Dialkylamino cyclopentadienyl ruthenium(II) complex-catalyzed α-alkylation of arylacetonitriles with primary alcohols†

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Aminocyclopentadienyl ruthenium complexes, $[(\eta^5\text{-}C_5H_4NMe_2)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ and $[(\eta^5\text{-}C_5H_4NEt_2)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$, are moderately active catalysts for α-alkylation of arylacetonitriles with primary alcohols; on the other hand, the analogous unsubstituted cyclopentadienyl ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ shows very low catalytic activity. On the basis of experimental results and theoretical calculations, rationalization for the much higher catalytic activity of the aminocyclopentadienyl complexes over that of the unsubstituted Cp complex is provided. In the catalytic systems with the former, it is possible to regenerate the active solvento complexes *via* protonation of the metal hydride intermediates and subsequent ligand substitution; this process is, however, very nonfacile in the catalytic system with the latter.

Introduction

α-Alkylated nitriles are an important class of compounds for their potential as versatile building blocks in the synthesis of amides, amidines, carboxylic acids, ketones, and biologically active compounds.[1] Traditional synthesis of these nitriles requires usage of alkyl halides and a stoichiometric amount of inorganic base; toxicity of the former constitutes a major drawback of this synthetic method. Direct catalytic alkylation of nitriles thus represents an attractive green reaction from both an economical and environmental point of view. Few examples of direct alkylation of nitriles with alcohols which are catalyzed by transition metals are known. The early ones being the Ru- and Rh-catalyzed reactions;[2] more recent ones include reactions catalyzed by the iridium complex $(Cp^*IrCl_2)_2$[3] and a novel Ru-grafted hydrotalcite.[4] In these reactions, aryl- and heteroaryl nitriles were used. Closely related reactions involving the addition of acetonitrile and other alkyl nitriles to aldehydes to yield β-hydroxynitriles have been reported; these reactions are catalyzed by ruthenium[5] and rhodium[6] complexes. β-hydroxynitriles are potential precursors for pharmaceutically important substances.[7]

We have recently reported that β-alkylation of secondary alcohols with primary alcohols are catalyzed by a number of ruthenium complexes, by virtue of their being able to affect respectively oxidation of the primary and secondary alcohols to aldehydes and methyl ketones, which then undergo aldol condensation under basic conditions.[8] Continuing our interest in ruthenium-catalyzed C–C bond formation reactions, we studied catalytic α-alkylation of nitriles with primary alcohols with these ruthenium complexes; however, they were found to be inactive or very poor catalysts for the reactions. Fortunately, we later found that a couple of aminocyclopentadienyl-ruthenium complexes are active catalysts for the reactions; we report here the findings of our work with these catalytic systems. We also provide, with the help of theoretical calculations, an explanation for the low catalytic activity of the analogous cyclopentadienyl-ruthenium species.

Experimental

Materials and general methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from sodium-benzophenone (tetrahydrofuran), sodium (diethyl ether, hexane and toluene), calcium hydride (dichloromethane, and acetonitrile) or P_2O_5 (C_6D_6 and $CDCl_3$); they were degassed prior to use. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ (USA). ^{1}H NMR spectra were obtained from a Bruker DPX-400 spectrometer at 400 MHz; chemical shifts (δ, ppm) were reported relative to residual peaks of the deuterated solvents used. $^{13}C\{^1H\}$NMR spectra were recorded with a Bruker DPX-400 spectrometer at 100.61 MHz; chemical shifts were internally referenced to $CDCl_3$ (δ = 77.7 ppm), C_6D_6 (δ = 128.1 ppm) or $(CD_3)_2CO$ (δ = 206.26, 29.84ppm). $^{31}P\{^1H\}$NMR spectra were recorded on a Bruker DPX-400 spectrometer at 161.70 MHz; chemical shifts were externally referenced to 85% H_3PO_4 in D_2O. All spectra were obtained at ambient probe temperature unless stated otherwise. Mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer with the samples dissolved in dichloromethane or acetone. The complexes $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$,[9] and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(CH_3CN)BF_4$ (**M3**),[10] were prepared according to literature methods. The organic products described in Table 3 are

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Table 1 Crystal data and structure refinement of $[(\eta^5\text{-}C_5H_4NMe_2)\text{-}Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (**M1**)

Empirical formula	$C_{45}H_{43}BF_4N_2P_2Ru$	
Formula weight	858.61	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	$a = 20.6849(5)$ Å	$\alpha = 90°$
	$b = 10.1795(2)$ Å	$\beta = 90°$
	$c = 19.2592(5)$ Å	$\gamma = 90°$
Volume	4055.25(16) Å^3	
Z	4	
Density (calculated)	1.406 Mg m^{-3}	
Absorption coefficient	0.518 mm^{-1}	
$F(000)$	1756	
Crystal size	$0.28 \times 0.24 \times 0.20$ mm^3	
Theta range for data collection	1.97 to 27.38°.	
Index ranges	$-26 \le h \le 26$, $-13 \le k \le 13$, $-24 \le l \le 23$	
Reflections collected	33629	
Independent reflections	8863 [R(int) = 0.0993]	
Completeness to theta = 27.44°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.736	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8863/1/496	
Goodness-of-fit on F^2	1.001	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0493$, w$R_2 = 0.0891$	
R indices (all data)	$R_1 = 0.1001$, w$R_2 = 0.1044$	
Absolute structure parameter	–0.05(4)	
Largest diff. peak and hole	1.279 and –1.099 e Å^{-3}	

Table 2 Selected bond distances (Å) and angles (°) for $[(\eta^5\text{-}C_5H_4NMe_2)\text{-}Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (**M1**)

Bond distances			
Ru(1)-C(1)	2.363(3)	C(1)-C(2)	1.435(4)
Ru(1)-C(2)	2.226(3)	C(1)-C(5)	1.429(6)
Ru(1)-C(3)	2.172(4)	C(2)-C(3)	1.418(5)
Ru(1)-C(4)	2.167(4)	C(3)-C(4)	1.390(5)
Ru(1)-C(5)	2.224(3)	C(4)-C(5)	1.433(5)
Ru(1)-N(1)	2.059(3)	N(1)-C(8)	1.145(5)
Ru(1)-P(1)	2.3413(9)	N(11)-C(1)	1.351(5)
Ru(1)-P(2)	2.3662(9)		

Bond angles			
C(1)-C(5)-C(4)	107.6(3)	C(6)-N(11)-C(7)	116.7(4)
C(1)-N(11)-C(6)	120.6(3)	C(8)-N(1)-Ru(1)	176.3(3)
C(1)-N(11)-C(7)	119.0(3)	N(1)-C(8)-C(9)	178.1(5)
C(3)-C(2)-C(1)	108.3(3)	N(1)-Ru(1)-P(1)	86.52(8)
C(3)-C(4)-C(5)	108.6(3)	N(1)-Ru(1)-P(2)	92.71(8)
C(4)-C(3)-C(2)	108.4(3)	P(1)-Ru(1)-P(2)	105.47(3)
C(5)-C(1)-C(2)	106.5(4)		

Hydrogen bond distances/Å			
D-H···A	d(D-H)	d(H···A)	d(D···A)
C(3)-H(3A)···F(1)	0.98	2.34	3.277(5)
C(4)-H(4A)···F(3)	0.98	2.66	3.202(5)

Hydrogen bond angles (°)	
D-H···A	∠(DHA)
C(3)-H(3A)···F(1)	158.9
C(4)-H(4A)···F(3)	115.3

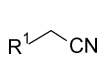
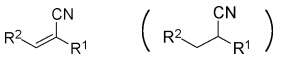
known and were characterized by comparing their ^{1}H NMR data with the reported ones.

