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CARBON–CARBON BOND ACTIVATION VIA FORMAL β-METHYL-ELIMINATION FROM [η^5-6,6-DIMETHYLCYCLOHEXADIENYL)Ru(DPPE)(CH_2Cl_2)]PF_6†‡

PETER T. DIMAURO and PETER T. WOLCZANSKI§

Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, NY 14853, U.S.A.

Abstract—Carbon–carbon bond activation has been observed through a formal β-methyl elimination from a 6,6-dimethylcyclohexadienyl (dmCh) ligand. Reflux of an EtOH solution of $RuCl_3 \cdot 3H_2O$, (dmCh)H (15 equiv.), and Zn dust (15 equiv.) afforded $(dmCh)_2Ru$ (**1**, 65–77%). Protonation of **1** with $HBF_4 \cdot Et_2O$ in ether provided $[(dmCh)_2RuH][BF_4]$ (**2**) in 77% yield; NMR spectra were consistent with either a terminal hydride or rapidly equilibrated agostic ground-state structure. Addition of CH_3CN to **2**, or protonation of **1** in CH_3CN, gave $[(\eta^5\text{-dmCh})Ru(NCCH_3)_3][BF_4]$ (**3**, 70%). Treatment of **3** with 2.0 equiv. PMe_3 or 1.0 equiv. dppe produced $[(dmCh)RuL_2(NCCH_3)][BF_4]$ (**4**, L = PMe_3; **5**, L = dppe), which were poor precursors to halide derivatives. Treatment of **1** with 12 M aqueous HCl in acetone generated $[(dmCh)RuCl]_n$ (**6**) in 55% yield. Addition of excess norbornadiene to **6** in hexane yielded (dmCh)Ru(NBD)Cl (**7**, 90%), which proved to be a ready precursor to $(dmCh)RuL_2Cl$ (**8**, L = PMe_3, 90%; **9**, L_2 = dppe, 53%) upon addition of the appropriate phosphine. Chloride abstraction from **8** with $TlPF_6$ afforded numerous $[(dmCh)Ru(PMe_3)_2(solvent)]PF_6$ [(**10**-solvent), solvent = CD_2Cl_2, CD_3NO_2, THF, 2-Me-THF] derivatives, but β-methyl elimination was not observed in subsequent thermolyses. A similar chloride abstraction from **9** produced $[(dmCh)Ru(dppe)(CD_2Cl_2)]PF_6$ ([**11**-CD_2Cl_2]PF_6); thermolysis of **11**-CD_2Cl_2 at 91°C for 12 h generated $[(\eta^6\text{-}C_7H_8)Ru(dppe)(CH_3)]PF_6$ (**12**), presumably via the coordinatively unsaturated precursor, [(dmCh)Ru(dppe)]PF_6 ([**11**]PF_6). The molecularity of the β-methyl elimination pathway remained elusive. Addition of 1.0 equiv. of $[Cp_2Fe][PF_6]$ to **1** in CD_3CN gave **3**-PF_6, while oxidation in CD_2Cl_2 provided $[(dmCh)Ru(\eta^6\text{-toluene})]PF_6$ (**13**-PF_6); cyclic voltammetry pinpointed the irreversible oxidation at ±0.85 V *vs* Ag/AgCl in THF. Three critical factors are responsible for β-methyl elimination from [**11**]PF_6: (1) coordinative/electronic unsaturation; (2) the compatability of ruthenium to both dmCh (precursor) and toluene (product) ligation; (3) an orbital with directionality appropriate to accept the migrating methyl group.

The activation of carbon–carbon single bonds represents an intriguing area of organometallic chemistry that has recently seen an influx of activity.[1] Carbon–carbon linkages are considered difficult to attack because they are generally hindered, and competitive C—H bond activation[2,3] pathways are

† Dedicated to my colleague and continual mentor John E. Bercaw on the occasion of his 50th birthday, and to Helmut Werner, whose elegant chemistry provided precedent for this work, on the occasion of his 60th birthday.

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§ Author to whom correspondence should be addressed.

typically available. Historically, such cleavage reactions were only observed for substrates possessing significant ring strain[4,5] (*e.g.* cyclopropanes),[6] and even then C—H bond activation pathways appear competitive.[7] Strained ring substrates contain C—C bonds that are more sterically accessible. For example, a $\sigma(C—C) \rightarrow d\sigma(Rh)$ bound intermediate is implicated in the rearrangement of a cyclopropyl hydride complex to a rhodacyclopropane; this electrophilic attack of the C—C bond clearly resembles related C—H bond scission events.[7] Strained ring C—C single bond additions to transition metal complexes represent formal oxidative addition reactions. Some recent efforts to revive strained ring activation chemistry have utilized biphenylene,[8] where the stronger sp^2 *vis-a-vis* sp^3 metal–carbon bonds formed upon oxidative addition provide additional thermodynamic impetus.[9]

In substrates without inherent strain, proximity effects have allowed C—C bond cleavage oxidative addition pathways to be revealed. The majority of these cases involve precoordination of dialkylcyclopentadienes, and subsequent C—C scission to provide $(\eta^5\text{-}C_5H_4R)MRL_n$ derivatives.[10,11] Complexation of 8-acyl-quinolines has also permitted RC=O(Ar) oxidative additions to occur. The interaction of the initially low valent Rh center with the carbonyl functionality suggests that the subsequent bond-breaking step is a migration of R akin to those occuring in Baeyer–Villager and related reactions;[12] olefin coordination may precede related cyclobutenone C—C bond oxidative additions.[13] A recent transformation makes use of a proximity effect reminiscent of Shaw's intramolecular C—H activation studies.[14] Milstein and co-workers have shown that an aryl—methyl bond may be cleaved when brought proximate to a Rh center by diphosphine chelation.[15]

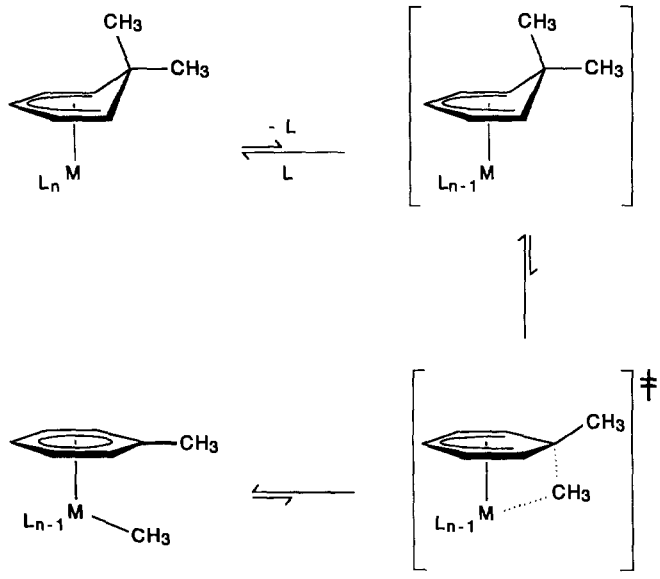
While all of the above examples involve oxidative addition, the most prevalent C—C single bond activations do not involve a formal change in metal oxidation state. Many transition metal and main group metal Lewis acids promote the electrophilic cleavage of carbon–carbon bonds.[4,16] In particular, strained ring openings represent a well-known, versatile synthetic organic method,[17] while other skeletal rearrangements resemble carbocation or superacid-mediated migrations.[18]

β-Alkyl-elimination reactions (*e.g.* $L_nMCH_2CH_2R \rightarrow L_nM(CH_2{=}CH_2)R$) are related to electrophilic activations because a coordinatively unsaturated metal is required. Observed principally in lanthanide systems, β-alkyl elimination has been proposed as a chain termination event in olefin oligomerizations (*e.g.* $Cp^*_2LuCH_2CHRR'$, $Cp^* = \eta^5\text{-}C_5Me_5$),[19] and represents a relatively low-energy pathway for skeletal hydrocarbon rearrangements (*e.g.* $Cp^*_2ScCH_2CHRR'$).[20] Ziegler–Natta polymerizations of methylenecyclobutane apparently utilize a propagation pathway that requires a ring-opening β-alkyl elimination.[21] Although low-coordinate, "hard" metal centers would appear to be the most likely candidates for β-alkyl elimination, Flood and coworkers have obtained evidence of this process via a putative $14e^-$ (2-methyl, 2-cyclobutylmethyl) $Pt(PMe_3)_2^+$ complex.[22] α-Alkyl-eliminations have also been proposed,[23] and a recent cyclohexadiene ring opening reaction mediated by manganese (I) possesses related features.[24]

Recognizing that a β-alkyl elimination reaction is likely to be endothermic (roughly, $\Delta H \approx 20$ kcal mol^{-1}),[25] enthalpic compensation may arise through aromatization of an appropriate substrate. An η^5-6,6-dimethylcyclohexadienyl (dmCh) ligand,[26,27] upon β-methyl elimination, will generate an η^6-toluene fragment that could possess the additional aromatic character necessary to drive this process (Scheme 1). Aromatic compensation is undoubtedly a critical factor in the aforementioned dialkylcyclopentadienyl C—C bond oxidative additions.[11,12] Maitlis' synthesis of $[Cp^*RhCl_2]_2$ from $RhCl_3$ via a solvent assisted C_2-extrusion from hexamethyl-Dewar-benzene provides a classic example.[28]

Crabtree has shown that it is not enough to simply coordinate a dialkylcyclohexadienyl; dehydrogenation studies of 1,1-dimethylcyclohexane yielded $(dmCh)IrHL_2^+$, but the lack of a vacant coordination site in this $18e^-$ complex, and its inert character, prevented β-methyl transfer relative to other degradation pathways. In this system, dialkylcyclopentadienyl C—C bond cleavage and other rearrangements were noted.[28] More recently, Chaudret has utilized the Cp^*Ru^+ fragment to dehydrogenate and aromatize six-membered ring substrates,[29] including several steroids.[30] Carbon–carbon bond activation has been observed, but the scissions that occur from incipient $18e^-$ [(cyclohexadienyl)$HRuCp^*]^+$ complexes apparently do not involve formal β-alkyl transfer to the ruthenium, and are attributed to homolysis or other radical-based mechanisms. Unusual, reversible C—C bond-making and bond-breaking reactions involving probable radical intermediates[31] have been proposed as electron storage systems.[32]

