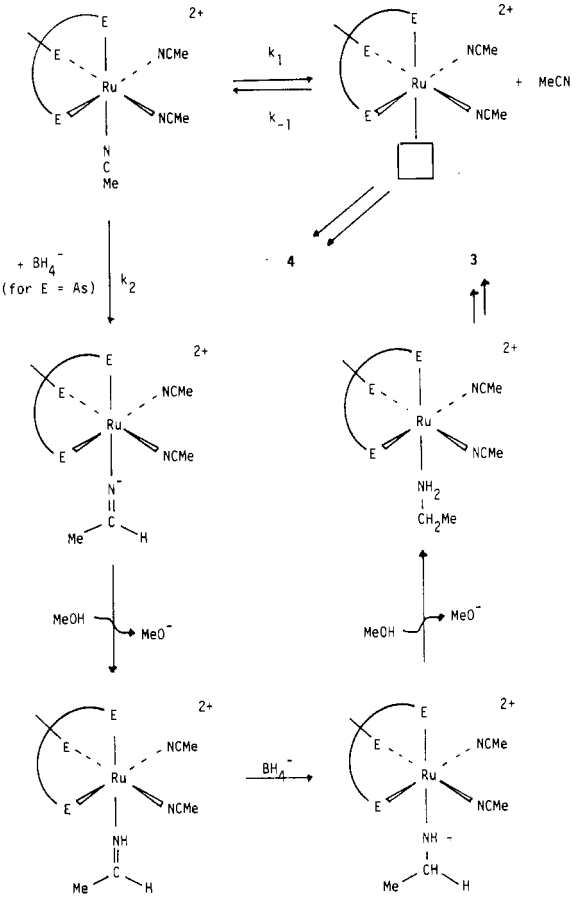
During the process of exploring new ruthenium solvento complexes with the facially coordinating coligand tripod $MeC(CH_2EPh_2)_3$ [tripod, E = P (triphos) or As (triars); see Scheme I], it became apparent that the newly synthesized tris(acetonitrile) complexes $[Ru(MeCN)_3(tripod)](CF_3SO_3)_2$ (tripod = triars (**1**) and triphos (**2**))[5] could potentially assist in the borohydride reduction of the coordinated nitrile. Thus, Crabtree and Pearman[6] report that the reaction of *fac*-$[Ru(MeCN)_3(PMePh_2)_3]^{2+}$ with $NaBH_4$ gives *mer*-$[RuH(BH_4)(PMePh_2)_3]$ with formation of 1 equiv of ethylamine. The results of this study are reported herein.

Results and Discussion

Reaction of 1 with Borohydride. On the basis of earlier work by Crabtree and Pearman,[6] treatment of **1** with $NaBH_4$ was expected to yield a hydride borohydride complex with concomitant reduction of nitrile. Although the addition of an 8-10 molar excess of $NaBH_4$ to a MeOH solution of **1** resulted in reduction of the coordinated acetonitrile, instead of a complex analogous to that of Crabtree and Pearman[6] the bis(amine) hydride $[RuH(NH_2CH_2Me)_2(triars)](CF_3SO_3)$ (**3**) was produced (eq 1). It has not proved possible to give a balanced equation for this reaction because the formation of **3** is always accompanied by 20-30% amounts of another as yet unidentified product, X. Further, it has been independently established that **3** reacts with BH_4^- with release of ethylamine and formation of X.

$$\underset{\mathbf{1}}{[Ru(MeCN)_3(triars)](CF_3SO_3)_2} \xrightarrow[MeOH]{NaBH_4} \underset{\mathbf{3}}{[RuH(NH_2CH_2Me)_2(triars)](CF_3SO_3)} \quad (1)$$

Scheme I[a]



[a] The tripod ligands represented are $MeC(CH_2EPh_2)_3$ (E = P (triphos), As (triars)).

(1) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley Interscience: New York, 1985; p 809 and references therein.
(2) Reference 1, p 815.
(3) Osby, J. O.; Heinzman, S. W.; Ganem, B. *J. Am. Chem. Soc.* **1986**, *108*, 67 and references therein.
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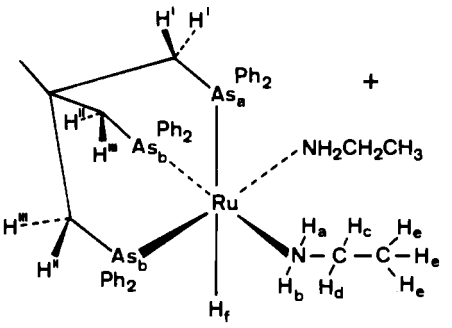


Figure 1. Atomic labeling scheme for compound **3**.

