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Journal of Organometallic Chemistry 690 (2005) 4640–4647
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

A comparison of Cp*- and Tp-ruthenium carbyne complexes prepared via site selective electrophilic addition to neutral ruthenium vinylidenes

Nicholas J. Beach, Andrew E. Williamson, Gregory J. Spivak *

Department of Chemistry, Lakehead University, 955 Oliver Road, Thunder Bay, Ont., Canada P7B 5E1

Received 10 May 2005; received in revised form 8 July 2005; accepted 11 July 2005
Available online 19 August 2005

Abstract

The synthesis and characterization of a series of ruthenium carbyne complexes supported by either pentamethylcyclopentadienyl (Cp*) or hydridotris(pyrazolyl)borate (Tp) ligands are discussed. Reacting the neutral ruthenium(II) vinylidenes [Cp*Cl(PPh_3)Ru(CCHR)] (**1**) or [TpCl(PPh_3)Ru(CCHR)] (**2**) with excess $HBF_4 \cdot Et_2O$ yields the ruthenium(IV) carbynes [Cp*Cl(PPh_3)Ru(CCH_2R)][BF_4] (**3**: R = ^{t}Bu, **3a**; R = ^{n}Bu, **3b**; R = Ph, **3c**), and [TpCl(PPh_3)Ru(CCH_2R)][BF_4] (**4**: R = ^{t}Bu, **4a**; R = ^{n}Bu, **4b**; R = Ph, **4c**). Complexes **3a** and **3b** are isolable solids, whereas **3c** and **4a–c** must be prepared and examined in solution at low temperatures using variable temperature NMR spectroscopy. In contrast, reactions of **1** or **2** (R = Ph) with MeOTf selectively yield the chloride abstracted products [Cp*(OTf)(PPh_3)Ru(CCHPh)] (**5**) or [Tp(OTf)(PPh_3)Ru(CCHPh)] (**6**), respectively, along with one equivalent of MeCl. When R = ^{t}Bu or ^{n}Bu, the reactions are much less selective. The relative stabilities of the complexes reported are compared and discussed.

Keywords: Ruthenium; Vinylidene; Carbyne; Electrophilic addition; Pentamethylcyclopentadienyl; Hydridotris(pyrazolyl)borate

1. Introduction

The hydridotris(pyrazolyl)borate ($HB(pz)_3$, or Tp) [1] and the cyclopentadienyl-type (C_5R_5, in particular C_5H_5, or Cp, and C_5Me_5, or Cp*) [2] ligand classes are featured prominently in transition metal chemistry as excellent spectator ligands since both classes typically bind strongly to metals, and they are also generally resistant towards nucleophilic and electrophilic attack. Several comparisons may be drawn between Tp and C_5R_5 ligands. For example, both ligand classes are isoelectronic, bear a net negative charge, and are capable of forming structurally analogous (e.g., half-sandwich) complexes and derivatives. One might also compare ring-slippage [3] in C_5R_5 ligands to the ability of the Tp ligand to dissociate a pendant pyrazolyl arm, where in each case an electron pair is removed from the metal, and a vacant site is created. There are, however, a number of notable differences between the two ligand classes as well. For example, the Tp ligand has a lower field strength compared to C_5R_5 [4]. The Tp ligand tends to bind to metals using its σ-donor orbitals, which contrasts the π-fashion established for C_5R_5 ligands. The Tp ligand is also bulkier, with a calculated cone angle [5] of about 180°, compared to 146° for Cp* and 100° for Cp. The thermal and chemical properties of their respective complexes are, in many cases, notably different [1c].

In recent years, a number of reports have appeared in the literature describing the synthesis of ruthenium carbyne complexes [6]. The majority of these reports

* Corresponding author. Tel.: +1 807 343 8297; fax: +1 807 346 7775.
E-mail address: greg.spivak@lakeheadu.ca (G.J. Spivak).

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doi:10.1016/j.jorganchem.2005.07.040

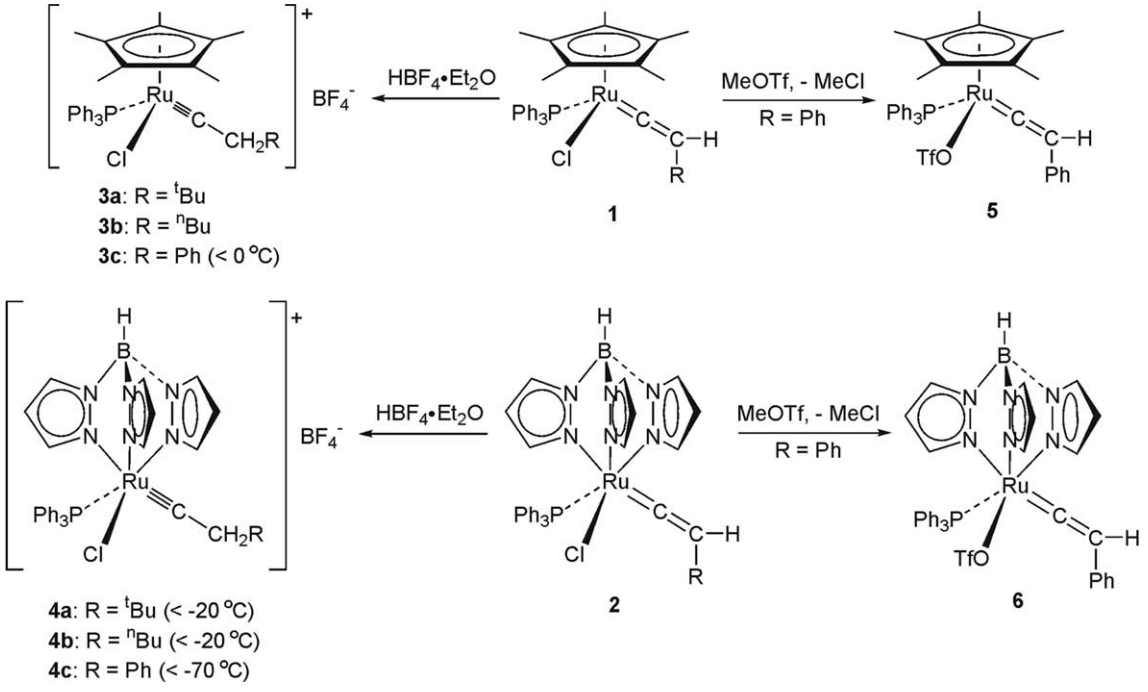
have centred on synthesis and reactivity. At the moment, little effort has been directed towards understanding those factors which control the stability of ruthenium carbynes. We recently communicated some preliminary results on the synthesis of ruthenium carbyne complexes prepared via selective electrophilic attack on vinylidene precursors [6j]. The complexes described in that report are supported by the Cp* ligand. We envisioned the Cp* ligand would serve as a better candidate than Cp for supporting the π-acid carbyne ligand [7], given its enhanced electron donating character. It has been suggested [4] that the Tp ligand is more closely related to the Cp* ligand than the Cp ligand. Within this context, we became interested in extending our work on ruthenium carbynes to include the Tp spectator ligand, with the intent to explore further those factors which influence the stability and reactivity of ruthenium carbyne complexes. The present study described herein, which builds upon our previous work [6j], compares the stability and reactivity of ruthenium carbyne complexes supported by either Cp* or Tp.