Syntheses and reactions

$(\eta^5\text{-}C_5H_4NMe_2)Ru(PPh_3)_2H$ (M4). A sample of $(\eta^5\text{-}C_5H_5)\text{-}Ru(PPh_3)_2Cl$ (0.50 g, 0.69 mmol) was added to a two-necked round bottom flask equipped with a dropping funnel, which was then evacuated and flushed with nitrogen for four cycles. Freshly degassed THF (50mL) was added to the flask. $LiN(Me)_2$ (0.18 g, 3.53 mmol) was added to the dropping funnel, followed by 20 mL of THF to dissolve it, the resulting solution was slowly added to the flask. The mixture was stirred at room temperature for 2 h. At the end of this period, 0.1 mL of H_2O was added to the reaction mixture. It was then evaporated to dryness under reduced pressure to produce a yellow colloidal material, 20 mL of freshly degassed toluene was then added, and the insoluble material was filtered off. The solvent was removed from the filtrate under reduced pressure to give a yellow paste; pre-cooled hexane (15 mL) was added to the residue, with stirring, to produce a yellow solid. The solid was collected by filtration and dried under vacuum at room temperature. Yield: 0.41 g (82%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.74 (m, 12H; PPh_3-*H*), δ 7.15-7.03 (m, 18H; PPh_3-*H*), δ 4.80, δ 3.00 (s, 2H, 2H; C_5H_4), δ 2.34 (s, 6H; –N(CH_3)$_2$), δ –10.30 (t, $J = 32$ Hz, 1H; Ru-*H*). ^{31}P{^{1}H}NMR (161 MHz, C_6D_6, 25 °C): δ 68.59 (s). ^{13}C{^{1}H}NMR (100.61 MHz, C_6D_6, 25 °C): δ 66.54 (t, $J = 5$ Hz, –*C*-N(CH_3)$_2$), δ 43.88 (s, –N(*C*H_3)$_2$). ESI-MS: m/z 734.15, $[M]^+$.

$(\eta^5\text{-}C_5H_4NEt_2)Ru(PPh_3)_2H$ (M8). To a solution of diethylamine (0.36 mL, 3.45 mmol) in freshly degassed THF (10 mL) cooled in an ice bath was added slowly n-butyllithium (1.7 mL, 2.7 mmol, 1.6 M in hexane); the solution was then allowed to warm to room temperature, and stirring was continued for 30 min. A sample of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (0.50 g, 0.69 mmol) was added to a two-necked round bottom flask, which was then evacuated and flushed with nitrogen for four cycles. Freshly degassed THF (50 mL) was added to the flask. Upon complete dissolution of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$, the lithium diethylamide solution just prepared was added and the mixture was stirred at room temperature for 2 h. At the end of this period, 0.1 mL of H_2O was added to the reaction mixture. It was then evaporated to dryness under reduced pressure to produce a yellow colloidal material; 20 mL of freshly degassed toluene was added, and the insoluble material was filtered off. The solvent of the filtrate were removed under reduced pressure to give a yellow paste; pre-cooled hexane (15 mL) was added to the residue, with stirring, to produce a yellow solid. The solid was collected by filtration and dried under vacuum at room temperature. Yield: 0.38 g (73%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.85-7.75 (m, 12H; PPh_3-*H*), δ 7.11-7.04 (m, 18H; PPh_3-*H*), δ 4.69, δ 3.27 (s, 2H, 2H; C_5H_4), δ 2.83 (q, $J = 7$ Hz, 4H; –N(CH_2CH_3)$_2$), δ 1.09 (t, $J = 7$ Hz, 6H;

Table 3 Ru(II)-catalyzed α-alkylation of arylacetonitriles with primary alcohols[a]

	nitrile	alcohol	products			% conversion[b]	
							
entry	**1**	**2**	**3**	**4**	mol% [Ru]	**M1**	**M2**	**M3**
1	**1a** R^1 = Ph	**2a** R^2 =Ph	**3a** (**4a**)		1%	37 (18)	38 (32)	7 (0)
2	**1a**	**2b** R^2 = 4-FC_6H_4	**3b** (**4b**)		1%	50 (19)	58 (21)	4 (0)
3	**1a**	**2c** R^2 = 2-$OMeC_6H_4$	**3c** (**4c**)		1%	16 (0)	27 (10)	4 (0)
4					2%	33 (24)	41 (14)	15 (0)
5	**1a**	**2d** R^2 = 4-$OMeC_6H_4$	**3d** (**4d**)		1%	22 (0)	35 (8)	3 (0)
6					2%	33 (11)	37 (15)	15 (0)
7	**1a**	**2e** R^2 = thiophen-2-yl	**3e** (**4e**)		1%	57 (6)	67 (7)	4 (0)
8	**1a**	**2f** R^2 = 2-furyl	**3f** (**4f**)		1%	40 (5)	49 (9)	3 (0)
9					2%	49 (4)	58 (9)	7 (0)
10[c]	**1a**	**2g** R^2 = Pr	**3g** (**4g**)		2%	31 (7)	23 (33)	11 (0)
11	**1b** R^1 = 4-$OMeC_6H_4$	**2a**	**3h** (**4h**)		1%	25 (0)	31 (0)	5 (0)
12					2%	36 (0)	40 (0)	16 (0)
13	**1b**	**2b**	**3i** (**4i**)		1%	26 (0)	34 (0)	6 (0)
14					2%	35 (0)	39 (0)	22 (trace)
15	**1c** R^1 = 4-FC_6H_4	**2a**	**3j** (**4j**)		1%	36 (31)	40 (38)	6 (0)

[a] Reaction conditions: catalyst (0.02 mmol), nitrile (1 or 2 mmol depend on mol% of cat.), alcohol (6 mmol), DBU (0.4 mmol), 120 °C, 24 h. [b] Conversion (based on nitrile) determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. Values in parenthesis indicate the conversion of the corresponding saturated products **4**. [c] 48 h.