The bands observed in the region 3300–1600 cm^{-1} are assigned to the NH stretches (3290 w, 3245 w cm^{-1}), bend (1600 w cm^{-1}), and the RuH stretch (1900 m cm^{-1}). These assignments are confirmed by the expected shifts observed for the fully deuteriated analogue **3**-d_5, which was synthesized by treatment of **1** with $NaBD_4$ in MeOH-d_1 (eq 2).

$$\underset{\mathbf{1}}{[Ru(MeCN)_3(triars)](CF_3SO_3)_2} \xrightarrow[MeOH\text{-}d_1]{NaBD_4} \underset{\mathbf{3}\text{-}d_5}{[RuD(ND_2CD_2Me)_2(triars)](CF_3SO_3)} \quad (2)$$

Although the ^1H NMR spectrum of **3** shown in Figure 2 appears to be rather complex at first sight, it can be interpreted in a straightforward manner if one assumes that the structure of this complex is as shown in Figure 1 and that the geometry around the ruthenium atom is rigid.

As this structure contains a plane of symmetry going through As_a and H_f and bisecting the As,bRuAs$_b$ angle, the methylene protons of the triars ligand will give rise to a singlet (H′) and AB quartet (H″H‴). The NMR parameters for triars and ethylamine are given in the Experimental Section. Integration, homonuclear proton decoupling experiments, and the ^{13}C NMR results confirm the assignments shown in Figure 2.

Further clarification is needed concerning two interesting spectral features of the amine ligands of **3**: (1) the amine (H_a and H_b) as well as the methylene protons (H_c and H_d) are inequivalent; (2) there is an upfield shift of the amine proton H_b relative to H_a of more than 2 ppm and a smaller (ca. 0.5 ppm) difference between the methylene protons. The former observation is simply a consequence of the overall molecular geometry, which requires that H_a/H_b and H_c/H_d form inequivalent (diastereotopic) pairs, while the methyl protons remain equivalent (only one signal observed for H_e). No significant change is observed by ^1H NMR at +80 °C (C_6D_6). Molecular models of **3** show that one possible conformation requires that protons H_b and H_d point directly into an open face of a phenyl substituent of As_b; i.e., the π-cloud of the phenyl ring effectively shields the protons such that they resonate at higher field. This would explain the anomalous chemical shift values noted above. Finally, the fact that the amine protons of **3** do not H/D exchange with added D_2O in CD_2Cl_2 solution even after 12 h at room temperature seems to be in accord with the notion that the same mechanism (presumably steric crowding at or near the metal center) which produces high-field NMR shifts may be responsible for the lack of facile H/D exchange.

In order to assess the source of the reducing equivalents in eq 1, the appropriate labeling studies were undertaken. The results are summarized in eq 3 and 4. Taken together, eq 2–4 permit

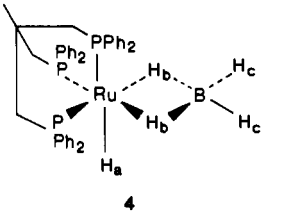
$$\underset{\mathbf{1}}{[Ru(MeCN)_3(triars)](CF_3SO_3)_2} \xrightarrow[MeOH]{NaBD_4} \underset{\mathbf{3}\text{-}d_3}{[RuD(NH_2CD_2CH_3)_2(triars)](CF_3SO_3)} \quad (3)$$

$$\underset{\mathbf{1}}{[Ru(MeCN)_3(triars)](CF_3SO_3)_2} \xrightarrow[MeOH\text{-}d_1]{NaBH_4} \underset{\mathbf{3}\text{-}d_2}{[RuH(ND_2CH_2CH_3)_2(triars)](CF_3SO_3)} \quad (4)$$

the following conclusions: (1) BH_4^- provides the hydride ligand as well as the methylene protons; (2) methanol serves as the source of amine protons; (3) β-H elimination from methanol (or methoxide) is not a source of reducing equivalents (β-H elimination of MeOH as a source of hydrides was a source of concern since a related complex, $[Rh(MeCN)_3(triphos)]^{3+}$, forms hydride complexes when dissolved in MeOH).[7]