Precedent for methyl migration from Mn to an arene ring ($(\eta^6\text{-}C_6H_6)Mn(CO)_2Me + PPh_3 \rightarrow$ (*endo*-$\eta^5\text{-}C_6H_5Me)Mn(CO)_2PPh_3$), the microscopic reverse of the desired reaction, has been established by Brookhart and co-workers.[33] In order to reverse the thermodynamics concerning this migration,



Scheme 1.

ruthenium was chosen as the target metal, due to its known affinity for arenes.[29,30,34,35] β-Methyl elimination from the dmCh ligand of a coordinatively unsaturated (dmCh)RuL_2^+ species is proposed to generate an $18e^-$ (η^6-toluene)RuL_2Me^+ derivative. The $16e^-$ target species, (dmCh)RuL_2^+, is formally isolobal[36] with another electron-rich metal fragment, $CpRe(PMe_3)_2$, that has exhibited C—H activation chemistry.[37] It is clear that a suitable empty *d*-orbital is apparently available to interact with the dmCh *endo*-methyl group, perhaps providing an electrophilic transition state stabilization for its transfer.[38–40]

Although dmCh–ruthenium derivatives were unknown prior to this work, other dienyl chemistry had been explored. Early work by Wilkinson and co-workers revealed that divalent $(\eta^5\text{-}C_6H_7)_2Ru$ was a product in the hydridic reduction of $(\eta^6\text{-}C_6H_6)_2Ru^{2+}$, but it rapidly isomerized to zero valent $(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}C_6H_8)$, the other product in the mixture.[41] In contrast, (η^6-1,3,5-cyclooctatriene)(η^4-1,5-COD)Ru is unstable with respect to hydrogen atom transfer and isomerization to bis(η^5-1,5-cyclooctadienyl)Ru.[42] Ernst and co-workers showed that bis(η^5-2,3,4-trimethyl-pentadienyl)Ru can be synthesized, albeit in low yield, using standard reductive ligation conditions (*i.e.* $RuCl_3$/Zn/EtOH/excess ligand). The structure of this thermally stable complex revealed two parallel, U-shaped pentadienyls in a gauche-eclipsed conformation.[43] Dehydrogenative[44] and dienyl anion-equivalent methods have also been used in the preparation of (dienyl)RuL_2X complexes.[45]

Finally, Werner *et al.* have shown that complexes such as $[(\eta^6\text{-}C_6H_6)Ru(PMe_3)_2CH_3][PF_6]$, prepared from alkylation of (benzene)$Ru(PMe_3)_2$ with CH_3I, are stable and isolable.[46] Since Werner's compounds are representative of products expected from β-methyl migration of the $16e^-$ target species, (dmCh)RuL_2^+, investigations into dmCh–ruthenium chemistry were initiated.

RESULTS AND DISCUSSION

Synthesis and characterization

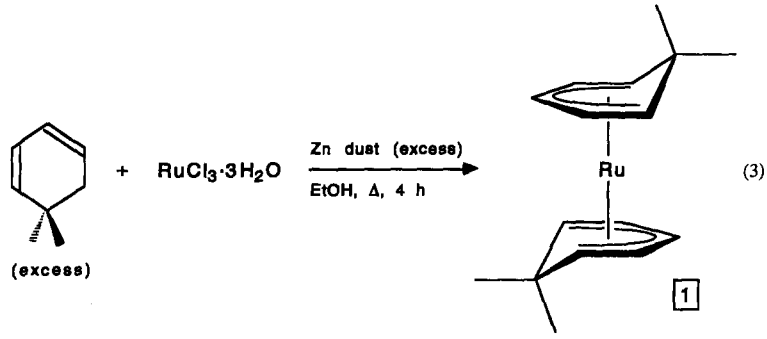
(1) $(dmCh)_2Ru$ (**1**). Initial attempts to prepare dmCh derivatives of ruthenium utilized $RuCl_2P_n$ ($n = 3$, $P = PPh_3$; $n = 4$, $P = PMe_3$)[47] and $[RuCl_2(diene)]_x$ (diene = norbornadiene, 1,5-COD)[48] as metathetical substrates. Treatment of the dihalides by varying amounts of K(dmCh)[26] proved problematic. Reduction to ruthenium metal was observed, and evidence of phosphine degradation owing to deprototation was noted for $P = PMe_3$. Using the milder $(dmCh)_2Mg \cdot xEt_2O$ ($x = 0$–2) reagent, prepared from 2.0 equiv. K(dmCh) and $MgBr_2$ (eq. (1)), reduction could be avoided, but only at the expense of additional substitution.

$$2K(dmCh) + MgBr_2 \xrightarrow[8\,h,\,25\,^\circ C]{Et_2O,\,-2KBr} (dmCh)_2Mg \cdot 2Et_2O \quad (1)$$

$$Ru(PPh_3)_3Cl_2 + (dmCh)_2Mg \cdot 2Et_2O \xrightarrow[25°C]{Et_2O,\ -MgCl_2} \underset{\mathbf{1}}{(dmCh)_2Ru} \quad (2)$$

Regardless of the stoichiometry, exposure of $Ru(PPh_3)_3Cl_2$[49] to $(dmCh)_2Mg \cdot xEt_2O$ afforded $(dmCh)_2Ru$ (**1**) in essentially quantitative yield according to ^1H NMR spectra of the crude reaction mixtures. When 1 equiv. of $(dmCh)_2Mg \cdot xEt_2O$ was employed (eq. (2)), **1** could be not completely separated from byproduct triphenylphosphine, despite attempts that included CuCl adduction of PPh_3, sublimation, chromatography on alumina I, or fractional crystallization.

Since separation procedures proved difficult, an alternative synthesis of **1** was sought. According to the standard reductive ligation conditions of Pertucci and Vitulli,[50] an ethanolic solution of $RuCl_3 \cdot 3H_2O$, 15 equiv. of (dmCh)H and 15 equiv. of Zn dust was refluxed for 4 h according to eq. (3). Subsequent crystallization from EtOH, followed by sublimation (50°C, 10^{-4} Torr) provided pale yellow crystalline **1** in 65–77% yield. Fortunately, the volatiles of the reaction mixture, including the (dmCh)H, were readily recycled. The yields achieved are significantly greater than those of a similar preparation of **1** by Kirss *et al.*[51] An analogous preparation by Ernst of $(\eta^5\text{-}2,3,4\text{-}Me_3C_5H_4)_2Ru$[43] was also less efficient; presumably, the endocyclic diolefin (dmCh)H is sterically resistant to polymerization reactions that divert 2,3,4-trimethyl-1,3-pentadiene from complexation. Syntheses of numerous related Cp*Ru(dienyl) and bis-dienyl species by Ernst and co-workers[52,53] have also utilized reductive ligation methodology.



Benzene solutions of **1** were stable to moist air for hours, according to monitoring by ^1H NMR spectroscopy, but solid **1** slowly darkened when stored in air at 25°C over a period of weeks. The complex was soluble in hydrocarbons, sparingly soluble in cold, polar solvents such as ethanol and acetonitrile, and insoluble in water. ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** (see Tables 1 and 2) were consistent with the proposed equivalent-ring structure, and no evidence of broadening due to ligand oscillation was seen at 25°C. The *anti*-eclipsed conformation is assigned on the basis of IR spectral studies, as previously presented for other $(dmCh)_2M$ congeners, but a *gauche*-eclipsed configuration, such as that possessed by bis(η^5-2,3,4-trimethyl-pentadienyl)Ru,[43] is equally likely. A similar structure has been proposed for the related (*endo*-η^5-1,2,3,4,5,6-C_6Me_6H)(exo-η^5-1,2,3,4,5,6-C_6Me_6H)Ru, recently prepared by Boekelheide *et al.*[54]

The UV–vis spectrum of **1**, while generally resembling that of Cp_2Ru, manifests a lower symmetry. A single *d-d* transition is observed at 350 nm (ε = 1300 M^{-1} cm^{-1}) in comparison to two *d-d* absorptions 322 nm (ε = 200 M^{-1} cm^{-1}) and 273 nm (ε = 150 M^{-1} cm^{-1}) for the Cp congener,[55] leading one to surmise that other, higher energy band(s) may be obscured. High intensity, charge transfer bands at 224 nm (ε = 26000 M^{-1} cm^{-1}) and 208 nm (ε = 25000 M^{-1} cm^{-1}, tentative) may reflect the substantial *d*-orbital/ligand orbital mixing indicative of greater covalency in ruthenium–dmCh bonding.[26,56] Corresponding charge transfer absorptions in Cp_2Ru are observed at 238 nm (ε = 2000 M^{-1} cm^{-1}) and 217 nm (ε = 4200 M^{-1} cm^{-1}). A greater spectral similarity to $(2,4\text{-}Me_2\text{-}C_5H_5)_2Ru$ is expected, since calculations on these "open" systems have revealed extensively mixed frontier orbitals,[57] but a detailed spectroscopic analysis has not been reported.