–N(CH_2CH_3)$_2$), δ –10.23 (t, J = 33 Hz, 1H; Ru-H). ^{31}P{^{1}H}NMR (161 MHz, C_6D_6, 25 °C): δ 69.04 (s). ^{13}C{^{1}H}NMR (100.61 MHz, C_6D_6, 25 °C): δ 65.70(t, J = 4 Hz,–C-N(CH_2CH_3)$_2$), δ 47.20 (s, –C–N(CH_2CH_3)$_2$), δ 13.73 (s, –C–N(CH_2CH_3)$_2$). ESI-MS: m/z 762.21, [M]$^+$.

[(η^5-$C_5H_4NMe_2$)Ru(PPh_3)$_2$(CH_3CN)]$^+BF_4^-$ (M1). A sample of (η^5-$C_5H_4NMe_2$)Ru(PPh_3)$_2$H (0.10 g, 0.14 mmol) was added to a two-necked round bottom flask which was degassed and flushed with nitrogen four times, freshly degassed THF (20 mL) was added to dissolve the complex, followed by the addition of HBF_4·Et_2O (25 μL, 1.5 mmol) and CH_3CN (1 mL). The solution was stirred at room temperature for 1 h, and evaporated to dryness under reduced pressure to yield a yellow paste. Hexane (5 mL) was added to the residue, with stirring, to produce a yellow solid. The solid was filtered off and washed with diethyl ether (2 × 2 mL). It was collected and dried under vacuum at room temperature. Yield: 89 mg (76%). Anal. Calcd (%) of $C_{45}H_{43}BF_4N_2P_2Ru$: C, 62.73; H, 5.03; N, 3.25. Found: C, 62.55; H, 5.09; N, 3.19. ^{1}H NMR (400 MHz, $(CD_3)_2O$, 25 °C): δ 7.46-7.39 (m, 6H; PPh_3-H), δ 7.31-7.25 (m, 24H; PPh_3-H), δ 4.28, δ 3.27 (s, 2H, 2H; C_5H_4), δ 2.88 (s, 6H; N(CH_3)$_2$), δ 2.28 (s, 3H; Ru-NCCH_3). ^{31}P{^{1}H}NMR (161 MHz, $(CD_3)_2O$, 25 °C): δ 46.22 (s) ^{13}C{^{1}H}NMR (100.61 MHz, $(CD_3)_2O$, 25 °C): δ 60.42 (t, J = 6 Hz, –C-N(CH_3)$_2$), δ 40.12 (s, –N(CH_3)$_2$). ESI-MS: m/z 734.15, [M–CH_3CN]$^+$.

[(η^5-$C_5H_4NEt_2$)Ru(PPh_3)$_2$(CH_3CN)]$^+BF_4^-$ (M2). A procedure similar to that for the synthesis of [(η^5-$C_5H_4NMe_2$)Ru(PPh_3)$_2$(CH_3CN)]$^+BF_4^-$ was followed, except that (η^5-$C_5H_4NEt_2$)Ru(PPh_3)$_2$H (0.10 g, 0.13 mmol) was used in place of (η^5-$C_5H_4NMe_2$)Ru(PPh_3)$_2$H. Yellow solid; yield: 83 mg (71%). Anal. Calcd (%) of $C_{47}H_{47}BF_4N_2P_2Ru$: C, 63.45; H, 5.32; N, 3.15. Found: C, 63.38; H, 5.39; N, 3.11. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.37-7.30 (m, 6H; PPh_3-H), δ 7.27-7.21(m, 12H; PPh_3-H), δ 7.19-7.11(m, 12H; PPh_3-H), δ 4.08, δ 3.04 (s, 2H, 2H; C_5H_4), δ 3.15 (q, J = 7 Hz, 4H;–N(CH_2CH_3)$_2$), δ 2.20 (s, 3H; Ru-NCCH_3), δ 1.11 (t, J = 7 Hz, 6H; –N(CH_2CH_3)$_2$). ^{31}P{^{1}H}NMR (161 MHz, $(CD_3)_2O$, 25 °C): δ 46.45 (s). ^{13}C{^{1}H}NMR (100.61 MHz, $(CD_3)_2O$, 25 °C): δ 59.95 (t, J = 6 Hz, –C-N(CH_2CH_3)$_2$), δ 45.85 (s, –C–N(CH_2CH_3)$_2$), δ 13.55 (s, –C–N(CH_2CH_3)$_2$). ESI-MS: m/z 762.19, [M–CH_3CN]$^+$.

(η^5-$C_5H_4NMe_2$)Ru(PPh_3)(Ph)(CO) (M5). A sample of [(η^5-$C_5H_4NMe_2$)Ru(PPh_3)$_2$H (0.50 g, 0.68 mmol) was loaded into a two-necked round bottom flask, which was then evacuated and flushed with nitrogen for four cycles. Degassed toluene (10 mL) and benzaldehyde (0.35 mL, 2.07 mmol) were then added and the resulting mixture was refluxed with stirring for 24 h. At the end of this period, the solution was cooled to room temperature and was evaporated to dryness under reduced pressure to yield a pale yellow paste. Hexane (5 mL) was added to the residue, with stirring at –78 °C, to produce a yellow solid. The solid was filtered off, and thoroughly dried under vacuum to give **M5** which was contaminated by free triphenylphosphine and phosphine oxide. **M5** was characterized by NMR spectroscopy. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.79-7.04(m, 20H; PPh_3-H, Ru–C_6H_5), δ 4.87, δ 4.53 (d, J = 2 Hz, 1H, 1H; C_5H_4), δ 4.18, δ 4.16 (s, 1H, 1H; C_5H_4), δ 2.23 (s, 6H; N(CH_3)$_2$).^{31}P{^{1}H}NMR (161 MHz, C_6D_6, 25 °C): δ 59.88 (s) ^{13}C{^{1}H}NMR (100.61 MHz, C_6D_6, 25 °C): δ 207.70 (d, $^2J_{PC}$ = 19 Hz, Ru-CO); δ 152.31 (d, $^2J_{PC}$ = 12 Hz, *ipso* C of Ru–C_6H_5).

***In situ* Preparation of HDBU$^+BF_4^-$.** The compound was synthesized according to the literature method with a slight modification.[11] HBF_4·Et_2O (0.58 mL, 3.6 mmol) was added to an ice-cooled solution of DBU (0.5 mL, 3.3 mmol) in Et_2O (10 mL). The reaction mixture was allowed to stir in the ice bath for 30 min. At the end of this period, the mixture was evaporated to dryness under reduced pressure to give a pale yellow oil. The resulting oil was washed with pentane (2 × 3 mL). It was collected and dried under vacuum at room temperature. Yield: 0.66 g (83%). ^{1}H NMR

(400 MHz, $CDCl_3$, 25 °C): δ 7.97 (s, 1H; N*H*), δ 3.58-3.53 (m, 4H), δ 3.41-3.39 (m, 2H), δ 2.69-2.67 (m, 2H), δ 2.09-2.037 (m, 2H), δ 1.76-1.70 (m, 6H).

