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A sterically demanding nucleophilic carbene: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). Thermochemistry and catalytic application in olefin metathesis

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Abstract

The sterically demanding nucleophilic carbene ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr, **4**) has been synthesized. The reaction of $[Cp^*RuCl]_4$ (**5**; $Cp^* = \eta^5\text{-}C_5Me_5$) with this ligand affords a coordinatively unsaturated $Cp^*Ru(IPr)Cl$ (**6**) complex. Solution calorimetric results in this system provide information concerning the electron donor properties of the carbene ligand. Steric parameters associated with this ligand are determined from the X-ray crystal structure study. The carbene ligand reacts with $RuCl_2(=C(H)Ph)(PCy_3)_2$ (**1**) to yield a mixed carbene–phosphine ruthenium complex $RuCl_2(=C(H)Ph)(IPr)(PCy_3)$ (**9**). A single-crystal X-ray diffraction study has been performed on **9**. The thermal stability of **9** has been studied at 60°C and its catalytic activity has been evaluated for the ring closing metathesis of diethyldiallylmalonate.

Keywords: Nucleophilic carbene; Thermochemistry; Olefin metathesis

1. Introduction

Tertiary phosphine ligands are useful in controlling reactivity and selectivity in organometallic chemistry and homogeneous catalysis [1] however, they often undergo significant P–C degradation at higher temperatures which, in certain catalytic processes, results in the deactivation of the catalyst [2]. Therefore there is a need for strongly nucleophilic (electron-rich) ligands that form stable bonds with metals. Carbene ligands have proven to behave as phosphine mimics [3].

The ruthenium carbene complex, $RuCl_2(=C(H)Ph)(PCy_3)_2$ (**1**) developed by Grubbs et al. is a highly efficient catalyst precursor in ring closing metathesis (RCM) and its use is widespread in organic and polymer chemistry [4]. Mechanistic studies have shown that the presence of a bulky tertiary phosphine ligand is mandatory for stabilizing reactive catalytic intermediate and/or preventing the decomposition of carbenes [4d, 5]. It has been shown that one of the phosphine ligands can be exchanged with one bulky nucleophilic carbene ligand such as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes (**2**)) to afford a mixed ligand system, $RuCl_2(=C(H)Ph)(IMes)(PCy_3)$ (**3**) [6]. When used in RCM, the catalyst precursor **3** shows significant activity and improved thermal stability compared to the parent complex **1** [6].

In a detailed study, we have examined steric and electronic properties of various nucleophilic carbene ligands by solution calorimetry and structural analysis [6a, 7]. We have also investigated the role of these ligands as catalyst precursors in ring closing metathesis (RCM) reactions [6a, 7]. In this paper we present the synthesis, structural characterization, and thermochemistry involving another bulky ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**4**). The electronic and steric properties of this ligand are compared to those of previously reported carbenes [6a, 7] and phosphines. This ligand is also utilized in the synthesis and catalytic behavior of very stable analogue to Grubbs' olefin metathesis catalyst.

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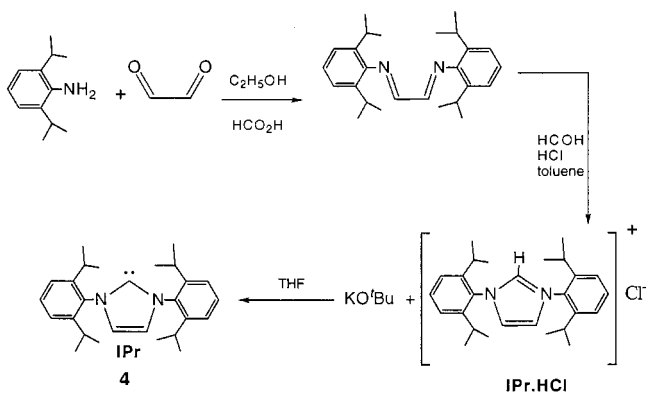
2. Results and discussion

2.1. Ligand synthesis

Although a number of 1,3-disubstituted imidazolium chlorides including the sterically hindered imidazolium chloride, 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) are available by established procedures [8], our numerous trials to synthesize the 1,3-diisopropylphenyl substituted product following this protocol have failed [9]. Herein, we report a modified procedure for the synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazoliumchloride (IPrHCl). Addition of glyoxal to 2,6-diisopropylaniline in absolute ethanol in the presence of catalytic amount of formic acid leads to the formation of the diazabutadiene as a yellow solid in good yields [10]. This compound reacts with paraformaldehyde and HCl in toluene to form 1,3-bis(2,6-diisopropylphenyl)imidazoliumchloride (IPrHCl) as an off-white solid in moderate yields. The carbene nucleophile IPr (**4**) is formed when IPrHCl is reacted with potassium *tert*-butoxide in THF [11]. Scheme 1 presents



Scheme 1.