When **1** was dissolved in Et_2O and combined with an excess of $HBF_4 \cdot Et_2O$ (eq. (4)), a bright yellow powder rapidly precipitated. Recrystallization from CH_2Cl_2/Et_2O provided yellow, air-sensitive $[(dmCh)_2RuH][BF_4]$ (**2**) in 77% yield. The 25°C $^{13}C\{^1H\}$ NMR spectrum of **2** revealed equivalent,

Table 1. ^{1}H NMR data [δ (J observed, Hz)][a] for (dmCh)RuL$_n$ complexes [dmCh = η^5-H$_a$C(CH$_b$)(CH$_c$)(CMe$_2$)(CH$_{c'}$)(CH$_{b'}$)]

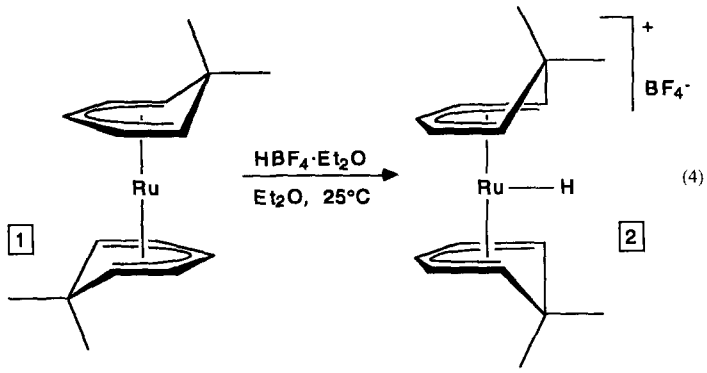
Compound	Me(*exo*)	Me(*endo*)	H_c,$H_{c'}$	H_b,$H_{b'}$	H_a	Others
$(dmCh)_2Ru$ (**1**)[b]	0.58 (s, 6 H)	1.41 (s, 6 H)	2.92 (dd, J = 6.6, 0.8, 4 H)	4.25 (dd, J = 6.7, 4.9, 4 H)	5.05 (tt, J = 4.8, 0.8, 2 H)	
$[(dmCh)_2RuH]BF_4$ (**2**)[c]	0.65 (s, 6 H)	1.60 (s, 6 H)	3.85 (dd, J = 6.6, 4.8, H)	5.04 (dd, J = 6.9, 5.4, 2 H)	6.44 (t, J = 5.2 Hz, 2 H)	−2.72 (qn, J = 4.8, 1 H Ru—H)
$[(dmCh)Ru(NCCH_3)_3]BF_4$ (**3**)[d]	0.29 (s, 3 H)	1.35 (s, 3 H)	2.27 (dd, J = 6.2, 0.9, 2 H)	4.28 (dd, J = 6.2, 4.7, 2 H)	5.61 (tt, J = 4.5, 0.9, 1 H)	1.96 (s, 3 H, CH_3CN)
$[(dmCh)Ru(PMe_3)_2NCCH_3]BF_4$ (**4**)[d]	0.56 (s, 3 H)	1.27 (s, 3 H)	2.90 (d, J = 6.5, 2 H)	4.52 (m, 2 H)	4.81 (t, J = 4.3, 1 H	1.29 (vt, J = 8.6, 18 H, PMe_3) 1.96 (br, 3 H, CH_3CN)
$[(dmCh)Ru(dppe)NCCH_3]BF_4$(**5**)[e]	0.58 (s, 3 H)	1.19 (s, 3 H)	3.44 (d, J = 6.9, 2 H)	4.58 (m, 2 H)	5.27 (t, J = 4, 1 H)	1.86 (t, J = 1.2, 3 H, CH_3CN) 2.25 (m, 2 H), 2.75 (m, 2 H), 7.4–7.8 (m, 20 H), dppe.
$[(dmCh)RuCl]_n$ (**6**)[f]	0.26 (bs, 6 H)	1.79 (s, 3 H) 1.84 (s, 3 H)	2.16 (d, J = 5.8, 2 H) 2.50 (d, J = 6.3, 2 H)	3.65 (dd, J = 4.9, 2 H) 3.93 (dd, J = 4.3, 2 H)	5.69 (t, J = 4.3, 1 H) 6.04 (t, J = 4.3, 1 H)	
(dmCh)Ru(NBD)Cl (**7**)[f,g]	0.49 (s, 3 H)	1.75 (s, 3 H)	3.36 (d, J = 7.3, 2 H)	4.26 (dd, J = 7.2, 4.8, 2 H)	5.30 (tt, J = 4.2, 1.0, 1 H)	0.81 (t, J = 1.1, 2 H, CH_2), 2.92 (br, 1 H, CH), 3.43 (br, 2 H, =CH), 3.88 (br, 1 H, CH), 4.40 (br, 2 H, =CH)
$(dmCh)RuCl(PMe_3)_2$ (**8**)[f,g]	0.67 (s, 3 H)	1.56 (s, 3 H)	2.52 (d, J = 6, 2 H)	4.11 (br t, J = 5, 2 H)	4.67 (br, 1 H)	1.11 (vt, J = 8.1, 18 H, PMe_3)
(dmCh)Ru(dppe)Cl (**9**)[c]	0.56 (br s, 3 H)	1.38 (v br s, 3 H)	3.10 (br, 2 H)	4.53 (br, 2 H)	4.38 (br, 1 H)	2.03 (m, 2 H), 2.77 (m, 2 H) 7.15–7.25, 7.25–7.4, 7.4–7.5 7.6–7.8 (m, dppe)
$[(dmCh)Ru(PMe_3)_2(THF\text{-}d_8)]PF_6$ [**10**-THF-d_8]PF_6[h]	0.38 (br s, 3 H)	1.17 (br s, 3 H)	2.40 (br d, J = 6, 2 H)	4.30 (br t, J = 5, 2 H)	5.39 (br, 1 H)	1.43 (br t, J = 7, 18 H)
$[(dmCh)Ru(PMe_3)_2(O_2NCD_3)]PF_6$ [**10**-CD_3NO_2]PF_6[i]	0.56 (br s, 3 H)	0.99 (br s, 3 H)	3.10 (br d, J = 6, 2 H)	4.68 (br t, J = 5, 2 H)	5.04 (br, m, 1 H)	1.40 (br t, J = 7, 18 H)
$[(dmCh)Ru(PMe_3)_2(CD_2Cl_2)]PF_6$ [**10**-CD_2Cl_2]PF_6[c]	0.51 (br s, 3 H)	1.27 (br s, 3 H)	2.67 (br, 2 H)	4.37 (br t, J = 6, 2 H)	5.32 (br, 1 H)	1.54 (br s, 18 H)
$[(dmCh)Ru(dppe)(CD_2Cl_2)]PF_6$ [**11**-CD_2Cl_2]PF_6[c]	0.60 (br s, 3 H)	1.27 (br s, 3 H)	3.36 (br, 2 H)	4.59 (br, 3 H)		1.94, 2.55 (br m, 2 H, dppe) 7.1–7.3, 7.3–7.5, 7.5–7.8 (br m, dppe)
$[(C_7H_8)Ru(dppe)Me]PF_6$ (**12**)[e]			5.94 (d, J = 5, 2 H)	6.07 (t, J = 5, 2 H)	5.73 (t, J = 5, 1 H)	−0.56 (t, J_{PH} = 6.4, 3 H, RuMe), 1.97 (t, J_{PH} = 0.5, 3 H, ArMe), 2.45 (m, 2 H, dppe), 2.90 (m, 2 H, dppe), 7.5–7.65, 7.7–7.85 (m, dppe)
$[(dmCh)Ru(\eta^6\text{-}C_7H_8)]BF_4$(**13**-$BF_4$)[c]	0.47 (s, 3 H)	1.27 (s, 3 H)	3.42 (d, J = 6.2, 2 H)	5.01 (dd, J = 5.0, 6.6, 2 H)	6.36 (t, J = 5.1, 1 H)	6.07 (m, J = 3.3, 1 H), 6.19 (d, J = 3.3, 2 H), 7.1–7.3 (m)

[a] All resonances are positive downfield to Me_4Si at 20 C unless otherwise noted. [b] C_7D_8. [c] CD_2Cl_2. [d] CD_3CN. [e] $(CD_3)_2CO$. [f] C_6D_6. [g] 50 C. [h] THF-d_8, 55 C. [i] CD_3NO_2.

Table 2. $^{13}C\{^1H\}$ NMR data [δ, J (Hz)][a] for (dmCh)RuL$_n$ derivatives [dmCh = η^5-H$_a$C(CH$_b$)(CH$_c$)(CMe$_2$)(CH$_{c'}$)(CH$_{b'}$), η^6-C$_7$H$_8$ = η^6-H$_a$C(CH$_b$)(CH$_c$)(CMe)(CH$_{c'}$)(CH$_{b'}$)]

Compound	Me(*exo*)	Me(*endo*)	CMe_2	C_c,$C_{c'}$	C_b,$C_{b'}$	C_a	Others
$(dmCh)_2Ru$ (**1**)[h]	31.50	34.73	37.10	48.39	83.16	80.95	
$[(dmCh)_2RuH]BF_4$ (**2**)[c]	30.95	33.99	40.37	60.11	89.03	90.36	
$[(dmCh)Ru(dppe)NCCH_3]BF_4$ (**5**)[d]	28.94	37.98	36.89	64.06	68.40	95.48	2.98 (CH_3CN), 27.80 (t, J = 20, CH_2) 129.8 (m), 131.3 (d, J = 16), 133.0 (dd, J = 4.8, 3.6), 136.0 (t, J = 21), dppe aryl
(dmCh)Ru(nor)Cl (**7**)[e]	25.92	40.32	35.69	59.92	80.48	98.11	48.30, 51.14 (CH), 51.66 (CH_2), 67.93, 71.21 (=CH)
(dmCh)Ru(dppe)Cl (**9**)[e,f]	26.80	36.42	35.60	60.79 (t, J = 10.4)	90.48	66.68	26.11 (t, J = 22, CH_2), 127.79 (t, J = 4.8), 128.05 (t, J = 4.9), 129.33 (d, J = 11.8), 131.96 (t, J = 5.9), 132.9 (t, J = 3.6), 133.57 (d, J = 4.4), 134.53 (t, J = 20), 138.45 (t, J = 18.7), dppe aryl
$[(C_7H_8)Ru(dppe)Me]PF_6$ (**12**)[c]	30.0		[g]	97.2 (t, J = 1.9)	91.96	91.7 (t, J = 3.7)	18.3 (t, J = 3),[h] 26.4 (t, J = 22), 128.1 (t, J = 4.5), 128.4 (t, J = 3.9), 129.3–129.6 (m), 129.7 (s), 131.5 (d, J = 7.8), 131.8 (t, J = 4.6), 132.3 (t, J = 5.0)

[a] All resonances positive downfield to Me_4Si at δ 0.00 (20°C). DmCh and toluene assignments are based on intensities and should be considered tentative.
[b] C_7D_8.
[c] CD_2Cl_2.
[d] $(CD_3)_2CO$.
[e] C_6D_6.
[f] −42°C.
[g] Not found, obscured.
[h] Tentative assignment.



symmetric rings, as did the ^{1}H NMR spectrum. The unique metal-hydride proton appeared at $\delta -2.72$ as a binomial quintet ($J = 4.8$ Hz), coupling to the H_1 and H_5 hydrogens of the rings, as shown by homonuclear decoupling and homonuclear two-dimensional (2D) J-resolved experiments. Upon cooling a CD_2Cl_2 solution to -65.5°C, the hydride quintet was unchanged ($J = 4.7$ Hz, $\nu_{1/2} \approx 1$ Hz), but the resonance shifted upfield ($\delta -3.05$); no perceptible change in $H_{1,5}$ was noted. Coupling of $C_{1,5}$ (δ 60.11, $^1J_{CH} = 164$ Hz) to the hydride was not observed by ^{13}C NMR at 20°C, but this particular resonance was broad ($\nu_{1/2} \approx 34$ Hz), thus a $J_{CH} < 30$ Hz may not have been resolved.