General procedure of catalytic α-alkylation of arylacetonitriles. The reactions were carried out in a 10 mL round-bottomed flask equipped with a reflux condenser topped with a nitrogen bypass. In a typical run, ruthenium complex (0.02 mmol) was loaded into the flask; it was then evacuated and filled with nitrogen for four cycles. Arylacetonitriles (1 or 2 mmol depending on mol% of cat.), primary alcohol (6 mmol) and DBU (0.4 mmol) were added to the flask *via* syringes and needles. The flask was heated in a silicon oil bath at 120 °C for 24 h. At the end of this period, the system was cooled to room temperature and 25mL 1,1,2,2-tetrachloroethane was added as internal standard; a 0.1 mL aliquot of the solution was removed and analyzed by ^{1}H NMR spectroscopy (in $CDCl_3$). Conversions of the reactions were obtained by measuring the integrations of the characteristic peaks of the products with reference to distinct peaks of the internal standard.

Monitoring of $[(\eta^5\text{-}C_5H_4NMe_2)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (M1) and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (M3)-catalyzed α-alkylation of benzyl cyanide with benzyl alcohol using ^{31}P{^{1}H}NMR spectroscopy. The reactions were carried out in 5 mm NMR tubes capped with rubber septa. In a typical run, the ruthenium complex (0.01 mmol, 1 mol%) was loaded to a tube; it was evacuated and filled with nitrogen for four cycles. Benzyl cyanide (1 mmol), benzyl alcohol (3 mmol) and DBU (0.2 mmol) were added to the tube *via* syringes and needles. The resulting solution was heated in a silicon oil bath at 120 °C. At different time intervals, the NMR tube was rapidly cooled down to room temperature and ^{31}P{^{1}H}NMR spectra of the solution were taken. The relative concentrations of the species present were obtained by comparing the integrations of their signals in the ^{31}P{^{1}H}NMR spectra.

Reactions of the metal hydrides M4 and M6 with $DBUH^+$ in the presence of CH_3CN. A weighted amount of hydride complex (0.01 mmol) was loaded into a 5 mm NMR tube capped with a septum; it was then evacuated and filled with nitrogen for four cycles. Freshly prepared $HDBU^+BF_4^-$ (0.12 g, 0.5 mmol) in THF (0.45 mL) was then added to the tube *via* syringe and needle. After complete dissolution of the complex, CH_3CN (26 μL, 0.5 mmol) was added. The resulting solution was heated in a silicon oil bath at 60 °C. At different time intervals, the NMR tube was cooled down to room temperature and ^{31}P{^{1}H} NMR spectra of the solution were taken. The relative concentrations of the complexes present were obtained by comparing the integrations of their signals in the ^{31}P{^{1}H}NMR spectra.

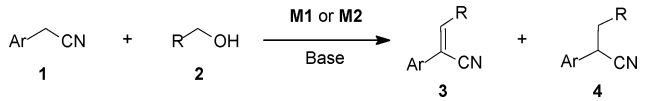
Crystallographic structure analysis of $[(\eta^5\text{-}C_5H_4NMe_2)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (M1). Yellow crystals suitable for the X-ray diffraction study for **M1** were obtained by layering of n-hexane onto a dichloromethane solution of the complex. A suitable crystal of the complex was mounted on a Bruker CCD area detector diffractometer and subjected to Mo-Kα radiation (λ = 0.71073 Å) from a generator operating at 50 kV and 30 mA. The intensity data of **M1** was collected in the range θ = 1.97–27.38°, with oscillation frames of ψ and ω in the range 0–180°. A total of 1756 frames in **M1** were taken in four shells. An empirical absorption correction of the SADABS (Sheldrick, 1996) program based on Fourier coefficient fitting was applied. The crystal structure was solved by Patterson function methods and expanded by difference Fourier synthesis, then refined by full-matrix least-squares on F^2 using the Bruker Smart and Bruker SHELXTL program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. The R and R_w values of **M1** are 0.0493 and 0.0891, respectively. Further crystallographic details and selected bond distances and angles for **M1** can be found in the Results and discussion section.

Computational details. In the DFT calculations, PMe_3 was used as a model for PPh_3. Geometry optimizations and frequency calculations have been performed for all species involved in the reaction at the Becke3LYP[12] level of density functional theory (no imaginary frequencies for an equilibrium structure and one imaginary frequency for a transition structure). The intrinsic reaction coordinate (IRC)[13] analysis was also carried out to confirm that all stationary points are smoothly connected to each other. Gibbs free energy at 298.15 K was obtained on the basis of the frequency calculations. The Ru and P atoms were described using the LANL2DZ basis set, a double-ζ valence basis set with the Hay and Wadt effective core potential (ECP).[14] For all other atoms, the 6-31G basis set was used.[15] Polarization functions were added for N (ζ_d = 0.864) and for P (ζ_d = 0.387). For those H bonded to Ru, polarization functions were also added (ζ_p = 1.100).[16] All calculations were performed with Gaussian 03 packages.[17]

Results and discussion

In view of the catalytic activity of ruthenium complexes in β-alkylation of secondary alcohols with primary alcohols, we studied catalytic α-alkylation of nitriles with primary alcohols using a number of Cp-Ru and Tp-Ru complexes (Tp = hydrotris(pyrazolyl)borate); however, they were found be inactive or very poor catalysts.

We then prepared the aminocyclopentadienyl-Ru complexes $[(\eta^5\text{-}C_5H_4NMe_2)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (**M1**) and $[(\eta^5\text{-}C_5H_4NEt_2)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (**M2**), and found that they are active for arylacetonitrile alkylation reactions (eqn (1)).

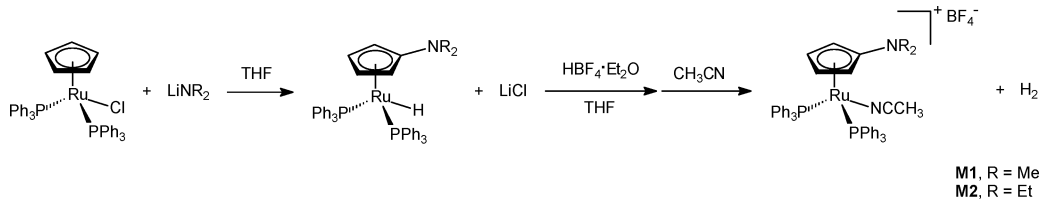


(1)

Preparation and characterization of complexes M1 and M2, and X-ray structure of M1

The aminocyclopentadienyl-ruthenium complexes **M1** and **M2** were prepared by protonation of the hydride precursors with $HBF_4{\cdot}Et_2O$ in the presence of acetonitrile; the hydride complexes were formed by reacting $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ with $LiNR_2$ (R = CH_3, C_2H_5) in THF (Scheme 1).