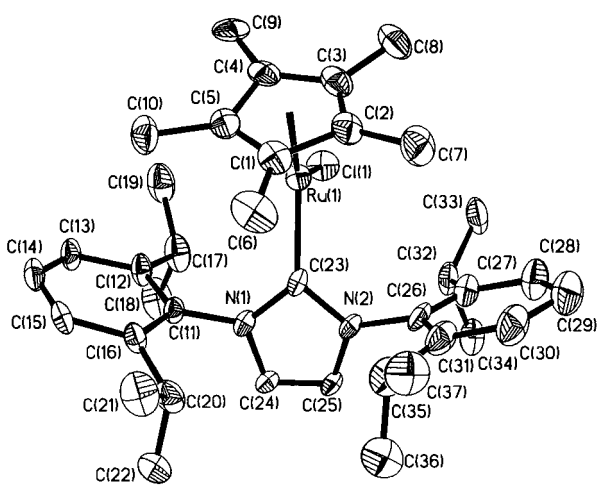
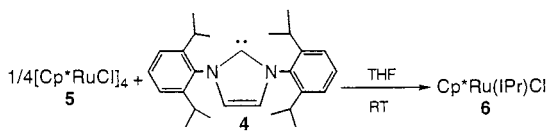


Fig. 1. ORTEP of Cp*Ru(IPr)Cl (**6**) with elipsoids drawn at 50% probability.

the synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr (**4**)).

2.2. The Cp*Ru(L)Cl system (L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IPr)

It has been shown that the versatile starting material $[Cp^*RuCl]_4$ [12] (**5**) ($Cp^* = \eta^5$-C_5Me_5) rapidly reacts with sterically demanding phosphines [13] as well as bulky carbene nucleophile (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene IMes (**2**)) [6a] to give deep blue 16-electron Cp*Ru(L)Cl complexes ($L = PR_3$ and IMes). Reaction of **5** with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr (**4**)) in THF proceeds rapidly, and a deep blue color appears instantaneously. A deep blue crystalline solid formulated as Cp*Ru(IPr)Cl (**6**) is isolated in 60% yield upon workup (Eq (1)).



(1)

The ^{1}H-NMR spectrum of **6** shows the resonances for the Cp* and the carbene ligand. The reaction depicted in Eq (1) is quantitative by NMR and therefore is suitable for calorimetric investigations [14]. When four equivalents of the carbene (**4**) react with one equivalent of the tetramer (**5**) in THF at 30°C, the measured enthalpy of reaction is exothermic by $-44.5(0.4)$ kcal mol^{-1}. Comparing this value to the previously measured reaction enthalpies involving **5** and PCy_3, P^iPr_3 [15] and IMes (**2**) [6a] indicates that the Ru–L stability decreases in the order shown in Eq (2). The IMes ligand (**2**) is by far the strongest binder of the four with the IPr (**4**) strength very close to that of PCy_3. Therefore, from an electronic point of view, the IPr ligand should be very similar to PCy_3.

$$\mathbf{5} + 4\,L \xrightarrow[RT]{THF} 4\ Cp^*Ru(L)Cl$$

L = PCy_3, $\Delta H = -41.9$ (0.2)
IMes, $\Delta H = -62.6$ (0.2)
IPr, $\Delta H = -44.5$ (0.4)
IMes (15.6) > IPr (11.2) > PCy_3 (10.5) (2)

The X-ray crystallography confirms the formulation of **6** (Fig. 1). The molecule has a pseudo piano stool structure with the Cp* ligand η^5-bonded to the ruthenium center. Crystallographic data are shown in Table 1 and selected bond lengths and bond angles for **6**, Cp*Ru(IMes)Cl (**7**) [6a] and $Cp^*Ru(PCy_3)Cl$ (**8**) [6a] are presented in Table 2. We have already defined a system for quantifying the steric factors in carbenes [7] which makes use of their fence-like structures. To gauge the steric factors, the height and the length of the fences