Reaction of 2 with Borohydride. Contrary to the results found for complex **1**, treatment of $[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (**2**) with $NaBH_4$ in methanol yields the expected hydride borohydride complex, $[RuH(BH_4)(triphos)]$[8] (**4**) (eq 5). Its postulated structure is shown here. The hydride stretches for **4**, which were

$$\underset{\mathbf{2}}{[Ru(MeCN)_3(triphos)](CF_3SO_3)_2} \xrightarrow[MeOH]{NaBH_4} \underset{\mathbf{4}}{[RuH(BH_4)(triphos)]} \quad (5)$$



4

confirmed by comparison with the fully deuteriated analogue, $[RuD(BD_4)(triphos)]$ (**4**-d_5), appear in the region expected for a bidentate BH_4^- ligand[9] (see Experimental Section). At low temperature (−70 °C) the ^1H NMR spectrum expected for structure **4** is seen. Thus, at δ 5.15 and −7.32 two broad singlets appear due to H_c and H_b, respectively, while H_a resonates at δ −4.50 as a broad doublet ($J_{PtransH}$ = 100 Hz) of triplets (J_{PcisH} = 16 Hz). At room temperature the peak assigned to H_c broadens into the base line, while the peak for H_b remains relatively unchanged. This broadening is probably due to quadrupolar $^{10}B/^{11}B$ relaxation effects.[10] The A_2X pattern observed in the $^{31}P\{^1H\}$ NMR spectrum of **4** agrees with the suggested structure.

Two compounds that have been recently reported are pertinent in discussing **4**: $[RuH(\eta^2\text{-}BH_4)(ttp)]$[10] and $[FeH(\eta^2\text{-}BH_4)(triphos)]$.[11] The former complex contains the meridionally coordinated ttp ligand ($PhP(CH_2CH_2CH_2PPh_2)_2$), thereby requiring the ruthenium to accept a meridional arrangement of bridging and terminal hydrides, while the latter complex has a structure identical with that proposed for **4**. The iron complex and **4** compare favorably spectroscopically in that the signals due to the bridging hydrides resonate downfield of those due to the terminal metal hydrides.[12] Interestingly, while the iron analogue of **4** undergoes global migration of *all* hydrides (bridging and terminal), NMR studies give no evidence of such a process occurring for **4** under similar conditions. It is noteworthy that at higher temperature, the spectra of samples of $[FeH(BH_4)(triphos)]$ contained signals due to an unidentified complex. Similar behavior was noted for **4**. In the latter case, this species proved to be $[(triphos)HRu(\mu\text{-}\eta^2\text{-}BH_4)RuH(triphos)^+]$, presumably formed by reaction with adventitious water.[8]

Solution Behavior of 1 and 2. In order to better understand the difference in reactivity between **1** and **2**, a more detailed spectroscopic study of the starting complexes became necessary. The ^1H NMR spectrum of **1** in MeOH-d_4 exhibits the expected pattern for a facially coordinated tris(acetonitrile). Similar geometries have been assigned for $[Ru(MeCN)_3(PMePh_2)_3]^{2+}$[6] and

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(8) This compound was reported earlier, but no synthetic or spectroscopic details were provided: Rhodes, L. F.; Venanzi, L. M.; Sorato, C.; Albinati, A. *Inorg. Chem.* **1986**, *25*, 3335.
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(10) Betts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 3898.
(11) Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Dalton Trans.* **1985**, 605.
(12) Jesson, J. P. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971; p 75.