2. Results and discussion

2.1. Synthesis of the carbynes $[Cp^*Cl(PPh_3)Ru(CCH_2R)][BF_4]$ (3) and $[TpCl(PPh_3)Ru(CCH_2R)][BF_4]$ (4)

The neutral ruthenium(II) vinylidenes [Cp*Cl(PPh_3)Ru(CCHR)] (**1**) [8] and [TpCl(PPh_3)Ru(CCHR)] (**2**) [9] undergo regioselective electrophilic attack at C_β of the vinylidene ligand when treated with an excess of $HBF_4 \cdot Et_2O$ to yield respectively the ruthenium(IV) carbynes $[Cp^*Cl(PPh_3)Ru(CCH_2R)][BF_4]$ (**3**: R = ^{t}Bu, **3a**; R = ^{n}Bu, **3b**; R = Ph, **3c**), and $[TpCl(PPh_3)Ru(CCH_2R)][BF_4]$ (**4**: R = ^{t}Bu, **4a**; R = ^{n}Bu, **4b**; R = Ph, **4c**), as illustrated in Scheme 1.

We wanted to probe further the mechanism of formation of carbynes **3** and **4**, and determine the course of electrophilic addition to **1** and **2** (i.e., distinguish kinetic vs. thermodynamic protonated products) using variable temperature NMR spectroscopy. Molecular orbital calculations suggest electrophiles might add selectively to C_β of a vinylidene ligand when bound to a late transition metal [10]. However, attack of the electrophile could occur initially at the electron-rich metal centre, yielding a hydrido vinylidene kinetic product [11]. Conceivably, electrophilic attack might also occur initially at a ligand (e.g., halide) [12]. In either case, intramolecular proton migration to C_β of the vinylidene ligand would yield the carbyne products observed. Carbynes **3** and **4** are formed rapidly, cleanly and quantitatively even at −70 °C (NMR). All display varying degrees of stability (vide infra). In all cases, electrophilic addition was observed to occur selectively at C_β of the vinylidene ligand under the conditions employed. Unfortunately, no intermediate species were observed under these conditions, hence the mechanism remains unclear. Similar difficulties in discerning kinetic vs. thermodynamic protonation sites have been reported for other ruthenium vinylidene systems [6f].



Scheme 1.

NMR spectroscopic data for complexes **3** and **4** were acquired in the range −70 to 22 °C depending on stability, and in all cases, they are consistent with the formation of a carbyne ligand. Key spectroscopic features for **3** and **4** include the signals attributed to the carbyne carbons, which appear as low-field (δ 340.6–355.2 ppm) doublets in their respective $^{13}C\{^1H\}$ NMR spectra due to coupling with the adjacent PPh_3 ligand. The measured $^2J_{PC}$ couplings (15.7–18.2 Hz) for **3** and **4** are lower compared to the parent vinylidenes **1** and **2** (19.2–24.4 Hz) [8,9] which suggests diminished backbonding with the PPh_3 ligand upon oxidizing the metal. Also, the relatively low values of $^2J_{PC}$ observed for **3** and **4** are consistent with a carbyne ligand located in a *cis* position with respect to the PPh_3 ligand. The two methylene hydrogens on C_β of the carbyne ligands are diastereotopic, due to the chiral ruthenium centres in complexes **3** and **4**. Consistent with this inequivalency, each of the carbyne methylene hydrogens in complexes **3a–c**, **4a** and **4c** appear as separate signals in their respective ^1H NMR spectra. Interestingly, this shift difference is very small and unresolved in the ^1H NMR spectrum of complex **4b**, where the signal for the carbyne methylene hydrogens appears as a complex multiplet within the temperature range −75 and −20 °C (the upper limit of stability for **4b**).

Carbynes **3** and **4** were observed to exhibit a range of stabilities (refer to Scheme 1). Most notably, compounds **3a** and **3b** are isolable orange solids, and may be obtained in almost quantitative yields as analytically pure samples after metathesis with $NaBAr^f_4$ ($Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$), to yield $[Cp^*Cl(PPh_3)Ru(CCH_2{}^tBu)][BAr^f_4]$ (**3a′**) [13] and $[Cp^*Cl(PPh_3)Ru(CCH_2^nBu)][BAr^f_4]$ (**3b′**) (more conventional anion salts such as $NaPF_6$ and $NaBPh_4$ generally require alcohols as solvents, in which **3a** and **3b** proved to be incompatible). Complexes **3a/3a′** and **3b/3b′** are stable for days when stored at room temperature under reduced pressure. In contrast, **3c**, **4a** and **4b** may be quantitatively prepared in solution at −70 °C, but rapidly decompose (when monitored via VT NMR spectroscopy) in the temperature range −20 to 0 °C. Complete decomposition occurs within hours at room temperature. Compound **4c** proved to be the least stable in the series, and begins to decompose within minutes, despite being prepared quantitatively and maintained at −70 °C.