Table 1
Crystallographic data for complexes **6** and **9**

	6	**9**
Formula	$C_{37}H_{50}ClN_2Ru$	$C_{52}H_{75}Cl_2N_2PRu$
f_w	724.42	931.08
Color	Blue	Pink–brown
Space group	*Cc*	*P*2(1)/*n*
a (Å)	12.2011(6)	20.4193(18)
b (Å)	31.1928(15)	11.1326(10)
c (Å)	10.5046(5)	22.2915(19)
α (°)	90	90
β (°)	94.2270(10)	107.449(1)
γ (°)	90	90
Volume (Å^3)	3987.0(3)	4834.1(7)
Z	4	4
D_{calc} (g cm^{-3})	1.207	1.279
R [a]	0.0281	0.0336
R_w [b]	0.0552	0.0603
Refined parameters	430	823
Data collected	29365	56 934
Unique data [$I>3\sigma$]	9873	11 106
Goodnes-of-fit on F^2	0.847	0.75

[a] $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.
[b] $R_w = \Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2$.

(A_L and A_H) are compared. A comparison between relevant bond distances in **6** and **7** indicate that the two structures are very similar despite their significant difference in reaction enthalpy (11.1 vs.15.6 kcal mol^{-1}, respectively). However, the steric parameters indicate a significant difference between the two with **6** being much more sterically demanding than **7** ($A_H = 137.6$ in **6** and 70.4° in **7**). The metrical parameters also illustrate the similarity between the structures of **6** and **8** which is also corroborated by the solution calorimetric results.

2.3. The $RuCl_2(=C(H)Ph)(PCy_3)(IPr)$ complex

2.3.1. Synthesis

We have shown that the IPr ligand (**4**) is sterically more demanding than either IMes (**2**) or PCy_3. Therefore, it is logical to predict that due to its steric bulk, IPr ligand could be capable of stabilizing the 14-electron ruthenium intermediate $RuCl_2(L)(=C(H)Ph)$ involved in olefin metathesis [4c, 5]. The complex

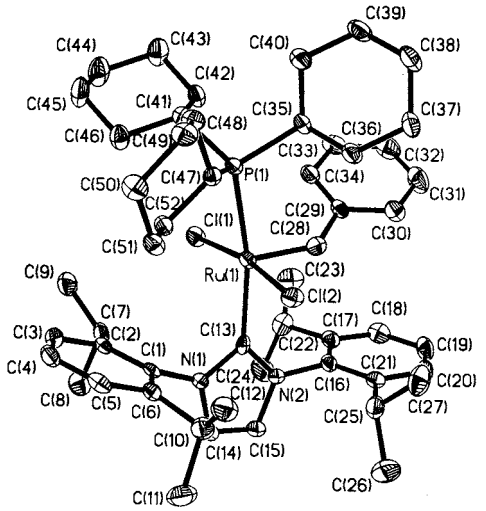
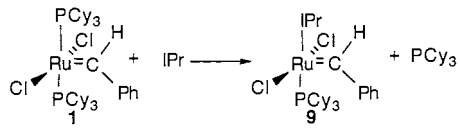


Fig. 2. ORTEP of $RuCl_2(=C(H)Ph)(PCy_3)(IPr)$ (**9**) with elipsoids drawn at 50% probability.

$RuCl_2(=C(H)Ph)(PCy_3)_2$ (**1**) reacts with IPr (**4**) in hexanes at 60°C to form $RuCl_2(=C(H)Ph)(PCy_3)(IPr)$ (**9**) as brown, air-stable microcrystals in moderate yield (Eq. (3)). Since the electron donating ability of IPr is similar to PCy_3, the driving force for the exchange reaction is small and the reaction does not take place at r.t. It is worth mentioning that even in the presence of excess IPr ligand, only one PCy_3 can be replaced.



(3)

The $^{31}P\{^1H\}$-NMR spectrum of **9** shows one singlet at 30.33 ppm due to one bound PCy_3 ligand. In the ^1H-NMR spectrum one can discern the relevant resonances for IPr as well as the very low field signal for the benzylidene proton at 20.04 ppm. The identity of this complex was further confirmed by a single-crystal X-ray diffraction study (Table 1). An ORTEP of **9** and selected metrical parameters are presented in Fig. 2 and Table 3.