Aminocyclopentadienyl-Fe hydride complexes $(\eta^5\text{-}C_5H_4NR_2)Fe(L_1)(L_2)H$ (R = CH_3, C_2H_5; L_1 = CO, L_2 = PR_3; L_1 = L_2 = PR_3) were prepared in a similar manner.[18] The ^{1}H NMR spectra of **M1** and **M2** show signals of the acetonitrile ligands at δ 2.28 and 2.20 ppm, respectively. A singlet that corresponds to the amino methyl groups in **M1** is seen at δ 2.88 ppm; on the other hand, the existence of amino ethyl groups



Scheme 1

of **M2** is confirmed by the observation of quartet (δ 3.15 ppm) and triplet (δ 1.11 ppm) signals which are present in a 2 : 3 ratio. The phosphine ligands of **M1** and **M2** appear as singlets at δ 46.22 and 46.45 ppm, respectively in their $^{31}P\{^{1}H\}$ NMR spectra.

Yellow crystals of **M1** suitable for X-ray diffraction study were obtained by layering hexane onto a CH_2Cl_2 solution of the complex. Fig. 1 shows the molecular structure of **M1**. The crystal data and refinement details are given in Table 1. Selected bond distances and angles are given in Table 2. The amino moiety is linked to the Cp ring *via* a short C(1)–N(11) bond (1.351(5) Å) which is shorter than the standard C(sp^2)–N(sp^3) single bonds (1.40–1.44 Å) but longer than typical C(sp^2)=N(sp^2) double bonds (1.25–1.28 Å).[19] The distance from Ru to the $N(CH_3)_2$-substituted Cp carbon (Ru–C(1), 2.363(3) Å) and to the two carbons in β positions from C(1) (Ru–C(3), 2.172(4) Å; Ru–C(4), 2.167(4) Å) are significantly longer and shorter, respectively, than the Ru–C(Cp) bonds found in the unsubstituted Cp complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (**M3**) (Ru–C(Cp) ≈ 2.21 Å).[20] The nitrogen atom is nearly coplanar with its substituents (sum of the angles around N, $\Sigma_N = 356.3°$); it sits 0.156 Å above the C_1–C_6–C_7 plane, which makes a small angle of 4.4° with the Cp ring. The structural properties of $\mathbf{M1}^+$ is in line with the structural data reported for the aminocyclopentadienyl-Fe complex $(\eta^5\text{-}C_5H_4NEt_2)Fe(PPh(OEt)_2)(CO)Br$[18] and for 1,1′-bis(dimethylamino)-titanocene dichloride.[21] The structure of **M1** shows hydrogen-bonding interactions between two of the fluorine atoms of the tetrafluoroborate anion and two of the Cp hydrogen atoms (H(3A)···F(1), 2.34 Å; H(4A)···F(3), 2.66 Å).

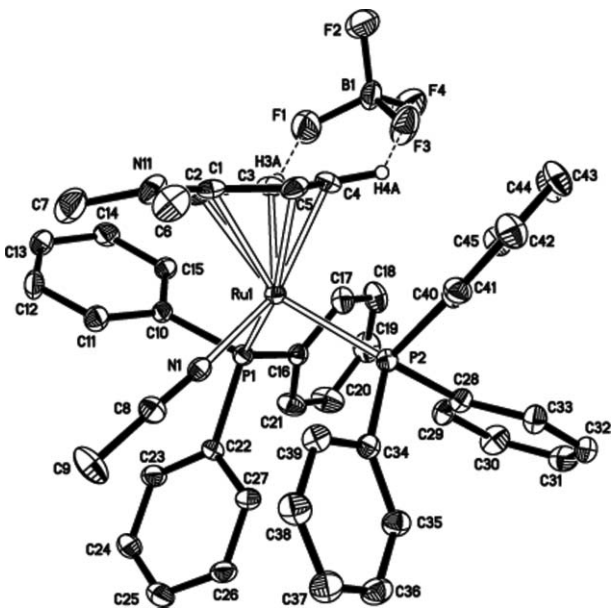


Fig. 1 ORTEP view (30% probability) of $[(\eta^5\text{-}C_5H_4NMe_2)Ru(PPh_3)_2\text{-}(CH_3CN)]^+BF_4^-$ (**M1**) showing the atom-labeling scheme.

Catalytic α-alkylation of arylacetonitriles with alcohols

The major products of the **M1**- and **M2**-catalyzed reactions are the unsaturated nitriles, and the saturated nitriles in some cases only appear as very minor products (Table 3). Product distributions in our study are quite different from those of the studies carried out by others; in their studies, the saturated nitriles are the overwhelming products.

The Cp complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(CH_3CN)]^+BF_4^-$ (**M3**) shows very low activity. Generally speaking, the complex with the diethylamino substituent on the Cp ring (**M2**) is more active than the one in which the Cp ring carries the dimethylamino group (**M1**). Benzyl alcohols with electron-donating substituents give lower overall conversions (entries 3–6), and the one containing an electron-withdrawing fluoro group affords higher conversion (entry 2). Alcohols containing heteroatoms seem to be less active than benzyl alcohol (entries 7–9), and alkyl alcohol is even less reactive (entry 10). Attachment of an electron-withdrawing fluoro group to the arylacetonitrile modestly increases the overall conversion (entry 15); on the other hand, the presence of an electron-donating substituent lowers the activity of the system (entries 11–14).

We are interested in understanding the large difference in catalytic activity between the systems based on the aminocyclopentadienyl complexes **M1**, **M2** and that based on the unsubstituted Cp complex **M3**. In a separate experiment, we learned that benzyl cyanide reacts, in the presence of DBU (40 mol%), with benzaldehyde to give the unsaturated nitrile **3a** in 88% conversion; no metal catalyst is needed for the reaction. The reaction, however, does not proceed in the absence of the base. It therefore seems that in the **M1**- and **M2**-catalyzed arylacetonitrile α-alkylation reactions, the major function of the metal complex is to affect dehydrogenation of the alcohol to yield the aldehyde, which then undergoes base-catalyzed condensation with the arylacetonitrile. In the presence of DBU, the complex reacts with alcohol to generate metal alkoxide, and subsequent β-elimination gives the aldehyde and the metal hydride species.