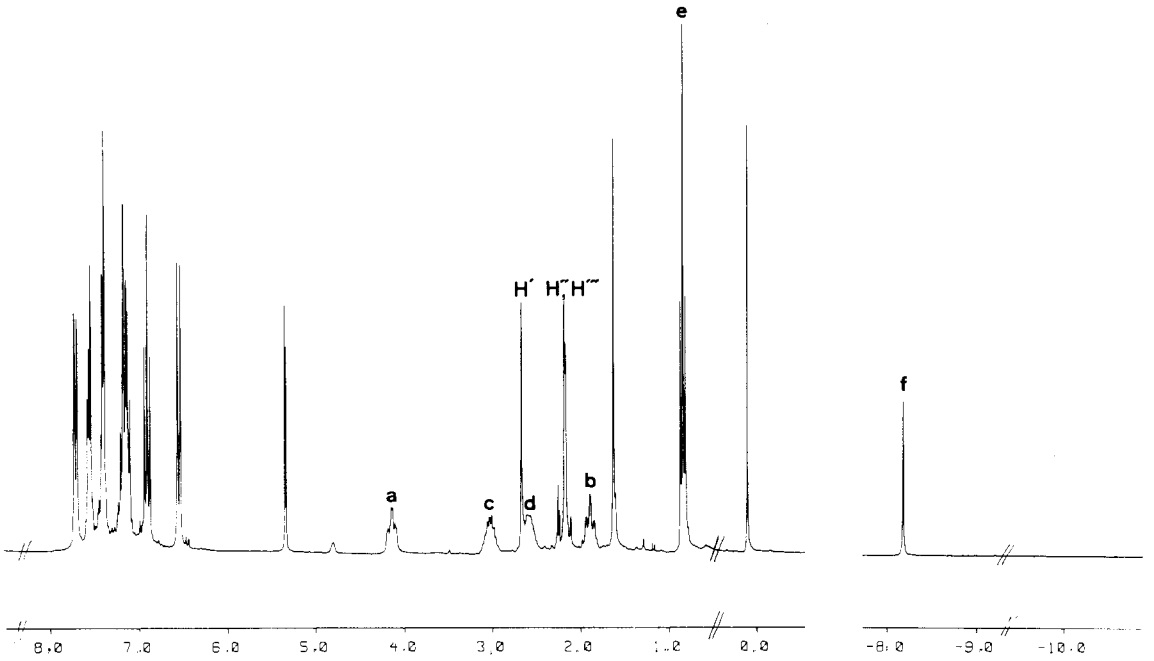


Figure 2. ^{1}H NMR spectrum (250 MHz) of compound **3**.

$[Os(MeCN)_3(PMe_2Ph)_3]^{2+}$.[13] In each case the peak for coordinated acetonitrile was observed between δ 2.35 and δ 2.10. The ^{1}H NMR spectrum of the osmium complex was recorded in MeCN-d_3, indicating that exchange of MeCN is, at best, very slow on the NMR time scale.

The complexities in deciphering the ^{1}H NMR spectrum of **2** in MeOH-d_4 have been mentioned elsewhere.[5] Specifically, at 250 MHz and room temperature one finds two broad peaks at δ 2.65 (6 H) and 1.73 (3 H) assigned to the methylene and methyl protons of the triphos ligands, respectively. In the region expected for acetonitrile two broad peaks are present (δ 2.36 (6 H) and 2.25 (3 H)). At −80 °C the signals become broader. However, at +60 °C, the methylene and methyl signals of triphos become sharper as the two peaks due to acetonitrile collapse to a broad singlet at δ 2.33 (weighted mean δ 2.32). Additional information concerning the fluxional process is provided by the ^{31}P{^{1}H} NMR spectrum of **2** in MeOH-d_4. At ambient temperature, a singlet at δ 28.45 (101.21 MHz) is seen. However, at −80 °C, two species, in the approximate ratio 3:1, are present; one exhibits a singlet at δ 28.22, while the other shows a doublet (δ 29.21, J_{PP} = 43 Hz, 2 P) and triplet (δ 36.64, J_{PP} = 43 Hz, 1 P). Since, at low temperature, no signal approaching that of free triphos (ca. δ −27.0) is observed in the ^{31}P{^{1}H} NMR spectrum, any exchange process involving a nonbonded (dangling) arm of the tridentate ligand can be excluded.[14]

Given the previously mentioned NMR data for **2**, it seems reasonable that **2** takes part in an equilibrium involving dissociation of acetonitrile to give either a mixed-solvent species (MeOH and MeCN) or a coordinatively unsaturated five-coordinate complex (eq 6). In the ^{1}H NMR spectrum of **2**, the methylene and methyl

$$[Ru(MeCN)_3(triphos)]^{2+} \overset{S}{\rightleftharpoons} [Ru(MeCN)_{3-x}(S)_x(triphos)]^{2+} + x\,MeCN \quad (6)$$

$$S = MeOH;\ x = 1 \text{ or } 2$$

protons of the triphos ligand for both species present in solution obscure one another. However, the low-temperature ^{31}P{^{1}H} NMR data suggest that the mixed-solvent species (or the 5-coordinate complex, A_2X pattern) and the tris(acetonitrile) species (singlet) are present in a 1:3 ratio, respectively. This interpretation is confirmed by ^{1}H NMR data in the acetonitrile region since the peak at δ 2.25 represents ca. 25% of the total acetonitrile present.