The coordination geometry around the ruthenium center is that of a distorted square pyramid with Cl(1)–Ru–Cl(2) angle of 170.42(2)° which is nearly lin-

Table 2
Selected bond lengths (Å) and bond angles (°) for Cp*Ru(IPr)Cl (**6**), Cp*Ru(IMes)Cl (**7**) and Cp*Ru(PCy_3)Cl (**8**)

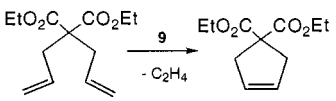
Complex	Steric parameters (A_L, A_H)	Ru–L	Ru–Cp*	Ru–Cl	C–Ru–Cl	C–Ru–Cp*	Cp*–Ru–Cl
6	150.7, 70.4	2.105	1.766	2.376	90.6	140.7	128.6
7	134.0, 137.6	2.086	1.754	2.371	89.32	141.5	129.2
8	115.8 [a]	2.383	1.771	2.378	91.2 [b]	138.9 [b]	129.9

[a] Phosphine cone angle.
[b] Replace C with P.

ear and close to the value for **3** (168.62°). The Ru–C(28) bond distance (1.817(3) Å) is shorter than that in **3** (1.838(3) Å) and **1** (1.851(21) Å). The other ruthenium carbene bond length, Ru–C(13), (2.088(2) Å) is longer than that of **3** (2.069(11) Å) which is in agreement with the difference in the reaction enthalpy between IMes and IPr. It is also much longer than that of Ru–C(28) and is in the range of ruthenium–carbon single bond distances. The isopropyl groups on the phenyl rings of the IPr ligand are pushed back indicating a fairly congested environment. This steric congestion may be at the origin of the longer than expected Ru–P bond distance in **9** (2.4554(7) vs. 2.419(3) Å in **3**).

3. Catalytic activity

The catalytic activity of **9** was tested by using the standard RCM substrate, diethyldiallylmalonate (Eq. (4)). When **9** is used as catalyst precursor ring closure is complete after 15 min at room temperature (r.t.). Under identical conditions, **3** and **1** show 92 and 85% conversion, respectively [6a].



(4)

We have already illustrated that the carbene complex **3** is much more thermally stable than the phosphine complex **1** (14 days vs. 1 h at 60°C) [6a]. When a solution of **9** is heated to 100°C in d_8-toluene under an inert atmosphere, signs of decomposition appear after 2 h. However, at lower temperatures (60°C) the complex is stable even after 2 weeks of continuous heating. The stability of **9** is closely related to that found for **3**.

4. Conclusion

In summary, we have shown that the nucleophilic carbene IPr acts as a phosphine mimic with reaction enthalpy similar to that of PCy_3 in the Cp*RuCl(L) system. The IPr ligand is much more sterically demanding than either IMes or PCy_3. It is capable of supporting catalysis in metathesis-active ruthenium systems. Owing to its large steric bulk, IPr ancillary ligand prevents/slows bimolecular carbene decomposition in the olefin metathesis 14-electron ruthenium intermediate, resulting in significant activity and thermal stability compared to phosphine containing catalysts.

Table 3
Selected bond lengths (Å) and bond angles (°) for $Cl_2Ru(=C(H)Ph)(PCy_3)(IPr)$ (**9**)

Ru–C(13)	2.088(2)	C(13)–Ru–Cl(2)	83.77(6)
Ru–Cl(1)	2.3822(7)	C(13)–Ru–P	164.60(7)
Ru–C(28)	1.817(3)	C(28)–Ru–Cl(2)	88.87(9)
C(28)–C(29)	1.478(4)	C(28)–Ru–Cl(1)	99.49(9)
Ru–P	2.4554(7)	C(28)–Ru–P	96.64(8)
Ru–Cl(2)	2.4008(7)	Cl(1)–Ru–Cl(2)	170.42(2)
C(28)–Ru–C(13)	97.56(10)	Cl(1)–Ru–P	93.06(2)

5. Experimental

5.1. General consideration

All manipulations involving organoruthenium complexes were performed under argon using standard high vacuum or Schlenk tube techniques, or in a MBraun glove box containing less than 1 ppm oxygen and water. Solvents were dried and distilled under argon before use employing standard drying agents [16]. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300 or 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction [17] or the enthalpy of solution of KCl in water [18]. The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described [19] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

5.2. NMR titrations

Prior to every set of calorimetric experiments, an accurately weighed amount (± 0.1 mg) of the organoruthenium complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF-d_8 was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by $^{31}P\{^1H\}$- and ^1H-NMR spectroscopy and the reactions were found to be rapid, clean and quantitative. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organometallic reactions investigated.