NMR monitoring of M1- and M3-catalyzed alkylation of benzyl cyanide with benzyl alcohol; comparison of rates of conversion of the metal hydrides to M1 and M3

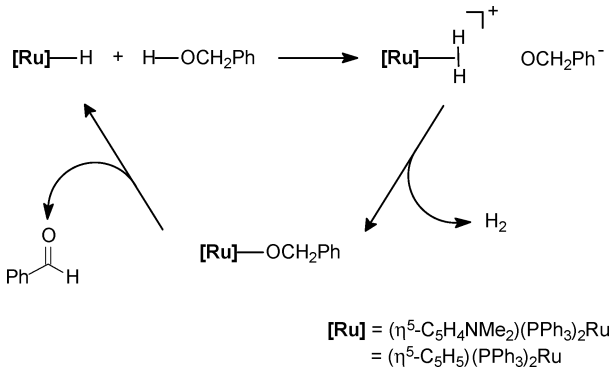
We monitored the **M1**- and **M3**-catalyzed alkylation of benzyl cyanide with benzyl alcohol with $^{31}P\{^{1}H\}$NMR spectroscopy. In the **M1**-catalyzed reaction, it was found that the metal hydride $(\eta^5\text{-}C_5H_4NMe_2)Ru(PPh_3)_2H$ (**M4**) was rapidly formed and it remained the major metal-containing species throughout the experiment;

small amounts of free phosphine and phosphine oxide due to complex decomposition were detected, their amounts increased with time. In addition, minute amounts of the carbonyl species (η^5-$C_5H_4NMe_2$)Ru(PPh_3)(Ph)(CO) (**M5**) and an unknown species were also detected. In the **M3**-catalyzed alkylation reaction, in which conversion was very low, the hydride complex (η^5-C_5H_5)Ru(PPh_3)$_2$H (**M6**) was the overwhelming species detected during the monitoring process, small amounts of free phosphine and phosphine oxide, indicative of a small degree of complex decomposition, were observed. Minute quantities of the carbonyl complex (η^5-C_5H_5)Ru(PPh_3)(Ph)(CO) (**M7**) and an unknown species were also formed. Formation of the phenyl carbonyl complexes **M5** and **M7** is probably due to benzaldehyde decarbonylation at the metal center. We have recently reported the synthesis of **M7**;[8] the aminocyclopentadienyl analogue **M5** is independently prepared in this study. Decarbonylation of aldehydes by transition metal complexes to form carbonyl complexes is well-established.[22] Aldehyde decarbonylation forming metal carbonyl species often causes catalyst deactivation.[22f,23]

Reactions of (η^5-$C_5H_4NMe_2$)Ru(PPh_3)$_2$H (M4) and (η^5-C_5H_5)Ru(PPh_3)$_2$H (M6) with DBUH$^+$ and with benzyl alcohol

We studied reactions of the hydride species **M4** and **M6** with DBUH$^+$$BF_4^-$ in THF in the presence of excess CH_3CN. It was found that at 60 °C **M4** in a THF solution containing 50 equiv each of DBUH$^+$$BF_4^-$ and CH_3CN was converted to **M1** (70%) after 30 min; the pseudo first order rate constant k was determined to be 0.0589 min^{-1}. On the other hand, under identical conditions, only a trace amount of **M3** was generated from **M6**. Reaction of **M4** with DBUH$^+$ first generated the η^2-dihydrogen intermediate **M-(H_2)**, it then came into equilibrium with the more stable and dominating dihydride tautomer. Formation of **M1** resulted *via* extrusion of H_2 from **M-(H_2)** and coordination of CH_3CN to the metal center (Scheme 2). Protonation of CpRu complexes to yield η^2-dihydrogen complexes as kinetic products which then come into equilibrium with the more stable metal dihydride is well-documented.[24]

It is known that transition-metal hydrides might be protonated by acidic alcohols to form η^2-dihydrogen complexes;[25] the dihydrogen ligand might then be displaced by the alkoxide. (Scheme 3). We looked into the possibility that the metal hydrides **M4** and **M6** would be protonated by benzyl alcohol to form the metal alkoxide which then *via* β-elimination generate the metal hydride and benzaldehyde (Scheme 4). It was found that heating



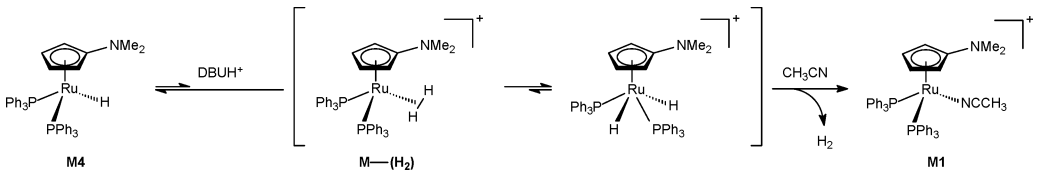
Scheme 4

a C_6D_5Cl solution of **M4** in the presence of 50 equiv of benzyl alcohol at 120 °C for 48 h only resulted in the formation of 0.2 equiv of benzaldehyde. $^{31}P\{^1H\}$NMR spectroscopy showed that **M4** basically remained unchanged although minute amounts of free phosphine, phosphine oxide and a couple of unknown species, probably due to **M4** decomposition, were observed. In the case of **M6**, under identical conditions, only a trace amount of benzaldehyde was generated; **M6** was recovered unchanged. These experiments seem to indicate that the reaction shown in Scheme 4 occurred to a negligibly small extent for **M4** and **M6**.

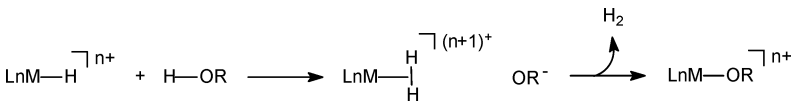
Theoretical calculations on the protonation of hydride complexes with DBUH$^+$ in CH_3CN

To gain support for the much more facile regeneration of the solvent complex from the hydride species in the case of the aminocyclopentadienyl complex in comparison to the non-substituted Cp-Ru system, theoretical calculations, performed at the Becke3LYP level of theory, on the displacement of H_2 from the dihydrogen complexes by CH_3CN (Schemes 2 and 5) were carried out.

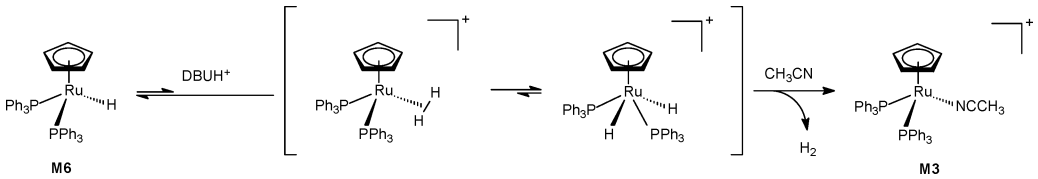
In the presence of DBUH$^+$, both **M4** and **M6** could be reversibly converted to the corresponding dihydrogen complexes and their dihydride tautomers; the equilibria would probably lie to the sides of the hydrides because after all DBUH$^+$ is a weak acid. We focus on the processes of the H_2/CH_3CN exchange of the two dihydrogen species. In the DFT calculations, PMe_3 is used as a model for PPh_3. Both dihydrogen complexes are 18-electron species and each contain an η^5-cyclopentadienyl ligand. Therefore, the H_2/CH_3CN exchange is expected to occur *via* either a dissociative mechanism or an associative mechanism involving a $\eta^5 \rightarrow \eta^3$ ring slippage of



Scheme 2



Scheme 3



Scheme 5

the cyclopentadienyl ligand, a well-known phenomenon for η^5-Cp transition metal complexes.[26] Our calculations show that the Cp ring slippage for the dihydrogen complexes is much less favorable than H_2 dissociation. The results are understandable because the dihydrogen is a weakly-coordinated ligand.