Given the preponderance of examples manifesting agostic interactions in related systems, these subtle spectral features may be revealing a fluxional process involving proton hopping between Ru and $C_{1,5}$, or one involving four equivalent agostic sites (*i.e.* Ru···H···$C_{1,5}$).[58] Treatment of $(\eta^5$-$C_7H_{11})_2Ru$ with HBF_4 resulted in a ground-state structure, $(\eta^5$-$C_7H_{11})(\eta^4$-$C_7H_{12})Ru$, that contains an agostic hydrogen residing between the metal and a pentadienyl CH_2 terminus.[59] In addition, an X-ray structure of the "hydride" showed that the ligands adopt a nearly gauche-eclipsed conformation, and perhaps contribute to the asymmetry observed in solution.[60] It is likely that the endocyclic dmCh ligand would manifest a lesser agostic interaction relative to the floppier open-ring, and large ring dienyl systems. No Ru—H stretch was observed in the IR spectrum of **2**, but absorptions expected for an agostic Ru···H···C fragment were not evident either. As a consequence of these observations and the literature precedent, **2** is presented as a classical hydride, but it is recognized that a weakly agostic ground-state structure is most probable.

In CD_2Cl_2, **2** exhibited great thermal stability, with no noticeable decomposition after >4 h at 98°C. Cationic hydride **2** did not react with CO (1/2 atm) at 25°C, but 1 equiv. of PMe_3 (pK_a ($HPMe_3^+$) = 8.65 in water)[61] caused quantitative deprotonation (eq. (5)), and

$$\underset{\mathbf{2}}{[(dmCh)_2RuH][BF_4]} + PMe_3 \rightleftharpoons \underset{\mathbf{1}}{(dmCh)_2Ru} + [HPMe_3][BF_4] \quad (5)$$

$$\underset{\mathbf{2}}{[(dmCh)_2RuH][BF_4]} + THF\text{-}d_8 \rightleftharpoons \underset{\mathbf{1}}{(dmCh)_2Ru} + HBF_4 \cdot THF\text{-}d_8 \quad (6)$$

no further reaction was observed upon heating. Upon dissolving **2** in THF-d_8, two sets of (η^5-dmCh) resonances were reproducibly observed in approximately equal amounts, implying partial deprotonation. One set was assigned to **1** upon comparison with a pure sample, while the second set, which included the requisite hydride quintet at $\delta -2.80$ ($^3J = 4.7$ Hz), corresponded to **2**. Equimolar proportions of **1** and **2** were combined in CD_2Cl_2, but no broadening or chemical shift changes from the pure materials were observed, hence proton transfer, if occurring, was relatively slow in the absence of a mediating Lewis base.

(2) $[(dmCh)RuL_n]^+$ *derivatives*. The addition of CH_3CN to a solution of **2** in CD_2Cl_2 at 25°C resulted in the immediate quantitative displacement of 5,5-dimethyl-1,3-cyclohexadiene and the formation of $[(\eta^5$-dmCh)$Ru(NCCH_3)_3][BF_4]$ (**3**, eq. (7)). Alternatively, **3** could be made by the addition of concentrated aqueous HBF_4 to an acetonitrile solution of **1** (eq. (8)).

$$\underset{\mathbf{2}}{[(dmCh)_2RuH][BF_4]} + (xs)\,CH_3CN \xrightarrow[25\,°C]{CH_2Cl_2} \underset{\mathbf{3}}{[(\eta^5\text{-dmCh})Ru(NCCH_3)_3][BF_4]} + C_8H_{12} \quad (7)$$

$$(\text{dmCh})_2\text{Ru} \xrightarrow[\text{HBF}_4/\text{H}_2\text{O}]{\text{CH}_3\text{CN, 25°C}} [(\eta^5\text{-dmCh})\text{Ru}(\text{NCCH}_3)_3][\text{BF}_4] + \text{C}_8\text{H}_{12} \quad (8)$$

1 → **3**

Isolated yields of the orange compound approached 70% by either route, after recrystallization from CH_3CN/Et_2O. Evidence of facile hydride migration to the dienyl, or displacement of an agostic bond, generating [(dmCh)Ru(η^4-5,5-Me_2-1,3-cyclohexadiene)]$^+$, was provided by the formation of **3**. Subsequent or concurrent nucleophilic attack at the 16e$^-$ diene complex by acetonitrile, followed by diene substitution, constitutes a straightforward mechanism. *tris*-Acetonitrile complex **3** was soluble in acetone, methylene chloride, and acetonitrile, and was stable in CD_2Cl_2 for 18 h at ~100°C. Analogous displacements have been previously observed.[59,60,62]

[(η^5-dmCh)Ru($NCCH_3$)$_3$][BF_4] (**3**) proved to be an excellent precursor to more electron-rich complexes. Treatment of an orange CH_3CN solution of **3** with 2.0 equiv. of PMe_3 at 25°C resulted in a rapid (~5 min) discharge of color, and provided a colorless oil spectroscopically identified as [(dmCh)Ru(PMe_3)$_2$($NCCH_3$)][BF_4] (**4**). Its ^{1}H NMR spectrum contained a

$$[(\eta^5\text{-dmCh})\text{Ru}(\text{NCCH}_3)_3][\text{BF}_4] + 2\text{L} \xrightarrow{\text{CH}_3\text{CN, 25°C}} [(\eta^5\text{-dmCh})\text{Ru}(\text{NCCH}_3)\text{L}_2][\text{BF}_4] \quad (9)$$

3

L = PMe_3, **4**; L_2 = dppe, **5**

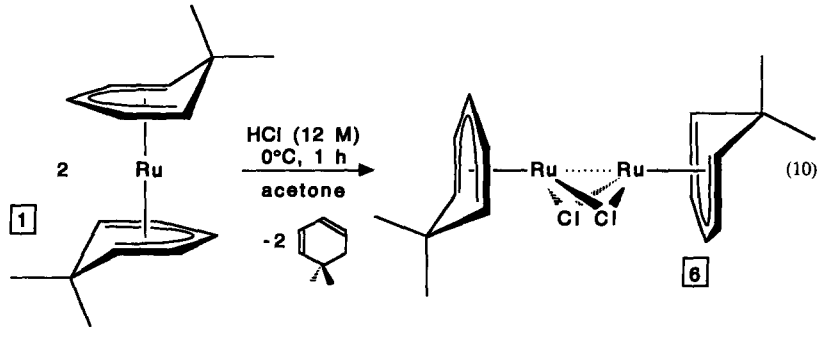
"virtual triplet" at δ 1.29 (J = 8.6 Hz) and a singlet corresponding to the bound acetonitrile at δ 1.96; a corroborating single resonance at δ 0.7 in the ^{31}P{^{1}H} spectrum was also observed. The substance was stable to 112°C for at least 6 h in CD_3CN, showing no sign of decomposition.

Addition of 1,2-bis(diphenylphosphino)ethane (dppe) to an acetonitrile solution of **3** at 25°C produced (3 h) colorless, crystalline [(dmCh)Ru(dppe)($NCCH_3$)][BF_4] (**5**) in 76% yield. A singlet at δ 68.0 in the ^{31}P{^{1}H} NMR spectrum, and typical dppe resonances accompanied by a methyl triplet at δ 1.86 (J_{PH} = 1.2 Hz) in the ^{1}H NMR spectrum, provided the key characterization. Dppe derivative **5** was robust, as evidenced by its stability in acetone-d_6 for 2 days at 120°C. Similar means have been utilized to prepare the Cp analogue.[63] Unfortunately, the parallel reaction of **3** with dmpe [1,2-bis(dimethylphosphino)ethane] under various conditions proved unsuccessful; in each instance, admixture of the reagents resulted in insoluble, presumably polymeric, colorless solids.

The [(dmCh)RuL_2($NCCH_3$)][BF_4] (L = PMe_3, **4**; L_2 = dppe, **5**) derivatives were considered to be incipient 16e$^-$ [(dmCh)RuL_2][BF_4] complexes upon loss of acetonitrile. The coordinatively unsaturated species were postulated to contain a *d*-orbital directed toward the saturated carbon of the dmCh ligand, thereby possessing the required geometry and electronic configuration to enable transfer of the methyl group to Ru (*i.e.* the desired β-alkyl-elimination). The related [CpRu(PPh_3)$_2$]$^+$ complex is considered to be an "unusually soft" electrophile that can function as an efficient σ- and π-acceptor.[64] Unfortunately, the acetonitrile ligands of **4** and **5** proved to be non-labile.