5.3. Calorimetric measurement for reaction between **5** and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr (**4**))

The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120°C, and then taken into the glove box. A 20–30 mg sample of $[Cp^*RuCl]_4$

was accurately weighed into the lower vessel, it was closed and sealed with 1.5 ml of mercury. Four ml of a stock solution of IPr [130 mg of IPr in 16 ml of THF] was added and the remainder of the cell was assembled, removed from the glove box and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organoruthenium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0°C (about 2 h), the reaction was initiated by inverting the calorimeter. At the end of the reaction, the vessels were removed from the calorimeter, taken into the glove box, opened, and analyzed using ^{1}H-NMR spectroscopy. Conversion to RuCp*(IPr)Cl was found to be quantitative under these reaction conditions. The enthalpy of reaction, -44.5 ± 0.4 kcal mol^{-1} represents the average of five individual calorimetric determinations.

5.4. Synthesis

The compounds $RuCl_2(=C(H)Ph)(PCy_3)_2$ (**1**) [4b], $[Cp^*RuCl]_4$ [12] (**5**) and $Cp^*Ru(PCy_3)Cl$ (**8**) [13] were synthesized according to literature procedures. Experimental synthetic procedures, leading to the isolation of unreported compounds are described below.

5.4.1. Stepwise synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (4)

5.4.1.1. Synthesis of bis(2,6-diisopropylphenyl)diazabutadiene [10]. A 250 ml round-bottom flask was charged with 100 g (0.56 mol) of 2,6-diisopropylaniline, 31.5 ml (0.28 mol, 40% in water) of glyoxal and 500 ml of absolute ethanol. A few drops of formic acid were added as catalyst. The color of the reaction mixture turned from colorless to yellow immediately, and a yellow precipitate appeared after a few hours. The reaction mixture was stirred for two days and the yellow solid was collected by filtration and washed with cold methanol to afford the analytically pure compound. Yield = 81.74 g (77.5%) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.28 (d, $J = 7.6$ Hz, 24H, $CH(CH_3)_2$, 3.03 (sep, $J = 6.4$ Hz, 4H, $CH(CH_3)_2$), 7.27 (m, 6H, $(CH(CH_3)_2)_2$–C_6H_3), 8.19 (s, 2H, NC*H*).

5.5. Synthesis of IPr·HCl

To a solution of bis (2,6-diisopropylphenyl)diazabutadiene (25 g, 66 mmol) in toluene (500 ml) was aded 2.0 g (66 mmol) of paraformaldehyde in solid form. The reaction mixture was heated to 100°C till most of paraformaldehyde was dissolved. It was then cooled to 40°C and 16.5 ml of HCl (66 mmol, 4 M in dioxane) was syringed in. The reaction mixture was heated to 70°C for 5 h during which time the color of the reaction mixture turned brown and a white precipitate appeared. It was then allowed to stir at r.t. for 36 h. The off-white precipitate was collected by filtration and washed with THF. Yield = 13.1 g (47%) ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 1.24 (d, $J = 7.2$ Hz, 12 H, $CH(CH_3)_2$), 1.27 (d, $J = 7.2$ Hz, 12 H, $CH(CH_3)_2$), 2.42 (sep, $J = 6.8$ Hz, 4 H, $CH(CH_3)_2$), 7.18 (t, $J = 7.2$ Hz, 2 H, p-C_6H_3), 7.4 (m, 4 H, m-C_6H_3), 7.80 (s, 2 H, NC*H*), 11.00 (s, 1 H, NC(*H*Cl)N).

5.6. Synthesis of IPr (4)

To a mixture of IPr.HCl (6.5 g, 15 mmol) and KO^{t}Bu (1.78 g, 16 mmol) was added THF (60 ml) at r.t. The color turned brown immediately and a white precipitate was formed. The reaction mixture was stirred for 4 h, the solvent was removed in vacuo and the residue was taken up in hot toluene (70°C). The reaction mixture was then filtered through Celite. Evaporation of the volatiles afforded a brown solid. Yield = 4.6 g (79%). ^{1}H-NMR (400 MHz, C_6D_6): δ 1.13 (d, $J = 9.2$ Hz, 12 H, $CH(CH_3)_2$), 1.23 (d, $J = 9.2$ Hz, 12 H, $CH(CH_3)_2$), 2.91 (sep, $J = 9.2$ Hz, 4 H, $CH(CH_3)_2$), 6.57 (s, 2 H, NC*H*), 7.11 (m, 4 H, m-C_6H_3), 7.22 (m, 2 H, p-C_6H_3).