The range of stabilities observed for **3** and **4** is likely linked to a number of factors. For instance, a series of EHMO studies conducted by Kirchner et al. [14] suggested electronegative π-donor co-ligands (e.g., chloride) might destabilize metal-based orbitals which are necessary to bind adjacent π-acid ligands sufficiently. In addition, the relative electron-donating properties of the Cp* and Tp co-ligands likely influence the overall stability of the carbyne complexes as well. IR spectroscopic studies suggest Cp and Cp* ligands are comparatively better donors with group 8 metals vs. Tp [15]. This is exemplified through the complexes $[LRuCl(CO)(PPh_3)]$ ($L = \eta^3$-Tp, $\upsilon_{CO} = 1965\ cm^{-1}$ [16]; $L = \eta^5$-Cp, $\upsilon_{CO} = 1958\ cm^{-1}$ [17]; $L = \eta^5$-Cp*, $\upsilon_{CO} = 1918\ cm^{-1}$ [18]). Similar effects have been observed in ruthenium dihydrogen complexes, where increasingly stronger donor co-ligands yield an increase in H–H separation [19]. Thus, $[CpRu(\eta^2\text{-}H_2)(dppe)]^+$ ($dppe = Ph_2PCH_2CH_2PPh_2$) has a more "stretched" H–H bond ($^1J_{HD} = 24.9$ Hz, $d(HH)_{calc} \sim 1.00$ Å) [19] than $[TpRu(\eta^2\text{-}H_2)(dppe)]^+$ ($^1J_{HD} = 32.5$ Hz, $d(HH)_{calc} \sim 0.88$ Å) [20]. An increase in electron density at the metal centre should also translate into longer C–C bonds for metal-bound π-co-ligands. For example, the average C–C distance observed for the η^4-butadiene ligand in $[TpRu(\eta^4\text{-}butadiene)Cl]$ ($d(CC)_{avg} \sim 1.348$ Å) [21] is smaller than those observed for $[Cp^*Ru(\eta^4\text{-}butadiene)X]$ ($X = OTf$, $d(CC)_{avg} \sim 1.376$ Å [22]; $X = CF_3CO_2$, $d(CC)_{avg} \sim 1.393$ Å [22]; $X = I$, $d(CC)_{avg} \sim 1.413$ Å [23]). Indeed, the better donor capacity of Cp* is reflected in the slightly stronger $^2J_{PC}$ couplings observed for the parent vinylidenes **1** (23.6–24.4 Hz) when compared to **2** (19.2–20.1 Hz), however this might also be a function of ligand size, where the higher steric requirements of the Tp ligand could be responsible for a slightly weaker $Ru\text{–}C_\alpha$ bond. Nonetheless, the accumulated evidence suggests Cp* should be better able to stabilize a strongly π-acidic carbyne ligand and formally Ru(IV) centre in carbynes **3** and **4**.

Clearly, the identity of the R group on the carbyne ligand has some influence on the overall stability of the carbyne complex as well. Using as guides the pK_a values for $[R_3PH]^+$ [24], enthalpies of protonation for R_3P [25], and the electronic parameter χ [26], the substituents $R = {}^tBu$ and ${}^nBu$ should be better able to stabilize the charge generated on C_β upon protonation, while $R = Ph$ would be the least effective in the series. Thus, carbyne **3a** (with Cp* and $R = {}^tBu$) is one of the more stable carbynes in the series, while **4c** (with Tp and $R = Ph$) is observed to be the least stable.

2.2. Reactions of 1 and 2 with MeOTf

Extending the scope of electrophilic addition reactions to include other electrophiles, in particular Me^+, revealed a different reaction course than that observed for H^+. As well, the reactions were comparatively slower (minutes) even at room temperature, and poor selectivity was observed (NMR) in most cases. For example, we observed that adding excess MeOTf to cooled (−78 °C) CD_2Cl_2 solutions of **1** in an NMR tube, followed by gradual warming to room temperature, yielded a number of interesting results when the reaction was monitored using VT NMR spectroscopy. With $R = {}^tBu$ or ${}^nBu$, the reactions proceeded with poor selectivity despite careful attention to reaction conditions, and afforded a mixture of products which could not be

confidently assigned. In contrast, when R = Ph the reaction proceeded cleanly under the same conditions, and quantitatively yielded the triflato vinylidene complex [Cp*(OTf)(PPh_3)Ru(CCHPh)] (**5**), along with one equivalent of MeCl within 30 min of mixing at room temperature, as determined by NMR spectroscopy (Scheme 1). Complex **5** may be isolated as a relatively stable brown solid in moderate yields (66%). The NMR spectra of **5** are similar to that of the parent chloro vinylidene [Cp*Cl(PPh_3)Ru(CCHPh)] [8]. For example, a low-field C_α vinylidene ligand doublet at δ 344.3 ppm with $^2J_{PC} = 22.1$ Hz (vs. δ 340.1 ppm and $^2J_{PC} = 24.4$ Hz for the chloride analogue) is observed in the $^{13}C\{^1H\}$ NMR spectrum of **5**, while the Cp* and vinylidene hydrogen signals resonate at δ 1.39 and δ 4.54 ppm (vs. δ 1.48 and δ 4.51 ppm for the chloride analogue), respectively. The $^{19}F\{^1H\}$ NMR spectrum of **5** shows a singlet at δ −79.1 ppm, consistent with coordinated OTf [27]. Similar observations were made when the MeOTf reactions were extended to include complexes **2** [28]. As with **1**, the reactions were slow. Room temperature NMR data of the products, including the evolution of MeCl (^1H NMR), suggested [Tp(OTf)(PPh_3)Ru(CCHR)] (R = ^{t}Bu or ^{n}Bu) formed as transient species in varying quantities, however they were very short-lived (minutes). With R = Ph, the complex [Tp(OTf)(PPh_3)Ru(CCHPh)] (**6**) formed almost quantitatively (see Section 4) within 90 min, but displayed lower stability ($t_{1/2} \approx 30$ h) compared to the Cp* analogue **5**.