(3) (dmCh)RuL_nX *derivatives.* Solutions of **4** were refluxed in THF with LiCl or NaI present, but only small amounts (5–10%) of (dmCh)Ru(PMe_3)$_2$X (X = Cl, I) were prepared, according to ^{1}H NMR spectral analysis of crude reaction mixtures. Consiglio reported a similar resistance to substitution in the Cp system,[65] hence an alternate route to halide derivatives was sought.

The synthesis of CpRu(1,5-COD)Cl,[66] suggested an analogous route to the desired dmCh halides. Treatment of **1** with anhydrous HCl (1.0 equiv.) in pentane or ether at 0°C resulted in a deep red solution that afforded a green–brown solid. Addition of PMe_3 to an ethereal solution of the substance resulted in (dmCh)Ru(PMe_3)$_2$Cl, contaminated



with a considerable quantity of *trans*-$(PMe_3)_4RuCl_2$.[47] To moderate the acidification and prevent cleavage of both rings, the reaction was repeated with aqueous HCl (12 M) in acetone. Upon solvent removal and recrystallization from pentane at −78°C, red, analytically pure [(dmCh)RuCl]$_n$ (**6**) was isolated in 55% yield (eq. (10)), manifesting the loss of the 5,5-Me_2-1,3-cyclohexadiene ligand. Exposure of **6** to $TlPF_6$ failed to liberate TlCl, providing evidence for strongly bound chlorides. [Cp*RuCl]$_4$,[35,67] [Cp*$RuCl_2$]$_n$,[68] and [Cp*Ru(OMe)]$_2$[69] are related oligomers, although none possess the extreme solubility of **6**, a property that has frustrated efforts to grow X-ray quality crystals. [(dmCh)RuCl]$_n$ (**6**) was extremely air-sensitive, turning black immediately upon exposure to air.

Two inequivalent dmCh ligands, each displaying a symmetry plane, are characterized by the ^{1}H NMR spectrum of **6** in C_6D_6. A binuclear [(dmCh)Ru]$_2$(μ-Cl)$_2$ conformation reminiscent of [Cp*Ru(OMe)]$_2$ is in accord with the spectra provided no mirror-plane contains the chlorides. The ^{1}H NMR spectrum of **6** in CD_2Cl_2 surprisingly reflected a structure with equivalent rings. It is not clear how the more polar, more donating (albeit weakly) solvent serves to change the nature of the complex, but disruption of a weak Ru···Ru interaction may alleviate any intermetallic dmCh–dmCh steric interactions. Coincident dmCh resonances are also plausible.

Addition of 1 equiv. dppe or dmpe to **6** in hydrocarbon solutions caused the immediate precipitation of bright yellow solids that were nearly insoluble in arene solvents. ^{1}H NMR spectroscopic studies indicated a complex mixture characteristic of oligomers containing Ru centers bridged by the bidentate phosphines. Redistribution to the desired chelate complexes was not effected upon heating for prolonged periods. Addition of excess norbornadiene (NBD) to

$$1/n\,[(\text{dmCh})\text{RuCl}]_n + \text{NBD (excess)} \xrightarrow{\text{hexane, 25°C}} \underset{\mathbf{6}}{} \qquad \underset{\mathbf{7}}{(\text{dmCh})\text{Ru(NBD)Cl}} \quad (11)$$

a hexane solution of **6** afforded a yellow precipitate characterized as (dmCh)Ru(NBD)Cl (**7**) in 90% yield (eq. (11)).

Like its analogue CpRu(COD)Cl,[66] **7** proved to be a convenient substrate for certain phosphine substitutions, although addition of dmpe still resulted in complex mixtures. Treatment of **7** with 2 equiv. PMe_3 in THF led to the precipitation of yellow (dmCh)Ru(PMe_3)$_2$Cl (**8**) in 90% isolated yield (eq. (12)), while reflux of **7** and 1 equiv. dppe in EtOH provided yellow (dmCh)Ru(dppe)Cl (**9**) in 53% yield (eq. (13)) upon recrystallization from toluene.

$$\underset{\mathbf{7}}{(\text{dmCh})\text{Ru(NBD)Cl}} + 2\,PMe_3 \xrightarrow{\text{THF, 25 C, 3 h}} \underset{\mathbf{8}}{(\text{dmCh})\text{Ru}(PMe_3)_2\text{Cl}} + \text{NBD} \quad (12)$$

$$\underset{\mathbf{7}}{(\text{dmCh})\text{Ru(NBD)Cl}} + \text{dppe} \xrightarrow{\text{EtOH, }\Delta\text{, 1 h}} \underset{\mathbf{9}}{(\text{dmCh})\text{Ru(dppe)Cl}} + \text{NBD} \quad (13)$$

Compound **9** displayed broad resonances in its NMR spectra, even when recrystallized. The spectra did not manifest any impurities, and high and low resolution fast-atom bombardment mass spectroscopy (FAB MS) analyses supported its formulation, hence the dppe complex was investigated without further purification.

(4) *β-Methyl-elimination from* (dmCh)RuL_n^+. bis-phosphine derivatives (dmCh)RuL_2Cl (L = PMe_3, **8**; L_2 = dppe, **9**) were considered candidates for generation of (dmCh)RuL_2^+ via halide abstractions, thereby providing a path for subsequent β-methyl elimination to give (η^6-toluene)RuL_2Me^+. Werner's (benzene)Ru(PMe_3)$_2Me^+$ is known to be stable,[46] hence **8** served as the initial precursor. A survey of chloride abstractions from **8** was conducted with 1 equiv. of $TlPF_6$ at 25°C in CD_2Cl_2, CD_3NO_2, THF-d_8, 2-Me-THF, and 2,5-Me_2-THF. Except for the treatment in 2,5-Me_2-THF, each reaction produced a soluble Ru-containing product in addition to precipitated TlCl. Although possessing a dielectric constant similar to THF and 2-Me-THF,[70] the disubstituted solvent is far less nucleophilic, a property apparently critical to solvation of the incipient (dmCh)Ru(PMe_3)$_2^+$ species.

Deuterated solvents permitted ready monitoring of the abstractions by ^{1}H NMR spectroscopy. In each instance, the new product was considered to be a solvento complex, (dmCh)Ru(PMe_3)$_2$(solvent)$^+$ (**10**-solvent, solvent = CD_2Cl_2, CD_3NO_2, THF, 2-Me-THF; eq. (14)), an assignment based on the familiar dmCh coupling pattern. When dissolved in CD_3NO_2, the yellow solid assigned as [**10**-2-Me-THF]PF_6 reverted to **10**-CD_3NO_2 and free 2-Me-THF, according to ^{1}H NMR spectral analysis. Furthermore, counterion binding by PF_6^- seemed unlikely, as the ^{1}H NMR spectrum of the metathesis product of **8** and $NaBPh_4$ in CD_3NO_2 was identical to **10**-CD_3NO_2 (eq. (15)). Thermolysis (90°C, 3 h) of **10**-solvent (solvent = CD_2Cl_2, THF, 2-Me-THF) resulted in extensive decomposition, includ-

ing evidence of ligand redistribution. The nitromethane derivative (**10**-CD_3NO_2) decomposed under slightly more moderate conditions (70°C, 3 h), but again no tractable products were obtained.

$$\underset{\mathbf{8}}{(\text{dmCh})\text{Ru}(\text{PMe}_3)_2\text{Cl}} + \text{TlPF}_6 \xrightarrow[-\text{TlCl}]{\text{solvent, 25°C}} [(\text{dmCh})\text{Ru}(\text{PMe}_3)_2(\text{solvent})]\text{PF}_6 \quad (14)$$
$$[\mathbf{10}\text{-solvent}]\text{PF}_6$$

$$\underset{\mathbf{8}}{(\text{dmCh})\text{Ru}(\text{PMe}_3)_2\text{Cl}} + \text{NaBPh}_4 \xrightarrow[-\text{NaCl}]{\text{CD}_3\text{NO}_2\text{, 25°C}} [(\text{dmCh})\text{Ru}(\text{PMe}_3)_2(\text{CD}_3\text{NO}_2)]\text{BPh}_4 \quad (15)$$
$$[\mathbf{10}\text{-}\text{CD}_3\text{NO}_2]\text{BPh}_4$$

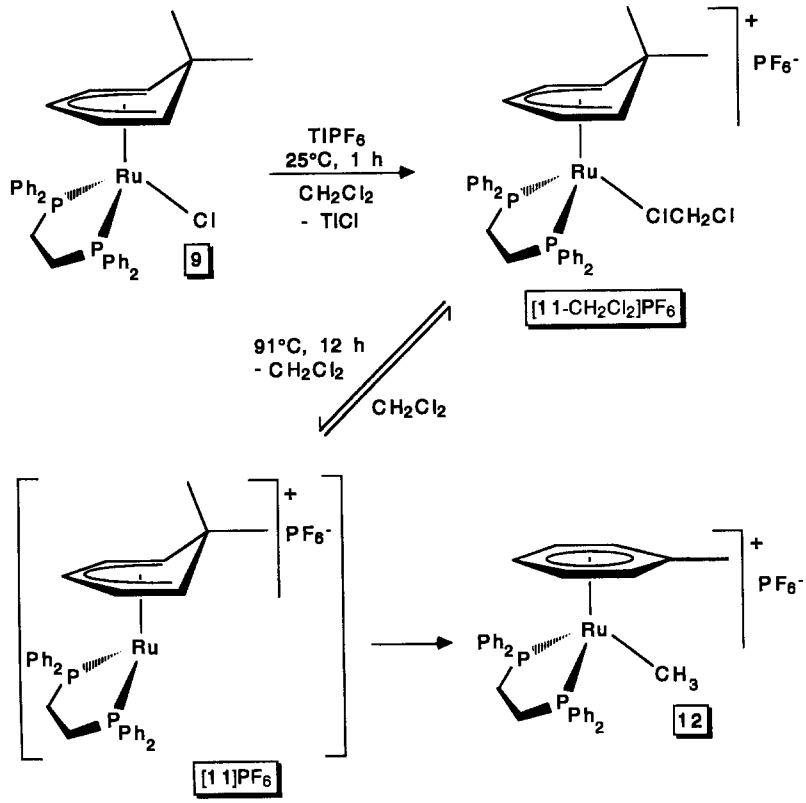
Attention then turned to the dppe derivative, (dmCh)Ru(dppe)Cl (**9**), in the hope that the chelating diphosphine[71] would render redistribution and related degradation pathways inoperative.[72] Noting that methylene chloride possesses a greater coordinating ability than PF_6^-,[73] **9** was subjected to $TlPF_6$ in CD_2Cl_2 by shaking equimolar quantities at 25°C for 1 h in a sealed NMR tube (Scheme 2). Colorless TlCl precipitated, and a single new product was observed by ^1H NMR spectroscopy. Two $^{31}P\{^1H\}$ resonances, a singlet for the equivalent phoshines of the dppe ligand (δ 60.2, bs), and a septet for solvated PF_6^- (δ 157.9, $^1J_{PF} = 714$ Hz), suggested that the desired solvento complex,[74] [(dmCh)Ru(dppe)(CD_2Cl_2)]PF_6 ([**11**-CD_2Cl_2]PF_6) had formed.