5.7. Synthesis of Cp*Ru(IPr)Cl (6)

A 50 ml flask was charged with **5** (100 mg, 0.092 mmol), IPr (140 mg, 0.364 mmol) and THF (10 ml). The clear deep blue solution was stirred at r.t. for 2 h after which the solvent was removed under vacuum. The residue was dissolved into 20 ml of warm hexanes, filtered and the resulting solution was slowly cooled to −78°C. The dark blue microcrystals were isolated by cold filtration, then washed with hexanes and finally dried under vacuum. Yield: 180 mg, 75%. ^{1}H-NMR (400 MHz, C_6D_6): δ 1.0 (br., 12 H, $CH(CH_3)_2$), 1.20 (s, 15 H, Cp*), 1.50 (br., 12 H, $CH(CH_3)_2$), 3.40 (sep, $J = 6.8$ Hz, 4 H, $CH(CH_3)_2$), 6.58 (s, 2 H, NC*H*C*H*N), 7.2–7.3 (m, 6 H, C_6H_4–$(CH(CH_3)_2)_2$). Calc. for $C_{49}H_{51}ClN_2Ru$: C, 67.30; H, 7.78; N, 4.24. Found: C, 67.00; H, 7.55; N, 4.25%.

5.8. Synthesis of $RuCl_2(=C(H)Ph)(PCy_3)$(IPr) (9)

To a slurry of IPr (110 mg, 0.282 mmol) in hexanes (20 ml) was added **1** (257 mg, 0.257 mmol). The reaction mixture was heated at 60°C for 3 h and then cooled to r.t. The volume of the solvent was then reduced to half and the reaction mixture was cooled to −78°C. Filtration of the pink precipitate, subsequent washing with cold hexanes (2×10 ml) and drying afforded the pink microcrystalline solid in 79% (190 mg) yield. ^{1}H-NMR (400 MHz, C_6D_6): δ 20.04 (s, 1 H,

Ru–C*H*), 7.30 (br, 2 H, *o*-C_6H_5), 7.21 (m, 1 H, *p*-C_6H_5), 7.03 (t, $J = 6.4$ Hz, 2 H, *p*-$C_6H_3(CH(CH_3)_2)$, 6.76 (br., 4 H, *m*-$C_6H_3(CH(CH_3)_2)$, 6.68 (s, 2 H, NC*H*C*H*N), 6.65 (m, 2 H, *m*-C_6H_5), 3.87(sep, $J = 6.8$ Hz, 1 H, $C_6H_3(CH(CH_3)_2)$, 3.43 (m, 1 H, $C_6H_3(CH(CH_3)_2)$, 2.40 (m, 2 H, $C_6H_3(CH(CH_3)_2)$, 1.64 (d, $J = 6.8$ Hz, 6 H, $C_6H_3(CH(CH_3)_2)$, (d, 6 H, $C_6H_3(CH(CH_3)_2)$, 1.01 (d, 6 H, $C_6H_3(CH(CH_3)_2)$, 0.98 (d, 6 H, $C_6H_3(CH(CH_3)_2)$, 1.49, 1.16–1.06, 0.90 (all m PCy_3). $^{31}P\{^1H\}$-NMR (400 MHz, C_6D_6): δ 30.33 (s). Anal. Calc. for $C_{52}H_{75}Cl_2N_2PRu$: C, 67.08; H, 8.12; N, 3.01. Found: C, 67.37; H, 8.34; N, 2.85%.

5.9. Ring closing metathesis procedure

In the dry box catalyst precursor (5 mol%) was accurately weighed in a Wilmad screw-capped NMR tube and dissolved in CD_2Cl_2 (0.4 ml). Diethyldiallyl malonate (0.02 g, 0.1 mmol) was added to the solution and the sealed NMR tube was kept at r.t. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks in the proton NMR spectrum. Product formation was confirmed by comparison with literature NMR data [4d].

6. X-ray diffraction measurements

A single crystal of **6** or **9** was coated with paratone oil and then sealed in a glass capillary tube. The X-ray data were collected at low temperature using graphite-monochromated Mo–K_α radiation on a Siemens P4 automated X-ray diffractometer. The structure was solved using direct methods (SHELXS-86) and refined by full matrix least-square techniques. Initial fractional coordinates for the Ru atom were determined by heavy-atom methods, and the remaining non-hydrogen atoms were located by successive difference Fourier calculations, which were performed with algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Crystallographic data can be found in the Table 1, and selected bond distances and bond angles are presented in Tables 2 and 3.

6.1. Supplementary material

Details of crystal structure determination for **6** and **9** (PDF).

Acknowledgements

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