Despite the slow production of **5** and **6**, we observed no evidence of carbyne formation. The rather large size of the Cp*, Tp and PPh_3 (cone angle = 145° [26b]) ligands likely prevent the comparatively larger CH_3^+ cation from accessing the vinylidene ligand. Even with [CpCl(PPh_2Ph')Ru(CCHPh)] (Ph′ = 2-methylphenyl) [29] which bears the smaller cyclopentadienyl ligand, MeCl evolution is still observed under similar conditions [30]. Bulky ligands are known to direct the site of electrophilic attack even with the smallest electrophile H^+ [12]. Direct attack of CH_3^+ on the chloride ligand [31] is certainly likely given the greater accessibility of the chloride lone pairs.

3. Concluding remarks

We have presented a study which describes the synthesis of a series of ruthenium carbyne complexes prepared via selective protonation of their respective neutral ruthenium chloro vinylidene precursor complexes. We have noted that the relative stabilities of the carbyne complexes examined may be traced, at least in part, to the supporting ligands. Our results suggest the Cp* ligand may be more effective than Tp in stabilizing ruthenium carbyne complexes. The range of stabilities observed among the carbynes studied also underscores the subtle effects of the identity of the substituents on the carbyne ligand, with alkyl ligands proving to be better candidates than aryl ligands. We have also described an interesting site selectivity in electrophilic addition reactions to the same ruthenium chloro vinylidene precursors. The accessibility of sites (i.e., chloride or vinylidene) available for attack by an electrophile are likely governed by sterics. Thus, smaller H^+ can access the vinylidene ligand, while larger CH_3^+ preferentially attacks chloride.

4. Experimental section

All experiments and manipulations were conducted under an inert atmosphere of prepurified N_2 using standard Schlenk and syringe techniques. Bulk solvents used in large-scale preparations were rigorously dried, and either distilled under nitrogen immediately prior to use, or stored over activated 4A molecular sieves in bulbs with Teflon taps: CH_2Cl_2 (CaH_2); C_6H_6, Et_2O and hexanes (sodium metal/benzophenone); MeOH (activated 4A molecular sieves). NMR solvents used in solution structure elucidations were dried with appropriate drying agents, vacuum distilled, freeze–pump–thaw degassed three times, and stored in bulbs with Teflon taps: $CDCl_3$ (anhydrous $CaCl_2$); CD_2Cl_2 (CaH_2); C_6D_6 (sodium metal). NMR spectra (^1H, ^{13}C, ^{31}P and ^{19}F) were obtained using a Varian Unity INOVA 500 MHz spectrometer, with chemical shifts (in ppm) referenced to residual protio solvent peaks (^1H and ^{13}C), external 85% H_3PO_4 (^{31}P) or external $CFCl_3$ (^{19}F). Elemental analyses were performed on a CEC 240XA analyzer by the Lakehead University Instrumentation Laboratory. With the exception of R = ^{n}Bu for **1** for which a synthesis is described below, the neutral vinylidenes **1** [8] and **2** [9] were prepared as described in the literature.

4.1. Synthesis of [Cp*Cl(PPh_3)Ru(CCH^nBu)]

The complex [Cp*RuCl(PPh_3)$_2$] (0.301 g, 0.379 mmol) was dissolved in benzene (30 mL) and treated with 5 equivalents of 1-hexyne (217 μL, 1.90 mmol) via syringe. The orange mixture was refluxed for 30 min while stirring. During this time, the solution turned deep red. Upon completion, the reaction mixture was cooled to room temperature and the volatiles were removed under reduced pressure. The crude product was recrystallized via slow diffusion from MeOH/CH_2Cl_2. Yield: 0.133 g (56%). Anal. Calc. for $C_{34}H_{40}ClPRu$: C, 66.26; H, 6.56. Found: C, 66.32; H, 6.81%. ^1H NMR (499.9 MHz, $CDCl_3$, 22 °C): δ 8.00–7.00 (m, 15H, Ph), 3.57 (t, 1H, $^3J_{HH} = 7.3$ Hz, RuCC*H*), 2.07, (m, 2H, RuCCH(^{n}Bu)), 1.45 (d, 15H, $^4J_{PC} = 1.5$ Hz, $C_5(CH_3)_5$), 1.16 (m, 2H,

RuCCH(^{n}Bu)), 1.01 (m, 2H, RuCCH(^{n}Bu)), 0.79 (t, 3H, $^3J_{HH} = 7.3$ Hz, RuCCH(^{n}Bu)). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): δ 334.7 (d, $^2J_{PC} = 24.4$ Hz, Ru*C*), 135.0–127.7 (s, Ph), 106.8 (s, RuC*C*H(^{n}Bu)), 100.8 (s, $C_5(CH_3)_5$), 33.94–13.96 (s, ^{n}Bu), 9.58 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): δ 50.9 (s, PPh_3).