Thermolysis of **11**-CD_2Cl_2 at 91°C for 12 h caused its disappearance ($t_{1/2} \approx 2$ h) with the concomitant emergence of a new set of resonances in the ^1H NMR spectrum, including a triplet at δ −0.58 ($J_{PH} = 6.2$ Hz) attributed to a ruthenium–methyl group. The $^{31}P\{^1H\}$ NMR spectrum (acetone-d_6) revealed a singlet at δ 78.4 in addition to the PF_6^- signal, consistent with the generation of [(η^6-C_7H_8)Ru(dppe)(CH_3)]PF_6 (**12**) upon formal β-methyl elimination from the putative coordinatively unsaturated precursor, [(dmCh)Ru(dppe)]PF_6 ([**11**]PF_6). The toluene–methyl derivative (**12**) was isolated as tan, air-stable microcrystals in 52% yield upon recrystallization from acetone/ether. A low-resolution FAB mass spectrum of a *m*-nitrobenzyl alcohol solution of **12** revealed a molecular ion for (η^6-toluene)Ru(dppe)$(CH_3)^+$ at *m/e* 607 (^{102}Ru), and the proper isotopic distribution of peaks for the formulation $C_{34}H_{35}P_2Ru^+$. In its ^1H NMR spectrum (acetone-d_6, Table 1), a clear separation of *ortho*, *meta*, and *para* protons was apparent.

Details regarding the β-methyl-elimination pathway from [(dmCh)Ru(dppe)(CH_2Cl_2)]PF_6[**11**-CH_2Cl_2]PF_6 to [(η^6-toluene)Ru(dppe)(CH_3)]PF_6 (**12**) remained elusive. Isolation of [**11**-CH_2Cl_2]PF_6 was attempted via evaporation of a filtered methylene chloride solution at 25°C, but the resulting yellow solid was not wholly soluble in CH_2Cl_2, CH_3CN, or acetone, and examination by ^1H NMR spectroscopy revealed partial decomposition. Rapid degradation of Lewis-acidic, cationic-PF_6 complexes has previously been observed.[75,76] Although not isolable, thermolyses of [**11**-CH_2Cl_2]PF_6 were conducted on both crude reaction mixtures and on centrifuged (TlCl-free) solutions in CH_2Cl_2, with no observable influence on the spectroscopic yield of **12**. NMR tubes containing equimolar quantities of (dmCh)Ru(dppe)Cl (**9**) and $TlPF_6$ (0.03–0.10 M) in CD_2Cl_2 were charged and sealed, and the formation of TlCl was noted. After centrifugation and removal of solids, the samples were resealed and thermolyzed at 91°C. In some cases, clean first-order decay ($\sim 10^{-3}$–10^{-4} s^{-1}) of [**11**-CH_2Cl_2]PF_6 was observed, and in others, inhibition of the reaction occurred at about one half-life. While the sporadic reactivity prevented further analysis, the conversion of [**11**-CD_2Cl_2]PF_6 to **12** is tentatively construed as a unimolecular β-alkyl elimination; bimolecular alkyl transfer pathways cannot be excluded.

Redox chemistry of $(dmCh)_2Ru$ (**1**)

Upon observation of the desired β-alkyl elimination in **9**, attempts to oxidatively induce similar reactivity in **1** were initiated based on the assumption that a 17e$^-$ species would be more prone to carbon–carbon bond scission. One equiv. of [Cp_2Fe][PF_6] was added to a CD_3CN solution of **1** in an NMR tube. Upon agitation of the tube at 25°C, the blue–purple color of the ferricinium was discharged within 5 min. Examination of the resulting light-orange colored solution by ^1H NMR spectroscopy revealed sharp resonances indicative of [(dmCh)Ru$(NCCD_3)_3$]PF_6 (**3**-PF_6), free toluene, and Cp_2Fe. Although not all of the lesser organic byproducts were identified, some of the observed olefinic peaks resulted from coupled dmCh (eq. (16)). Extrusion of a pentadienyl radical upon one-electron oxidation of a *pd* complex has been noted previously.[77] Oxidation of **1** with 1.0 equiv. [Cp_2Fe][PF_6] in CD_2Cl_2 at 25°C rapidly yielded a pale-yellow solution comprising a complex mixture of at least two (dmCh)-containing products. One of the products was the cation (dmCh)Ru(η^6-toluene)$^+$(**13**-PF_6), arising from the cleavage of a C—C bond in a dmCh ligand (eq. (17)). The fate of the CH_3 fragment remains unknown. Toluene complex **13**-BF_4 was prepared independently via reflux of [(dmCh)Ru$(NCCD_3)_3$]BF_4 (**3**) and C_7H_8 in CD_2Cl_2



Scheme 2.

(eq. (18)). A related electrochemically- and chemically-reversible carbon–carbon cleavage in a diruthenium-bound cyclooctatetraene ligand has been reported;[78] two-electron oxidation of the electronically unsaturated $CpRu(\mu\text{-}\eta^4:\eta^4\text{-COT})RuCp$ resulted in the scission of an endocyclic C—C bond, while reduction of the product regenerated the starting material.

$$(dmCh)_2Ru + [Cp_2Fe][PF_6] \xrightarrow[25°C]{CD_3CN} \underset{\mathbf{1}}{} [(dmCh)Ru(NCCD_3)_3]PF_6 (3\text{-}PF_6) + C_7H_8 + C_{16}H_{22} + \cdots + Cp_2Fe \quad (16)$$

$$(dmCh)_2Ru + [Cp_2Fe][PF_6] \xrightarrow[25°C]{CD_2Cl_2} \underset{\mathbf{1}}{} [(dmCh)Ru(\eta^6\text{-}C_7H_8)]PF_6 + Cp_2Fe + \cdots \quad (17)$$
$$\mathbf{13}\text{-}PF_6$$

$$[(dmCh)Ru(NCCD_3)_3]BF_4 + C_7H_8 \xrightarrow{CD_2Cl_2} \underset{\mathbf{3}}{} [(dmCh)Ru(\eta^6\text{-}C_7H_8)]BF_4 \quad (18)$$
$$\mathbf{13}\text{-}BF_4$$

The cyclic voltammogram of **1** was consistent with the chemical results (Fig. 1, Ag/AgCl/THF at 0.0 V). While no reduction was observed until solvent breakdown (> -2.25 V), scanning positive resulted in the appearance of an irreversible wave centered at $+0.85$ V. Subsequent scans in the potential window -0.2 V to -1.4 V showed several irreversible waves due to reduction of electrogenerated oxidation products(s). The combined chemical and CV evidence supports a $1e^-$ oxidation of **1**, based on the consumption of 1 equiv. of fericenium. The possibility that some ferricenium was consumed by oxidation of the degradation products of $\mathbf{1}^+$ seems unlikely, since repeated cyclic voltammograms showed no current passed in the vicinity of 0.8 V (Cp_2Fe/Cp_2Fe^+ couple = 0.82 V *vs* Ag/AgCl/THF) other than for oxidation of **1**, and no indication of any obscured peaks was noted.

Related organoruthenium(II) species have exhibited similar reactivity upon oxidation. One-electron oxidation of decamethylruthenocene (Cp_2^*Ru) at $-25°C$ in CH_2Cl_2 was reported by O'Hare and co-workers[79] to yield $[(\eta^6\text{-}1,2,3,4\text{-tetramethylfulvene})RuCp^*]^+$ and Cp_2^*Ru via proton loss and e^--transfer. The unmethylated ruthenocinium ion, Cp_2Ru^+, is not known to exist; instead, oxidation of Cp_2Ru has been determined by coulometric methods to proceed directly to

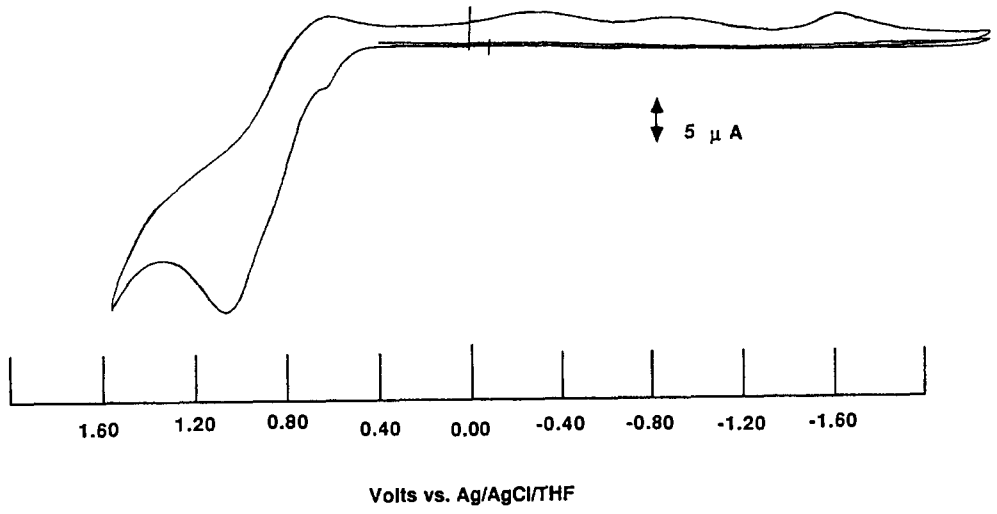


Fig. 1. Cyclic voltammogram of $(dmCh)_2Ru$ (**1**) in THF: [**1**] = 0.6 mM, $[^nBu_4BF_4]$ = 0.2 M, scan rate = 200 mV s^{-1}.