Fig. 2 shows the energy required to dissociate H_2 from **A** to give (**A′** + H_2) is 17.3 kcal mol^{-1}. After H_2 dissociation, **A′** takes in CH_3CN to form **M1'**, which is more stable than **A** by 7 kcal mol^{-1}. The activation barrier for the dissociative mechanism was estimated by calculating the H_2 dissociation energy, which is the upper limit for a dissociative ligand substitution reaction. Fig. 3 shows the corresponding energy profile calculated for the dihydrogen complex **B**, the H_2 dissociation energy was found to be 21.3 kcal mol^{-1}.

The metal fragment **A′** derived from H_2 dissociation from **A** is relatively more stable than the metal fragment **B′** generated by H_2 dissociation from **B**. Therefore, the H_2 dissociation process from the complex **A** is more favorable. The electron donating NMe_2 moiety on the Cp ring contributes to stabilizing the electron deficient 16-e$^-$ metal fragment **A′**. For complex **B**, in the absence of an NMe_2 substituent, H_2 dissociation is much less favorable. Brookhart and co-workers carried out a detailed mechanistic study on the [CpFe(CO)(PPh_3)]$^+$-catalyzed silane alcoholysis and revealed that displacement of the H_2 ligand of the η^2-dihydrogen intermediate by silane is probably the rate-determining step.[27] A density functional study showed that introduction of an amino substituent at the Cp ring of the catalyst lowers the barrier of the H_2/silane exchange step; it is rationalized by the π-donating capability of the amine group which makes the Cp ring more electron-rich, resulting in better stabilization of the electron-deficient iron center upon H_2 dissociation.[28]

Proposed mechanism for the catalytic α-alkylation of arylacetonitrile with primary alcohol

Taken together, a mechanism is proposed for the **M1**- or **M2**-catalyzed α-alkylation of arylacetonitriles with primary alcohols (Scheme 6). In the presence of a base (DBU) and the metal

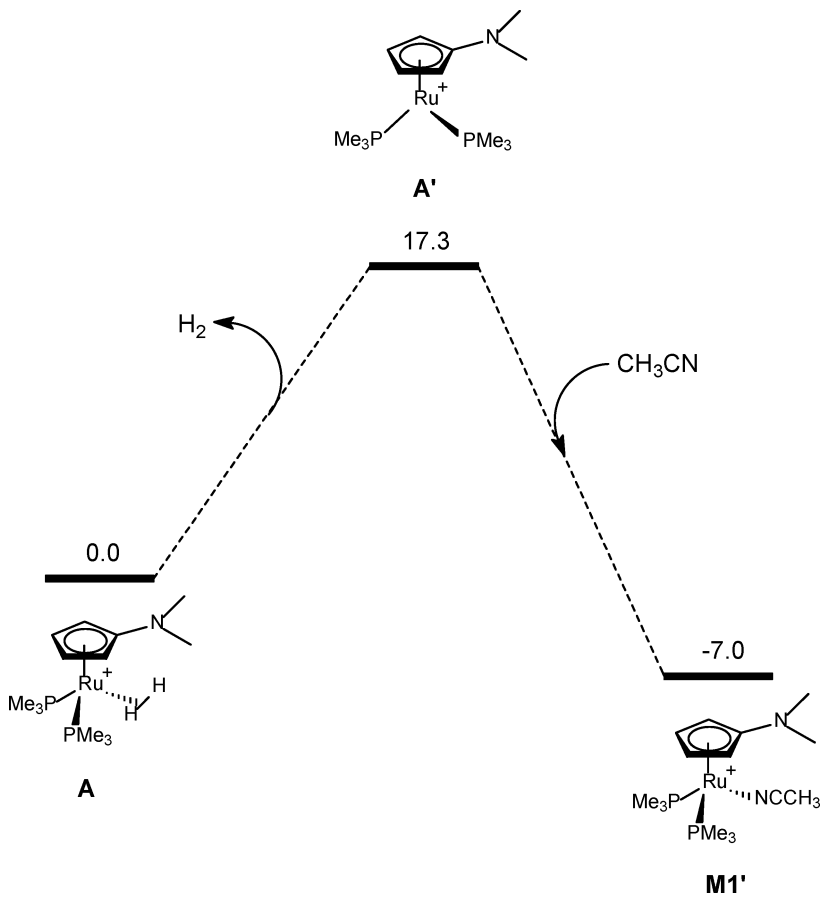


Fig. 2 Energy profile calculated for the H_2/CH_3CN ligand exchange in the complex **A**. The calculated relative electronic energies are given in kcal mol^{-1}.