4.2. Synthesis of [Cp*RuCl(CCH$_2$(^{t}Bu))(PPh$_3$)][BF$_4$] (3a)

0.223 g (0.362 mmol) of [Cp*RuCl(CCH^{t}Bu)(PPh$_3$)] was dissolved in CH_2Cl_2 (3 mL) and the solution was cooled to −78 °C. To the cooled, deep red solution was added a slight excess of HBF_4 in Et_2O (55 μL of 54 wt% solution, 0.399 mmol) followed by stirring at this temperature for about 10 min. An immediate colour change from red to orange–brown was observed. The solution was allowed to warm to room temperature gradually (about 30 min), and then the volatiles were removed under reduced pressure. The orange residue was washed with Et_2O (4 × 5 mL) and dried under reduced pressure. All attempts to recrystallize the product were frustrated by the high solubility of this complex yielding oils, hence sufficiently pure samples for elemental analysis could not be obtained. Yield: 0.229 g (90%). ^1H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.79–7.30 (m, 15H, Ph), 3.11 (dd, 1H, $^2J_{HH} = 20.3$ Hz, $^4J_{PH} = 1.1$ Hz, RuCCH_aH$_b$(^{t}Bu)), 1.86 (dd, 1H, $^2J_{HH} = 20.3$ Hz, $^4J_{PH} = 3$ Hz, RuCCH$_a$$H_b$(^{t}Bu)), 1.65 (d, 15H, $^4J_{PH} = 2$ Hz, $C_5(CH_3)_5$), 0.97 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, 22 °C): δ 351.0 (d, $^2J_{PC} = 15.7$ Hz, Ru*C*),134.8–129.3 (s, Ph), 110.5 (s, $C_5(CH_3)_5$), 67.4 (s, RuC*C*H$_2$(^{t}Bu)), 36.6 (s, *C*Me$_3$), 30.4 (s, C(CH_3)$_3$), 10.0 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 39.0 (s, PPh_3).

4.3. Synthesis of [Cp*RuCl(CCH$_2$(^{n}Bu))(PPh$_3$)][BF$_4$] (3b)

A procedure analogous to that for the synthesis of **3a** was employed for the synthesis of **3b**, except using [Cp*Cl(PPh$_3$)Ru(CCH^{n}Bu)] (prepared as above) as the precursor. Unfortunately, as with **3a**, all attempts at recrystallizing **3b** yielded only oily products. Yield: 0.195 g (88%). ^1H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.66–7.39 (m, 15H, Ph), 2.35 (m, 1H, $^2J_{HH} = 20.5$ Hz, RuCCH_aH$_b$(^{n}Bu)), 1.86 (m, 1H, $^2J_{HH} = 20.5$ Hz, RuCCH$_a$$H_b$(^{n}Bu)), 1.56 (d, 15H, $^4J_{PH} = 1.9$ Hz, $C_5(CH_3)_5$), 1.48–1.09 (m, 6H, RuCCH$_2$(^{n}Bu)), 0.77 (t, 3H, $^3J_{HH} = 7$ Hz, Ru/CCH$_2$(^{n}Bu)). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, 22 °C): δ 349.4 (d, $^2J_{PC} = 17.1$ Hz, Ru*C*), 135.8–129.2 (s, Ph), 110.6 (s, $C_5(CH_3)_5$), 66.1 (s, RuC*C*H$_2$(^{n}Bu)), 31.6 (s, ^{n}Bu), 24.3 (s, ^{n}Bu), 22.2 (s, ^{n}Bu), 13.7 (s, ^{n}Bu), 10.0 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 38.6 (s, PPh_3).

4.4. Low-temperature observation of [Cp*RuCl(CCH$_2$(Ph))(PPh$_3$)][BF$_4$] (3c)

0.0324 g (0.0509 mmol) of [Cp*RuCl(CCHPh)(PPh$_3$)] was dissolved in CD_2Cl_2 (0.4 mL) in a 5 mm NMR tube fitted with a rubber septum and attached to a vacuum line. The deep red solution was cooled to −78 °C and then treated with 7.4 μL of a 54 wt% solution of HBF_4 in Et_2O (0.0537 mmol) via syringe. An instant colour change from deep red to orange was observed. The sample was immediately transferred to a pre-cooled (−75 °C) NMR probe, and data were collected immediately. Complex **3c** was observed to form immediately. ^1H NMR (499.9 MHz, CD_2Cl_2, −75 °C): δ 7.58–6.95 (m, 20H, Ph), 4.05 (d, 1H, $^2J_{HH} = 20.5$ Hz, RuCCH_aH$_b$Ph), 3.52 (d, 1H, $^2J_{HH} = 20.5$ Hz, RuCCH$_a$$H_b$Ph), 1.60 (d, 15H, $^4J_{PH} = 1.5$ Hz, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, −75 °C): δ 340.6 (d, $^2J_{PC} = 16.3$ Hz, Ru*C*), 133.9–126.8 (s, Ph), 110.9 (s, $C_5(CH_3)_5$), 59.7 (s, RuC*C*H$_2$Ph), 10.0 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, −75 °C): δ 38.6 (s, PPh_3).