Cp_2Ru^{2+} in a two-electron process. The resulting dication was then found to decompose in acetonitrile.[80]

Interestingly, the electrochemical behavior of **1** deviated from that of its first row congener, $(dmCh)_2Fe$ (**14**).[26] A reversible oxidation was observed at +0.36 V (*vs* Ag/AgCl/THF at 200 mV sec^{-1}, 25°C, ΔE_p = 230 mV) for **14**, thereby resembling that of ferrocene, which is generally taken to be the benchmark of reversible redox reactions in non-aqueous solvents.[81] In contrast, oxidation of Ernst's "open" and "half-open" analogues, $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2Fe$ and $CpFe(2,4\text{-}Me_2C_5H_5)$, is reversible only with rapid scan speeds at −40°C.[82] Presumably the $17e^-$ pentadienyl-containing oxidation products can dimerize easily at their termini, while dmCh species are relatively stable with respect to that particular decomposition.

CONCLUSIONS

The goal of this work, the observation of β-methyl elimination from the 6,6-dimethylcyclohexadienyl (dmCh) ligand, came to fruition after a lengthy investigation[26,27] into suitable precursor molecules. While it was gratifying to detect methyl transfer from $[(dmCh)Ru(dppe)(CH_2Cl_2)]PF_6$ ($[\mathbf{11}\text{-}CH_2Cl_2]PF_6$) to give $[(\eta^6\text{-toluene})Ru(dppe)(CH_3)]PF_6$ (**12**), presumably via the $16e^-$ electrophile $[(dmCh)Ru(dppe)]PF_6$ ($[\mathbf{11}]PF_6$), the failure to adequately determine the molecularity of this event is disappointing. Given Chaudret's C—C cleavage reactions that apparently arise from homolysis or related radical pathways,[30] the possibility of binuclear Me^- transfers cannot be discounted. Nonetheless, a formal β-alkyl elimination has resulted from this study.

It is plausible that phosphine lability, a process observed to interfere in Bercaw and co-workers study of $Cp^*Ru(PMe_3)_2X$ chemistry,[83] may influence the above chemistry to a certain extent. The broad NMR spectral signatures of (dmCh)Ru(dppe)Cl (**10**) may reflect reversible ligand loss, or hindered ring rotation about the Ru(dppe)Cl moiety. However, since the ultimate alkyl-elimination was verified, possible dynamic processes were not deemed critical enough to investigate. What then, are the crucial factors involved in the β-transfer of an alkyl group from dmCh?

Initial efforts[26] focused on the generation of electronically unsaturated complexes that would increase their electron density upon transfer of the β-methyl from dmCh. However, sandwich derivatives such as $(dmCh)_2M$ (M = Ti, V, Cr etc.) decomposed at relatively high temperatures via pathways that do not invoke β-alkyl transfer. Subsequent attempts to prepare suitable precursors to $(dmCh)Mo(CO)_3^+$ were unsuccessful, perhaps because the carbonyl ligands provide poor electronic support for putative $16e^-$ transient. In the process, the excellent donor ability of the dmCh ligand via its directed set of p(C)-based orbitals—affording better ligation than Cp, but worse than pentadienyl[26]—was probably underestimated.

This ruthenium study succeeded because the delicate balance necessary to ensure a relatively low-level energetic pathway for β-alkyl elimination was finally achieved. The phosphine donors (dppe) helped offset or limit the donor ability of dmCh, while still imparting stabilization to both the start-

ing dmCh derivative, [**11**-CH_2Cl_2]PF_6, and the final toluene complex, **12**. Ruthenium also proved to be an apt choice because of its noted affinity for π-hydrocarbon ligands, especially arenes (*vide supra*). Most importantly, the choice of a ligand system that establishes a critical, directional metal orbital cannot be emphasized enough. Principally through precedent established by Brookhart in related manganese systems[33] and others,[38] an appropriate empty *d*-orbital is available to mediate the β-alkyl-elimination reaction. Specific electrophilic interactions of this type are obviously critical to olefin polymerization reactions, and serve the same purpose in facilitating this microscopically reverse process.[38-40]

EXPERIMENTAL

General considerations

All manipulations were performed using either glovebox or high vacuum line techniques. Ethereal and hydrocarbon solvents were distilled from purple sodium benzophenone ketyl and vacuum transferred from same. CH_3CN, CD_3CN, C_6D_6, CD_3NO_2, THF-d_8, and CD_2Cl_2 were dried over activated 4 Å molecular sieves, vacuum transferred and stored under N_2. $RuCl_3 \cdot 3H_2O$ (Alfa or Aldrich), $HBF_4 \cdot Et_2O$, PMe_3, $TlPF_6$ (Aldrich), aqueous HBF_4 and HCl (Mallinkrodt) were used without further purification. Dppe (1,2-bis(diphenylphosphino)ethane) was purchased from Aldrich, recrystallized from acetone, and dried under vacuum ($\sim 10^{-4}$ Torr) before use. Norbornadiene (Aldrich) was passed through alumina I and distilled under vacuum immediately prior to use. $[Cp_2Fe]PF_6$,[84] K(dmCh) was prepared using published procedures, and (dmCh)H was synthesized via modification of previous methods.[26]

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ (referenced to H_3PO_4 (aq.) at 0.0 ppm (25°C); secondary external references used: PCl_3 at δ 219.0; $P(OMe)_3$ at δ 140.4) NMR spectra were recorded on Varian XL-200, XL-400 and Brüker WM 300 spectrometers (see Tables 1 and 2 for additional details). Infrared spectra were obtained on a Mattson Alpha Centauri instrument. Elemental analyses were conducted by Analytische Laboratorien, Elbach, or by Oneida Analytical, Whitesboro, NY. Electrochemical measurements were recorded using a BAS-CV-27 instrument and Soltec 6423S X-Y recorder. Reference electrodes were locally prepared and consisted of cracked glass bead outer shells containing a silver wire, in contact with a saturated solution of AgCl/$[Me_4N]Cl$ in THF. The Cp_2Fe/Cp_2Fe^+ couple (+0.82 V, with ΔE_p typically ~ 300 mV) was used to calibrate each reference electrode. All cyclic voltammograms were recorded in a single compartment cell using platinum disc working electrode, platinum wire counterelectrode, and 0.1 M $[^nBu_4N]BF_4$ as supporting electrolyte. FAB MS was performed by a Kratos MS-50 double-focussing spectrometer, using nitrobenzyl alcohol as solvent and Xe (8 kV) bombardment gas.

Preparation of (dmCh)H

To obtain high yields in subsequent reactions, (dmCh)H had to be prepared by modification of the previously described procedure. To a sample of crude, dry 5,5-dimethyl-1,3-cyclohexanediol (prepared by reduction of 45 g (0.32 mol) dimedone as previously described)[26] was added reagent grade acetone (150 cm^3) and *p*-toluenesulfonic acid monohydrate (16 g, 0.084 mol). The solution was refluxed for 2.5 h, cooled, and neutralized with an aqueous solution of staturated $NaHCO_3$, resulting in two phases. The organic layer was separated, diluted with Et_2O (100 ml), washed with eight 30 cm^3 portions of water and dried over Na_2SO_4. Distillation through a Vigreaux column (10 cm) separated most of the Et_2O (34°C, 1 atm); vacuum transfer (25°C, 10^{-4} Torr) of the residue onto sodium, followed by another such transfer, yielded an ethereal solution of diene (~ 50% yield from dimedone) free of isomeric impurities. Spectra are as previously described.

Preparation of $(dmCh)_2Mg \cdot xEt_2O$

To a flask containing $MgBr_2$ (472 mg, 2.57 mmol) and solid (dmCh)K (750 mg, 5.1 mmol) at −78°C was added 25 cm^3 diethyl ether. The reaction mixture was stirred for 1 h, allowed to warm to 25°C, and stirred an additional 8 h. The resulting colorless slurry was filtered, reduced to ~ 5 cm^3, and ~ 10 cm^3 pentane was added. Reduction of solution volume to 5 cm^3, followed by crystallization at −78°C afforded colorless crystals of $(dmCh)_2Mg \cdot 0.3Et_2O$ (479 mg, 71%). The amount of solvent varied for each preparation. ^1H NMR (C_6D_6) δ 0.63 (s, 6H, Me), 1.06 (s, 6H, Me), 3.88 (dd, $^3J = 7.3$, $^4J = 1.8$ Hz, 4 H, H_c, $H_{c'}$), 4.92 (tt, $^3J = 6.5$, $^4J = 2$ Hz, 2 H, H_a), 6.47 (dd, $^3J = 7$, $^3J = 6.4$ Hz, 4 H, H_b, $H_{b'}$).

Preparation of $(dmCh)_2Ru$ (**1**)

To a 100 cm^3, two-neck flask was added $RuCl_3 \cdot 3H_2O$ (1.18 g, 4.77 mmol based on analysis of metal content; 40.89% w/w Ru) and absolute ethanol (35 cm^3). The solution was degassed by three freeze–pump–thaw cycles, and stirred at 25°C.