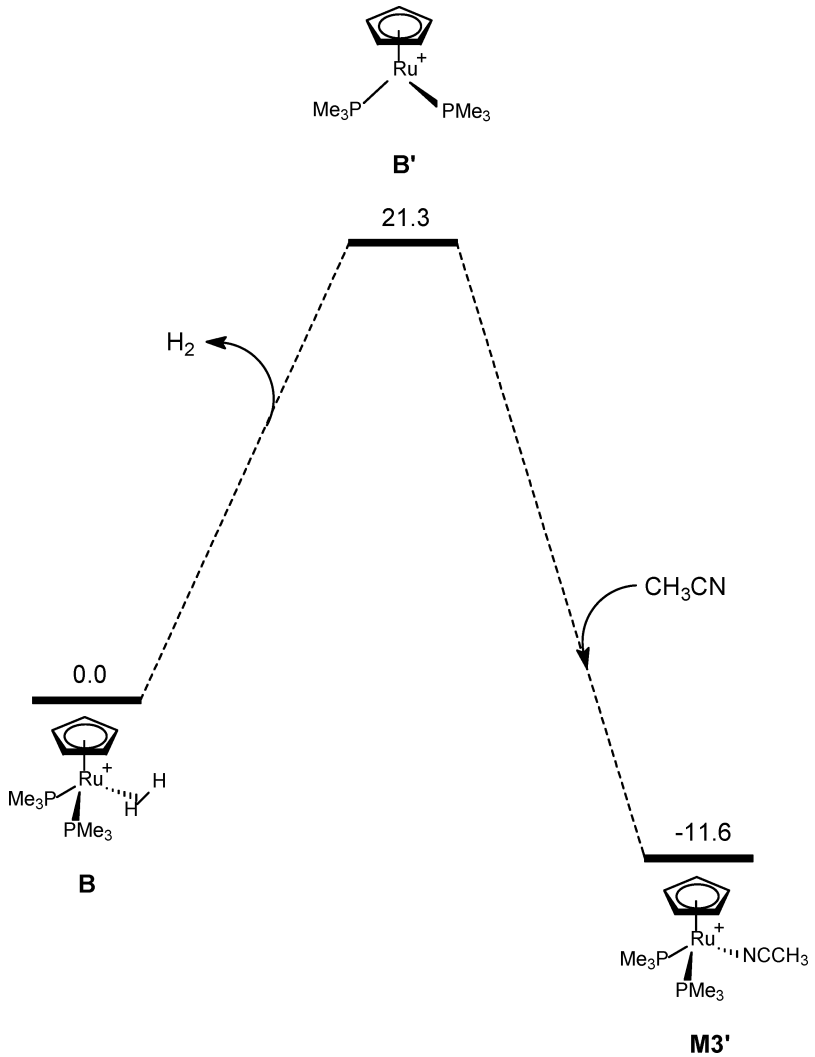


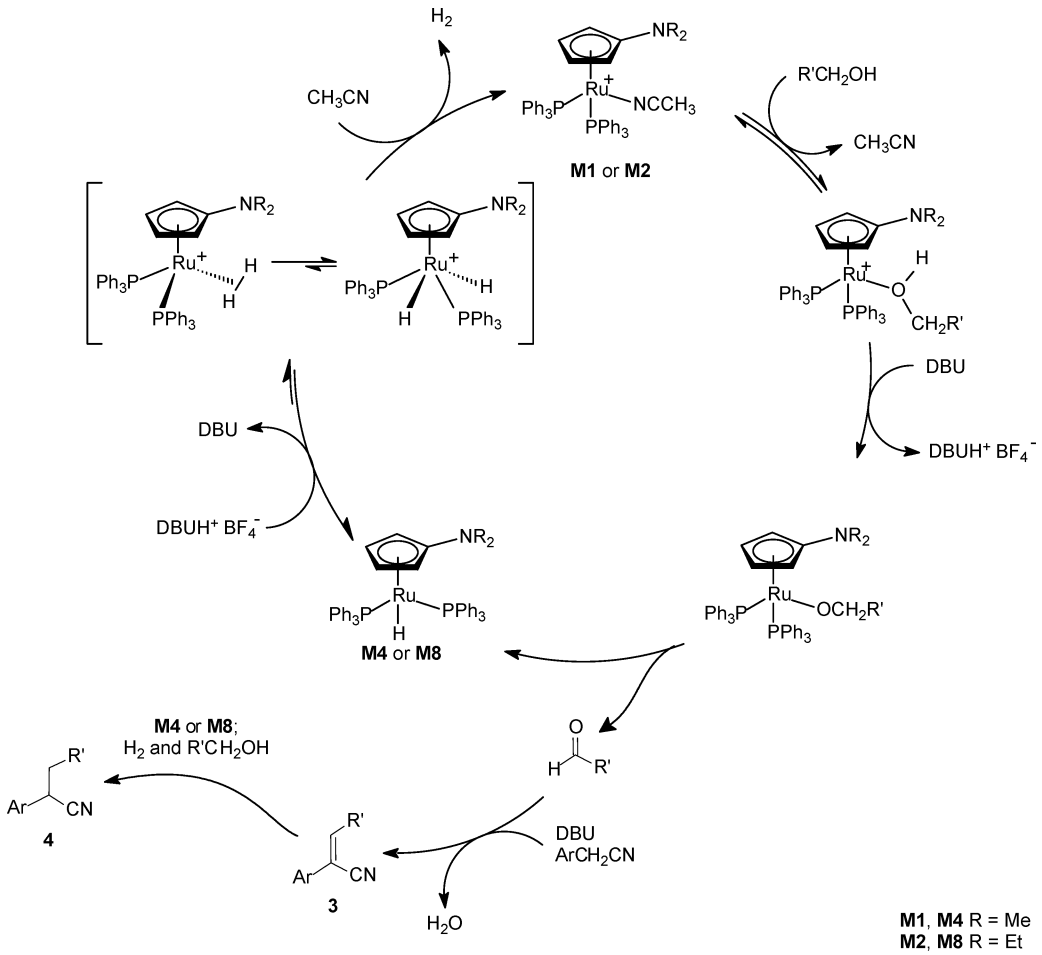
Fig. 3 Energy profile calculated for the H_2/CH_3CN ligand exchange in the complex **B**. The calculated relative electronic energies are given in kcal mol^{-1}.

complex, the alcohol is oxidized to aldehyde while the metal complex is converted to a hydride species (η^5-$C_5H_4NMe_2$)$Ru(PPh_3)_2H$ (**M4**) or (η^5-$C_5H_4NEt_2$)$Ru(PPh_3)_2H$ (**M8**). The aldehyde, by the action of the base, undergoes Knoevenagel condensation with the arylacetonitrile to afford the unsaturated nitrile **3**. The crucial and slow step is the regeneration of the solvent complex **M1** or **M2** *via* protonation of the hydride species **M4** or **M8** (with $DHUH^+$) and subsequent H_2/CH_3CN exchange. This process is very slow for the analogous Cp hydride species **M6**, and this is probably the major reason for the unsubstituted Cp system **M3** being a poor catalyst for the α-alkylation reactions. In the **M1**- or **M2**-catalyzed reaction, the barrier of the ligand exchange step is lowered with increased electron density at the metal center; this is probably the reason for **M2**, which contains the more electron-donating diethylamino group, being more active than **M1** bearing the dimethylamino substituent on the Cp ring. The electron-donating nature of the amino group is also illustrated by the nitrogen atom being coplanar with its substituents, as shown in the X-ray structure of **M1**; the sp^2-hybridized nitrogen atom can better donate its lone pair into the ring. The initially formed unsaturated nitrile **3** could be reduced *via* **M4**- or **M8**-catalyzed hydrogenation and *via* reversible insertion into the Ru–H bond of **M4** or **M8** and subsequent protonation by the alcohol. The reduction of **3** is not complete, probably due to the very low concentration of H_2 in the system and the sluggishness of the alcohol protonation step.

Benzyl alcohols with electron-withdrawing and electron-donating substituents giving higher and lower conversions, respectively, is in consonance with the fact that the aldehyde with a more electrophilic carbon center undergoes condensation with arylacetonitrile more readily than the ones with less electrophilic carbon centers. Lower conversion with 4-methoxyphenylacetonitrile is probably attributable to its less readiness to be deprotonated by the base to generate the α-cyano carbanion, which is the nucleophile attacking the aldehyde carbon in the condensation reaction.

Conclusion

Few examples of transition metal-catalyzed α-alkylation of nitriles with primary alcohols, which is a green and atom-economical reaction to yield α-alkylated nitriles, are known to date. Success of



Scheme 6

this reaction lies in the ability of the metal to catalyze oxidation of the alcohol to aldehyde. Moreover, readiness of the nitrile, which is usually an aryl- or heteroarylacetonitrile, to undergo condensation with the aldehyde is also important. We have demonstrated in this work that the aminocyclopentadienyl ruthenium complexes are moderately active catalysts for α-alkylation of arylacetonitriles with primary alcohols. The main thrust of our work lies on our being able to provide supports, both experimental and theoretical, for the proposed mechanism which accounts for the much higher catalytic activity of the aminocyclopentadienyl ruthenium complexes over the non-substituted analogous Cp-Ru complexes, and this is important from the point of view of basic organometallic chemistry.

Acknowledgements

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