4.5. Synthesis of [Cp*RuCl(CCH$_2$(^{t}Bu))(PPh$_3$)]-[B(Ar^f)$_4$] (3a′)

Complex **3a** (0.229 g, 0.325 mmol) in CH_2Cl_2 (8 mL) was treated with $NaBAr^f_4$ (0.386 g, 0.436 mmol) in Et_2O (4 mL) via cannula at room temperature. The addition was accompanied by the immediate formation of a white precipitate. After about 20 min of stirring, the solvents were removed under reduced pressure and the product was extracted from the resultant orange residue with CH_2Cl_2 (3 × 12 mL). Filtration of the combined extracts through Celite and removal of the solvent from the filtrate under reduced pressure yielded the analytically pure product as a dark orange–brown solid. Yield: 0.463 g (96%). Orange crystals of **3a′** could be grown via slow diffusion (CH_2Cl_2/hexanes) at −20 °C. Anal. Calc. for $C_{66}H_{53}BClF_{24}PRu \cdot CH_2Cl_2$: C, 51.40; H, 3.55. Found C, 51.21; H, 3.75%. The presence of solvent was confirmed spectroscopically. ^1H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.75–7.45 (m, 27H, Ph and $C_6H_3(CF_3)_2$), 2.51 (d, 1H, $^2J_{HH} = 20.3$ Hz, RuCCH_aH$_b$(^{t}Bu)), 1.76 (d, 1H, $^2J_{HH} = 20.3$ Hz, RuCCH$_a$$H_b$(^{t}Bu)), 1.61 (d, 15H, $^4J_{PH} = 1.5$ Hz, $C_5(CH_3)_5$), 0.99 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, 22 °C): δ 348.3 (d, $^2J_{PC} = 15.7$ Hz, Ru*C*), 161.9 (q, $^1J_{BC} = 49.6$ Hz, C_{ipso} of Ar^f), 135.0 (s, C_{ortho} of Ar^f), 134.5–129.5 (s, Ph), 129.0 (m, C_{meta} of Ar^f), 124.8 (q, $^1J_{CF} = 271$ Hz, *C*F$_3$ of Ar^f), 117.7 (s, C_{para} of Ar^f), 110.6 (s, $C_5(CH_3)_5$), 67.1 (s, RuC*C*H$_2$(^{t}Bu)), 36.9 (s, *C*Me$_3$), 30.4 (s, C(CH_3)$_3$), 10.1 (s, $C_5(CH_3)_5$). $^{19}F\{^1H\}$ NMR (470.2 MHz, CD_2Cl_2, 22 °C): δ 63.2 (s, C*F*$_3$ of Ar^f). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 38.3 (s, PPh_3).

4.6. Synthesis of [Cp*RuCl(CCH$_2$(^{n}Bu))(PPh$_3$)][B(Ar^f)$_4$] (**3b′**)

A procedure analogous to that for the synthesis of **3a′** was employed for the synthesis of **3b′**, except using **3b** as the precursor. Complex **3b′** was isolated as a dark orange–brown solid. Unfortunately, the extreme solubility of **3b′** confounded all attempts at obtaining sufficiently pure samples for elemental analysis. Yield: 0.407 g (99%). ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.66–7.39 (m, 27 H, Ph and $C_6H_3(CF_3)_2$), 2.35 (m, 1H, $^2J_{HH}$ = 20.5 Hz, RuCCH_aH$_b$(^{n}Bu)), 1.86 (m, 1H, $^2J_{HH}$ = 20.5 Hz, RuCCH$_a$$H_b$(^{n}Bu)), 1.56 (d, 15H, $^4J_{PH}$ = 1.9 Hz, C$_5$(CH_3)$_5$), 1.48–1.09 (m, 6H, RuCCH$_2$(^{n}Bu)), 0.77 (t, 3H, $^3J_{HH}$ = 7 Hz, RuCCH$_2$(^{n}Bu)). ^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2, 22 °C): δ 347.0 (d, $^2J_{PC}$ = 17.1 Hz, Ru*C*), 162.0 (q, $^1J_{BC}$ = 49.6 Hz, C$_{ipso}$ of Ar^f), 135.0 (s, C$_{ortho}$ of Ar^f), 135.8–128.1 (s, Ph), 129.1 (m, C$_{meta}$ of Ar^f), 124.8 (q, $^1J_{CF}$ = 271 Hz, *C*F$_3$ of Ar^f), 117.7 (s, C$_{para}$ of Ar^f), 110.7 (s, *C*$_5$(CH$_3$)$_5$), 66.1 (s, RuC*C*H$_2$(^{n}Bu)), 31.6 (s, ^{n}Bu), 24.3 (s, ^{n}Bu), 22.1 (s, ^{n}Bu), 13.5 (s, ^{n}Bu), 10.1 (s, C$_5$(*C*H$_3$)$_5$). ^{19}F{^{1}H} NMR (470.2 MHz, CD_2Cl_2, 22 °C): δ −63.2 (s, C*F*$_3$ of Ar^f). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 38.6 (s, *P*Ph$_3$).

4.7. Low-temperature observation of [TpRuCl(CCH$_2$(^{t}Bu))(PPh$_3$)][BF$_4$] (**4a**)

0.0333 g (0.0480 mmol) of [TpRuCl(CCH(^{t}Bu))(PPh$_3$)] was degassed in an NMR tube fitted with a rubber septum, and dissolved in CD_2Cl_2 (0.4 mL) under N_2. The deep red solution thus formed was then cooled to −78 °C and treated with 9 μL of a 54 wt% solution of HBF_4 in Et_2O (0.0653 mmol) via syringe. The sample was then rapidly transferred to a precooled (−70 °C) NMR probe and immediate acquisition of data was then carried out. Quantitative conversion to **4a** was observed at −70 °C. The sample was slowly warmed to room temperature. Product decomposition began at −20 °C with complete decomposition into unidentified species observed after several hours. ^{1}H NMR (499.9 MHz, CD_2Cl_2, −70 °C): δ 7.97 (d, 1H, $^3J_{HH}$ = 1.5 Hz, Tp), 7.84 (s, 2H, Tp), 7.76 (s, 1H, Tp), 7.29 (s, 1H, Tp), 7.6–7.2 (m, 15H, Ph), 6.35 (s, 1H, Tp), 6.20 (d, 1H, $^3J_{HH}$ = 1.5 Hz, Tp), 6.02 (t, 1H, $^3J_{HH}$ = 2 Hz, Tp), 5.97 (t,1H, $^3J_{HH}$ = 1.5 Hz, Tp), 3.08 (d, 1H, $^2J_{HH}$ = 21 Hz, RuCCH_aH$_b$(^{t}Bu)), 2.94 (d, 1H, $^2J_{HH}$ = 21 Hz, RuCCH$_a$$H_b$(^{t}Bu)), 1.00 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, −70 °C): δ 355.2 (d, $^2J_{PC}$ = 16.5 Hz, Ru*C*), 146.9 (s, Tp), 143.7–132.9 (m, Ph), 138.5 (s, Tp), 138.1 (s, Tp), 137.4 (d, $^3J_{PC}$ = 2.9 Hz, Tp), 126.3 (s, Tp), 125.9 (s, Tp), 108.6 (s, Tp), 107.6 (d, $^4J_{PC}$ = 1.9 Hz, Tp), 107.0 (s, Tp), 70.8 (s, RuC*C*H$_2$(^{t}Bu)), 35.4 (s, *C*Me$_3$), 31.1 (s, C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, −70 °C): δ 23.9 (s, *P*Ph$_3$).