In order to test this hypothesis and to better understand the relative rates of MeCN exchange in **1** and **2**, equal amounts of MeCN-d_3 (3 equiv) were added to temperature-equilibrated equimolar MeOH-d_4 solutions of **1** and **2**. The exchange was then followed by ^{1}H NMR. Within 5 min the methylene and methyl proton signals of triphos in **2** became sharp and ca. 50% of the acetonitrile intensity was present as free acetonitrile (δ 2.01), the other half appearing as coordinated (δ 2.35). In the case of **1**, only ca. 6% of the total acetonitrile content appears at δ 2.01 (free acetonitrile) after the same time period. After 1.5 h in solution, **1** had still not exchanged 50% of coordinated acetonitrile for free. Thus, the exchange rate for **2** is at least 18 times faster than that for **1**.

In view of the differing rates of exchange for complexes **1** and **2** in MeOH and the reduction of bound acetonitrile in **1** to amine, it became increasingly of interest to learn the fate of acetonitrile in the $NaBH_4$ reduction of **2**. Even after taking special procautions to limit the loss of low-boiling ethylamine (bp 16 °C; see Experimental Section), no amine was detected when the volatile components were analyzed by GC. When the reduction of **2** was followed by ^{1}H NMR, all the MeCN present (coordinated or free) before reaction was released as free MeCN (as determined by integration against toluene internal standard), thus ruling out the possibility of a side reaction rendering ethylamine nonvolatile.[15] Isolation of the inorganic product after GC and ^{1}H NMR analysis gave yields as good as, or better than, the synthetic-scale reactions. Equation 5 can therefore be written as

$$[Ru(MeCN)_3(triphos)](CF_3SO_3)_2 + 2NaBH_4 \overset{MeOH}{\rightarrow} [RuH(BH_4)(triphos)] + 3MeCN + \text{“}\tfrac{1}{2}(B_2H_6)\text{”} + 2NaCF_3SO_3 \quad (7)$$

Mechanistic Considerations. Initially, it was hoped that detailed analysis of eq 1 and 7 would allow for a unified mechanism that could explain how the observed products were formed. Although many questions remain, several conclusions can be drawn from the previously presented results.

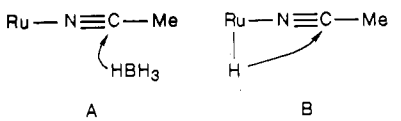
(13) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.

(14) This is not the case for $[CdI_2(triphos)]$, where, at low temperature, two signals are observed: δ −25.5 and −29.6. The latter resonance can be unambiguously assigned to a dangling arm of triphos since (a) the chemical shift value resembles that of free triphos (δ −27.0) and (b) the other signal has ^{113}Cd and ^{111}Cd satellites of 918 and 877 Hz, respectively: Chaloupka, S.; Magyar, B. I.; Venanzi, L. M., unpublished results.

(15) Ethylamine is known to react with BH_3 to form an adduct. See ref 4.

First of all, it seems reasonable that the significant difference in acetonitrile exchange rates for **1** and **2** plays an important role in determining the nature of the product(s). The reason for this rate difference probably lies in the higher expected trans effect of P over As.[16] As a consequence of the facile solvent exchange[17] in the phosphine complex **2**, it is suggested that borohydride preferentially substitutes acetonitrile with subsequent formation of **4** (see Scheme I where E = P); i.e., $k_1 > k_2$. Conversely, for the arsine complex (E = As) as a result of the slow exchange for **1**, the rate of BH_4^- attack at the carbon of the coordinated nitrile is faster than its substitution rate; i.e., $k_2 > k_1$. (Interestingly, a related compound, $[Ru(MeCN)_3(PMePh_2)_3](BF_4)_2$, which displays ^1H NMR signals consistent with coordinated MeCN, reacts with $NaBH_4$ to yield a 1:2 ethylamine:acetonitrile ratio).[6]

A probable mechanism of reduction of the nitrile ligands in **1**, which is in agreement with all the above data, is also presented in Scheme I. Presumably, coordination to ruthenium polarizes the nitrile and activates the β-carbon toward nucleophilic attack.[18] Successive additions of hydride and proton to the β-carbon and the nitrogen, respectively, would yield the observed amine complex. The intermediate imine complex has been postulated in other nitrile reduction mechanisms.[19] The labeling studies mentioned earlier unambiguously prove that BH_4^- is the source of hydrides at the β-carbon position. However, the hydrides may be introduced directly[3] (case A) or indirectly (via a 1,3 metal hydride shift from



metal to β-carbon)[20] (case B). Since in both cases the original source of hydride is BH_4^-, the mechanism in Scheme I is still valid.