Deoxygenated 5,5-dimethyl-1,3-cyclohexadiene (7.75 g, 71.6 mmol; admixture with 2.85 g diethyl ether according to ^{1}H NMR spectra) was added via syringe, followed by 4.68 g (71.6 mmol) of zinc dust. The reaction mixture briefly turned blue–green, concomitant with the generation of heat. The resulting red–brown slurry was refluxed for 4 h, and the ethanol was removed. The residue was triturated with hexane, then extracted with hexane (2 by 75 cm^3). Filtration through glass wool followed by evaporation yielded a waxy yellow solid, which was crystallized from cold (−78°C) ethanol. Sublimation (50°C, 10^{-4} Torr) afforded pale yellow crystalline **1** (1.153 g, 77%). Anal. found: C, 61.05; H, 6.92. Anal. calc. for $C_{16}H_{22}Ru$: C, 60.97; H, 7.03.

Preparation of [(dmCh)RuH]BF_4 (**2**)

To a stirred solution of **1** (352 mg, 1.12 mmol) in diethyl ether (20 cm^3) was added $HBF_4 \cdot Et_2O$ (480 mg of 85% w/w acid in ether, 2.5 mmol) at 25°C. A yellow solid precipitated upon rapid stirring. After 1 h, pentane (20 cm^3) was added; the solid was filtered, washed with pentane, and dried under high vacuum, providing 360 mg **2** (80%). Anal. found: C, 47.80; H, 5.78. Anal. calc. for $C_{16}H_{23}BF_4Ru$: C, 47.66; H, 5.75.

Preparation of [(dmCh)Ru($NCCH_3$)$_3$]BF_4 (**3**)

(a) To solid **2** (403 mg, 1.00 mmol) was added dry acetonitrile (10 cm^3) at 25°C. The resulting orange solution was stirred 10 min, filtered, reduced in volume to ~2 cm^3, and ~10 cm^3 of diethyl ether was added. Upon stirring rapidly, a yellow solid was dispersed, collected, washed with diethyl ether, and dried under vacuum, providing **3** (370 mg, 89%).

(b) To acetonitrile (15 cm^3) was added **1** (291 mg, 0.923 mmol), and the light yellow solution was cooled to 0°C. Aqueous HBF_4 (290 mg of 48% w/w solution; 1.59 mmol) was added via tared syringe, and the solution immediately darkened to an orange color. Workup proceeded as in (a) to yield **3** (233 mg, 60%). Anal. found: C, 40.10; H, 4.72; N, 9.86. Anal. calc. for $C_{14}H_{20}N_3BF_4Ru$: C, 40.21; H, 4.82; N, 10.05.

Preparation of [(dmCh)Ru(PMe_3)$_2$($NCCH_3$)]BF_4 (**4**)

To a CH_3CN solution of **3** (34 mg, 0.082 mmol) was added 2 equiv. of distilled PMe_3 (0.16 mmol) at 25°C. Stirring for 3 h resulted in discharge of the starting yellow color. Filtration and removal of solvent yielded a colorless oil of >95% purity by ^{1}H NMR spectroscopy. The yield was nearly quantitative by NMR analysis. $^{31}P\{^1H\}$ NMR (CD_3N) δ 0.7 (s).

Preparation of [(dmCh)Ru(dppe)($NCCH_3$)](BF_4) (**5**)

To a CH_3CN solution of **3** (224 mg, 0.536 mmol) was added dppe (213 mg, 0.535 mmol) at 25°C. Upon stirring for 3 h, the yellow color was discharged. Filtration, removal of solvent, and washing with diethyl ether provided 298 mg of white solid **5** (75.6%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 68.0 (s). Anal. found: C, 58.60; H, 5.34; N, 2.21. Anal. calc. for $C_{36}H_{38}NBF_4P_2Ru$: C, 58.87; H, 5.21; N, 1.91.

Preparation of [(dmCh)RuCl]$_n$ (**6**)

To a solution of **1** (346 mg, 1.10 mmol) in reagent grade acetone (20 ml) was added concentrated aqueous HCl (90 μl of 12 M solution; 1.1 mmol) at 0°C. The solution immediately turned red–brown. Upon stirring for 1 h, then warming to 25°C, the solvent was removed to afford a brick-red solid and traces of a green solid. Trituration with pentane, followed by filtration, reduction in volume to ~5 cm^3, and cooling to −78°C gave brick-red microcrystals of **6** (146 mg, 54.6%). Anal. found: C, 39.65; H, 4.65; Cl, 14.55. Anal. calc. for $C_8H_{11}ClRu$: C, 39.43; H, 4.55; Cl, 14.55.

Preparation of (dmCh)Ru(NBD)Cl (**7**)

To a stirred solution of **6** (297 mg, 1.22 mmol) in hexane at 25°C was added an excess of NBD (0.5 cm^3, 5 mmol). A bright yellow solid precipitated immediately, leaving the solution colorless. The substance was washed with hexane, recrystallized from diethyl ether, and dried under vacuum to yield **7** (370 mg, 90%), as yellow crystals. Anal. found: C, 53.64; H, 5.70. Anal. calc. for $C_{15}H_{19}ClRu$: C, 53.65; H, 5.70.

Preparation of (dmCh)Ru(PMe_3)$_2$Cl (**8**)

To a 25 cm^3 flask containing **7** (45 mg, 0.13 mmol) and THF (10 cm^3) at −78°C was distilled PMe_3 (0.34 mmol) via a gas bulb. The reaction mixture was allowed to warm to 25°C and stirred for 3 h. Upon removal of solvent, trituration with hexane, and drying under vacuum, **8** (46 mg, 90%) was obtained as a yellow powder. $^{31}P\{^1H\}$ NMR (C_6D_6) δ −1.53 (s). Anal. found: C, 42.63; H, 7.22. Anal. calc. for $C_{14}H_{29}ClP_2Ru$: C, 42.48; H, 7.38.

Preparation of (dmCh)Ru(dppe)Cl (**9**)

To a 25 cm^3 flask containing **7** (297 mg, 0.88 mmol) and dppe (352 mg, 0.88 mmol) was distilled absolute ethanol (20 cm^3). The reaction mixture was refluxed for a period of 1 h. Upon cooling, bright yellow crystals deposited, and were collected by filtration. The product was repeatedly extracted with toluene ($\sim$15 cm^3), filtered, and recrystallized. Washing with hexane followed by drying under vacuum provided **11** (298 mg) in 52.5% yield. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 65.5 (s). High-resolution FAB mass spectrum (positive ion), calculated *m*/e for $^{12}C_{34}{}^1H_{35}{}^{31}P_2{}^{35}Cl^{96}Ru$: 636.0978. Found: 636.0941. Low-resolution FAB mass spectrum, *m*/e (relative intensity) for $C_{34}H_{35}P_2Cl^{102}Ru$: 642, M^+ (41.9%); 627, $(M-CH_3)^+$ (100%); 607 $(M-Cl)^+$ (89.9%); 499 $(M-C_8H_{12}Cl)^+$ (86.2%). Isotopic envelope for M^+ peak, *m*/e (relative intensity): 636 (14%), 637 (10%), 638 (13%), 639 (37.9%), 640 (48.9%), 641 (69.7%), 642 (100%), 643 (57.8%), 644 (76.1%), 645 (29.6%). Anal. found: C, 64.57; H, 4.99. Anal. calc. for $C_{34}H_{35}ClP_2Ru$: C, 63.60; H, 5.49.

Preparation of [(η^6-toluene)Ru(dppe)CH_3]PF_6 (**12**)

To a thick-walled glass bomb reactor containing **9** (246 mg, 0.38 mmol) and $TlPF_6$ (134 mg, 0.38 mmol) was distilled dry CH_2Cl_2 (15 cm^3). The bomb sealed with a teflon needle-valve, and immersed in a 91°C oil bath. After 6 h, the reactor was allowed to cool, and the supernatant was removed via syringe under an argon counterflow, filtered, and evaporated to a brown powder. Recrystallization from acetone/ether (1:2) at 0°C afforded 143 mg of **12** (52.3% yield). $^{31}P\{^1H\}$ NMR (acetone-d_6, 20°C) δ 78.4 (s), 164.3 (sep, $^1J_{PF}$ = 708 Hz). Low-resolution, positive ion FAB mass spectrum, *m*/e for $C_{34}H_{35}P_2{}^{102}Ru$ (relative intensity): 607, M^+ (100%); 499 $(M-C_8H_{12})^+$ (32%). Isotopic envelope for M^+ peak, *m*/e (observed/calculated relative intensity): 603 (7.6/5.8%), 604 (37.6/34.3%), 605 (44.6/45.2%), 606 (56.4/58.4%), 607 (100/100%), 608 (34.7/34.5%), 609 (53.8/54.1%), 610 (16.6/18.9%), 611 (3.5/3.4%). Anal. found: C, 54.37; H, 4.80. Anal. calc. for $C_{34}H_{35}F_6P_3Ru$: C, 54.33; H, 4.69.

NMR tube scale preparation of [(dmCh)Ru(dppe)(CD_2Cl_2)]PF_6 ([**11**-CD_2Cl_2]PF_6)

To an NMR tube containing **9** (10 mg, 0.016 mmol) and $TlPF_6$ (5 mg, 0.015 mmol) was added CD_2Cl_2 (0.4 cm^3). After shaking for 1 h at 25°C, followed by centrifugation, the reaction was complete, providing a yellow solution of [**11**-CH_2Cl_2]PF_6 ($\sim$90%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20°C) δ 60.2 (br s, $v_{1/2}$ = 60 Hz), 157.9 (septet, $^1J_{PF}$ = 714 Hz).

NMR tube scale preparation of [(dmCh)Ru(PMe_3)$_2$(solvent)]PF_6 ([**10**-solvent]PF_6)

The procedure above was followed for NMR spectral observation of all solvent complexes.

NMR tube scale preparation of [(dmCh)Ru(η^6-C_7H_8)]BF_4 (**13**-BF_4)

To an NMR tube containing **3** (10 mg, 24 μmol) and toluene (24 μmol) was distilled 0.4 ml CD_2Cl_2 (0.4 cm^3). After sealing the tube, the resulting yellow solution was heated to 91°C for 1 h, providing **13**-BF_4 in >95% yield (^1H NMR).

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