4.8. Low-temperature observation of [TpRuCl(CCH$_2$(^{n}Bu))(PPh$_3$)][BF$_4$] (**4b**)

0.0428 g (0.0617 mmol) of [TpRuCl(CCH(^{n}Bu))(PPh$_3$)] in an NMR tube fitted with a rubber septum was dissolved in CD_2Cl_2 (0.35 mL) under N_2. The sample was cooled to −78 °C and then treated with 12 μL of a 54 wt% solution of HBF_4 in Et_2O (0.0648 mmol) via syringe. An instant colour change from deep red to orange–brown was observed. The sample was rapidly transferred to a precooled (−75 °C) NMR probe, and NMR data were collected immediately. Complex **4b** was formed immediately and quantitatively at −75 °C. The sample was slowly warmed to room temperature. Product decomposition began at −20 °C, with complete decomposition occurring within hours. ^{1}H NMR (499.9 MHz, CD_2Cl_2, −70 °C): δ 7.89 (d, 1 H, $^3J_{HH}$ = 1.5 Hz, Tp), 7.84 (d, 1 H, $^3J_{HH}$ = 2 Hz, Tp), 7.82 (d, 1H, $^3J_{HH}$ = 2.5 Hz, Tp), 7.77 (s, 1H, Tp), 7.62–7.28 (m, 15H, Ph), 7.09 (s, 1H, Tp), 6.36 (s, 1H, Tp), 6.21 (d, 1H, $^3J_{HH}$ = 2Hz, Tp), 5.99 (m, 2H, $^3J_{HH}$ = 2Hz, Tp), 3.12–2.96 (m, 2H, RuCCH_2(^{n}Bu)), 1.92 (br m, 2H, RuCCH$_2$(^{n}Bu)), 1.55 (br m, 2H, RuCCH$_2$(^{n}Bu)), 1.10 (br m, 2H, RuCCH$_2$(^{n}Bu)), 0.73 (t, 3H, $^2J_{HH}$ = 7 Hz, RuCCH$_2$(^{n}Bu)). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, −70 °C): δ 351.2 (d, $^2J_{PC}$ = 17.5 Hz, Ru*C*), 146.8 (s, Tp), 143.5–129.3 (m, Ph), 138.2 (s, Tp), 138.1 (s, Tp), 137.2 (s, Tp), 126.6 (s, Tp), 126.2 (s, Tp), 108.3 (s, Tp), 107.7 (d, $^4J_{PC}$ = 3 Hz, Tp), 106.9 (s, Tp), 58.1 (s, RuC*C*H$_2$(^{n}Bu)), 32.0 (s, RuCCH$_2$(^{n}Bu)), 23.2 (s, RuCCH$_2$(^{n}Bu)), 22.5 (s, RuCCH$_2$(^{n}Bu)), 14.2 (s, RuCCH$_2$(^{n}Bu)). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, −70 °C): δ 26.4 (s, *P*Ph$_3$).

4.9. Low-temperature observation of [TpRuCl(CCH$_2$(Ph))(PPh$_3$)][BF$_4$] (**4c**)

0.0239 g (0.0335 mmol) of [TpRuCl(CCH(Ph))(PPh$_3$)] in an NMR tube fitted with a rubber septum was dissolved in CD_2Cl_2 (0.4 mL) under N_2. The resulting deep red solution was then cooled to −78 °C and treated with 5 μL of a 54 wt% solution of HBF_4 in Et_2O (0.0363 mmol) via syringe. A rapid colour change from deep red to orange–brown was observed. The cooled sample tube was then transferred immediately to a precooled (−70 °C) NMR probe and data were acquired immediately. Complex **4c** was observed to have formed immediately and quantitatively at −70 °C. Slow decomposition of **4c** began almost immediately at −70 °C. Slowly warming the solution to room temperature only accelerated the decomposition of **4c**, which was observed to be complete after about 2 h at room temperature. ^{1}H NMR (499.9 MHz, CD_2Cl_2, −70 °C): δ 7.81 (d, 1H, $^3J_{HH}$ = 2 Hz, Tp), 7.77 (s, 1H, $^3J_{HH}$ = 2.5 Hz, Tp), 7.60–7.25 (m, 20 H, Ph), 7.23 (s, 1H, Tp), 7.21 (s, 1H, Tp), 6.32 (s, 1H, $^3J_{HH}$ = 2 Hz, Tp), 6.20 (d, 1H,

$^3J_{HH} = 2.5$ Hz, Tp), 5.97 (t, 1H, $^3J_{HH} = 2.5$ Hz, Tp), 5.95 (t, 1H, $^3J_{HH} = 2.5$ Hz, Tp), 5.93 (m, 1H, $^3J_{HH} = 1$ Hz, Tp), 4.66 (dd, 1H, $^4J_{PH} = 2$ Hz, $^2J_{HH} = 20$ Hz, RuCCH_aH$_b$(Ph)), 3.83 (dd, 1H, $^4J_{PH} = 2$ Hz, $^2J_{HH} = 20$ Hz, RuCCH$_a$$H_b$(Ph)). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, −70 °C): δ 341.4 (d, $^2J_{PC} = 17.8$ Hz, Ru*C*), 147.1 (s, Tp), 143.4 (s, Tp), 138.0–129.5 (m, P*Ph*$_3$), 137.4 (d, $^3J_{PC} = 2.9$ Hz, Tp), 131.5 (s, RuCCH$_2$(*Ph*)), 130.2 (s, RuCCH$_2$(*Ph*)), 128.6–128.1 (m, RuCCH$_2$(*Ph*)), 126.5 (s, Tp), 126.1 (s, Tp), 122.9 (s, Tp), 108.3 (s, Tp), 106.8 (d, $^4J_{PC} = 2.9$ Hz, Tp), 63.7 (s, RuC*C*H$_2$(Ph)). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, −70 °C): δ 26.6 (s, *P*Ph$_3$).