Finally it is interesting to note that a species related to **1** and **2**, $[RuCl(MeCN)_3(dppb)]^+$, containing the chelating phosphine 1,4-bis(diphenylphosphino)butane, was found to be catalytically active in the H_2 reduction of MeCN under mild conditions,[21] as well as being hydrogenated with H_2, under base-assisted conditions, to $[RuH(C_2H_5NH_2)_3(dppb)]^+$.

Experimental Section

All manipulations were carried out in a Dri-Lab (Vacuum Atmospheres Co.) glovebox or by using standard Schlenk techniques. MeOH was dried over Mg and distilled under nitrogen, while CH_2Cl_2 was dried over CaH_2 and distilled. Elemental analyses were performed by the Microanalytical Section of the ETH Zürich. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer as CsI pellets. The ^1H NMR spectra were recorded at 250.13 MHz on a Bruker WM-250 instrument, while ^{31}P NMR spectra were recorded at either 36.43 or 101.26 MHz on a Bruker HX-90 or on a Bruker WM-250 instrument, respectively. The ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument operating at 62.80 MHz. The ^{13}C and ^1H NMR were referenced to external Me_4Si, while the ^{31}P NMR spectra were referenced to external H_3PO_4 with a positive sign indicating a chemical shift downfield of the reference. A Carlo Erba 2400 V gas chromatograph equipped with a 3380 A Hewlet-Packard integrator was used for analysis of volatile organics. The separation was performed on a 3 m × 0.3 cm column packed with the 10% poly(ethylene glycol) (PEG) 20M on Chromosorb P-NAW (150–177-μm particles) which was modified with 6% KOH (w/w relative to PEG). The chromatographic conditions were as follows: injector, 150 °C; detector, 200 °C (FID); oven, 112 °C (isothermal); carrier gas, nitrogen (9 mL/min). Complexes **1** and **2** were prepared as previously described.[5] Sodium borohydride (Fluka) was used as purchased.

While a parallel reaction can take place between $NaBH_4$ and methanol,[22] this reaction and its products are irrelevant to the postulated reaction pathway on the basis of selective labeling experiments which show that (1) the hydrogen atoms on nitrogen come from CH_3OH (see eq 3), (2) the hydrogen atoms on the CH_2 group come from the BH_4^- (eq 4), and (3) there is no H/D exchange between the solvent system and the coordinated ethylamine (see Discussion).

$[RuH(NH_2CH_2Me)_2(triars)](CF_3SO_3)$ (3). Solid $NaBH_4$ (0.075 g, 2.0 mmol) was added slowly to a stirred MeOH solution (10 mL) of $[Ru(MeCN)_3(triars)](CF_3SO_3)_2$ (0.25 g, 0.20 mmol). The $NaBH_4$ slowly dissolved with concomitant gas evolution. The small amount of precipitate formed was filtered off. A $MeOH/H_2O$ mixture (5 mL, 1:1 v/v) was added to the filtrate with formation of an off-white solid. This was filtered out, washed (H_2O, MeOH, Et_2O), and dried. Yield: 0.14 g (0.13 mmol), 65%. Anal. Calcd for $C_{46}H_{54}N_2F_3O_3SAs_3Ru$: C, 50.32; H, 4.97; N, 2.55. Found: C, 49.86; H, 4.85; N, 2.64. IR (CsI; cm^{-1}): ν(NH) 3290 w, 3245 w; ν(RuH) 1900 m; δ(NH) 1600 w. ^1H NMR (CD_2Cl_2): δ 7.68 d (2 H), 7.67 d (2 H), 7.53 d (2 H), 7.52 d (2 H), 7.37 m (6 H), 7.12 m (8 H), 6.88 t (4 H), 6.53 d (2 H), 6.52 d (2 H), 4.15 d (13 Hz) of d (13 Hz) of d (3 Hz, 2 H), 3.01 quartet (8 Hz) of d (13 Hz) of d (13 Hz) of d (3 Hz, 2 H), 2.63 s (2 H), 2.54 quartet (8 Hz) of d (13 Hz) of d (13 Hz, 2 H), 2.18 d (14 Hz, 2 H), 2.10 d (14 Hz, 2 Hz), 1.84 t (13 Hz, 2 H), 1.59 s (3 H), 0.81 t (8 Hz, 6 H), −8.18 s (1 H). $^{13}C\{^1H\}$ (C_6D_6): δ 51.79 ($NH_2CH_2CH_3$), 41.42 ($NH_2CH_2CH_3$). $^1H\{^1H\}$ measurement gave the following coupling constants: J_{ab} = 13 Hz, J_{ac} = 3 Hz, J_{ad} = 13 Hz, J_{bc} = 13 Hz, J_{bd} < 2 Hz (not observed), J_{cd} = 13 Hz, J_{ce} = 8 Hz, J_{de} = 8 Hz.