4.10. Synthesis of [Cp*Ru(OTf)(CCHPh)(PPh$_3$)] (5)

In a 10 mL Schlenk tube containing a stir-bar, 0.0460 g (0.0723 mmol) of [Cp*Cl(PPh$_3$)Ru(CCHPh)] was dissolved in CH_2Cl_2 (0.5 mL) and treated with 25 μL (0.221 mmol, 3 equivalents) of MeOTf via syringe. An almost immediate colour change from deep red to dark brown with formation of some brown solid was observed. The reaction mixture was stirred at room temperature for 30 min, at which point the volatiles were removed under reduced pressure. The resultant brown solid was then washed with hexanes (4 × 5 mL) and allowed to dry in vacuo. Yield: 0.0360 g (66%). Anal. Calc. for $C_{37}H_{36}F_3O_3PRuS{\cdot}2CH_2Cl_2$: C, 50.93; H, 4.39. Found: C, 51.67; H, 4.64%. The presence of solvent was confirmed spectroscopically. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.39–6.89 (m, 20 H, Ph), 4.54 (s, 1H, RuCC*H*), 1.39 (d, 15H, $^4J_{PH} = 2.0$ Hz, C$_5$(C*H*$_3$)$_5$). ^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2, 22 °C): δ 344.3 (d, $^2J_{PC} = 22.1$ Hz, Ru*C*), 134.2–125.2 (s, Ph), 118.9 (q, $^1J_{CF} = 318$ Hz, *C*F$_3$SO$_3$), 115.2 (s, *C*$_5$(CH$_3$)$_5$), 103.4 (s, RuC*C*HPh), 9.88 (s, C$_5$(*C*H$_3$)$_5$). ^{19}F{^{1}H} NMR (470.2 MHz, CD_2Cl_2, 22 °C): δ −79.1 (s, C*F*$_3$SO$_3$). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 47.5 (s, *P*Ph$_3$). IR (cm^{-1}): 1481 (m), 1436 (m), 1383 (w), 1315 (m, ν(SO$_3$)), 1261 (m), 1225 (m), 1202 (m), 1155 (s), 1092 (m), 1070 (m), 1029 (s).

4.11. Synthesis of [TpRu(OTf)(CCHPh)(PPh$_3$)] (6)

0.0323 g (0.0452 mmol) of [TpCl(PPh$_3$)Ru(CCHPh)] in an NMR tube fitted with a rubber septum was dissolved in CD_2Cl_2 (0.35 mL) under N_2. This deep red solution was then treated with 16 μL MeOTf (0.141 mmol), and a colour change to orange–brown occurred instantly. The sample was allowed to mix (tumbling) for 1.5 h. The NMR data collected after this time indicated nearly quantitative conversion to complex **6**. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 8.38 (d, 1H, $^3J_{HH} = 2.3$ Hz, Tp), 7.94 (d, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 7.71 (d, 1H, $^3J_{HH} = 2.3$ Hz, Tp), 7.66 (m, 1H, $^3J_{HH} = 1.5$ Hz, Tp), 7.45–7.03 (m, 20H, Ph), 6.90 (d, 1H, $^3J_{HH} = 1.5$ Hz, Tp), 6.88 (d, 1H, $^3J_{HH} = 1$ Hz, Tp), 6.77 (d, 1H, $^3J_{HH} = 1.5$ Hz, Tp), 6.45 (d, 1H, $^3J_{HH} = 2.3$ Hz, Tp), 6.18 (t, 1H, $^3J_{HH} = 2.3$ Hz, Tp), 6.14 (t, 1H, $^3J_{HH} = 2.3$ Hz, Tp), 5.75 (t, 1H, $^3J_{HH} = 2.3$ Hz, Tp), 5.40 (d, 1H, $^4J_{PH} = 3.5$ Hz, RuCC*H*(Ph)). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 22 °C): δ 377.4 (d, $^2J_{PC} = 17.3$ Hz, Ru*C*), 147.1 (s, Tp), 145.6 (d, $^3J_{PC} = 1.9$ Hz, Tp), 143.4 (s, Tp), 137.6 (s, Tp), 136.3 (s, Tp), 135.4 (d, $^4J_{PC} = 2.9$ Hz, RuCCH(*Ph*)), 134.3–130.3 (m, P*Ph*$_3$), 134.1–133.9 (m, RuCCH(*Ph*)), 131.1–130.2 (m, RuCCH(*Ph*)), 128.8–128.5 (m, RuCCH(*Ph*)), 126.9 (s, Tp), 126.1 (s, Tp), 118.9 (q, $^1J_{CF} = 319.3$ Hz, *C*F$_3$SO$_3$), 113.8 (s, RuC*C*H(Ph)), 106.7 (s, Tp), 106.2 (s, Tp), 105.7 (d, $^4J_{PC} = 2.9$ Hz, Tp). ^{19}F{^{1}H} NMR (470.2 MHz, CD_2Cl_2, 22 °C): δ −78.9 (s, C*F*$_3$SO$_3$). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 37.4 (s, *P*Ph$_3$). IR (cm^{-1}): 1435 (m), 1409 (m), 1399 (m), 1312 (s, ν(SO$_3$)), 1245 (sh), 1225 (s), 1212 (s), 1165 (s), 1117 (m), 1092 (m), 1076 (w), 1050 (s), 1028 (s).

Acknowledgements

We gratefully acknowledge financial support from the Lakehead University Senate Research Committee, and the Natural Sciences and Engineering Research Council of Canada.

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