$[RuH(BH_4)(triphos)]$ (4). Solid $NaBH_4$ (0.11 g, 2.9 mmol) was slowly added to a MeOH solution (5 mL) of $[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (0.42 g, 0.37 mmol). The slurry evolved gas and over a 5-min period deposited a yellow precipitate, which was filtered out, washed (MeOH and Et_2O), and dried. Yield: 0.18 g (0.24 mmol), 65%. Anal. Calcd for $C_{41}H_{44}BP_3Ru$: C, 66.39; H, 5.99. Found: C, 65.27; H, 6.10. IR (CsI; cm^{-1}): $\nu(BH_t)$ 2382 s, 2310 m; $\nu(BH_b)$ and ν(RuH) 1919 m, br; $\nu(RuH_b)$ 1395 m, br; $\delta(BH_2)$ 1169 s. ^1H NMR (CD_2Cl_2, −70 °C): δ 7.50 t, br (4 H), 7.23 t, br (4 H), 7.10 m (6 H), 6.23 m (16 H), 5.15 s, br (2 H), 2.20 m (6 H), 1.60 br, s (3 H), −4.50 d (J_{PH} = 100 Hz) of t (J_{PH} = 16 Hz, 1 H), −7.32 s, br (2 H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 58.1 d (J_{PP} = 19 Hz, 2 P), 14.83 t (J_{PP} = 19 Hz, 1 P).

For gas chromatographic analysis of the volatiles, the reaction was carried out as above except that the flask was cooled to −5 °C, equipped with a condenser, and the borohydride was added via a side arm so as to minimize loss of volatiles. Before isolation of the inorganic complex, the organic species were vacuum-transferred and stored at −5 °C in a vacuum-tight flask equipped with a Teflon stopcock until analysed by GC.

For ^1H NMR analysis of the reaction mixture, an NMR tube was filled with $[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (0.01 g, 0.0087 mmol) and dissolved in MeOH-d_4 (0.3 mL) and CD_2Cl_2 (0.1 mL). After the mixture was cooled to −5 °C, $NaBH_4$ (0.0026 g, 0.07 mmol) was added and the solution was immediately capped. The ^1H NMR spectrum (−10 °C) of the resulting mixture was taken within 5 min. Yield of **4**: 0.005 g (0.0067 mmol), 77%.

Deuteriated Compounds. The deuteriated compounds **3**-d_5, **3**-d_3, **3**-d_2, and **4**-d_5 were prepared as described above with use of the appropriate deuteriated reagent (i.e., MeOH-d_1, $NaBD_4$, or D_2O).

Solvent Exchange in 1 and 2. Samples of **1** (0.011 g, 0.087 mmol) and **2** (0.010 g, 0.087 mmol) were added to two NMR tubes that were filled with 0.4 mL of MeOH-d_4 and equilibrated to +21 ± 1 °C. A ^1H NMR spectrum was taken of each sample at 22 °C. Then a 1.6-μL sample of MeCN-d_3 (3 equiv) was added to each, and the exchange process was followed by ^1H NMR spectroscopy.

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Registry No. **1**, 109124-78-9; **2**, 103500-16-9; **3**, 109124-80-3; **4**, 103500-11-4; $NaBH_4$, 16940-66-2; MeCN, 75-05-8.

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