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Reactions of $[Cp^*Ru(H_2O)(NBD)]^+$ with alkynes

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Formal $[2+2+2]$ addition reactions of $[Cp^*Ru(H_2O)(NBD)]BF_4$ (NBD = norbornadiene) with $PhC{\equiv}CR$ (R = H, COOEt) give $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C_9H_8R)]$ BF_4 (1a, R = H; 2a, R = COOEt). Treatment of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with $PhC{\equiv}C{-}C{\equiv}CPh$ does not give $[2+2+2]$ addition product, but $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C{\equiv}C{-}C{\equiv}CPh)]$ BF_4(3a). Treatment of 1a, 2a, 3a with $NaBPh_4$ affords $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C_9H_8R)]$ BPh_4 (1b, R = H; 2b, R = COOEt) and $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C{\equiv}C{-}C{\equiv}CPh)]$ BPh_4(3b). The structures of 1b, 2b and 3b were determined by X-ray crystallography. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: $[2+2+2]$ addition reaction; norbornadiene; ruthenium; alkyne

INTRODUCTION

The discovery and development of novel cycloaddition reactions continues to attract considerable attention.[1–15] Metal-catalyzed cycloaddition reactions are of particular interest due to the mild reaction conditions and unique reactivity and selectivity imparted by the metal and its ligands.[16–19] The homo Diels–Alder reaction is a six-electron $[2+2+2]$ process which occurs under thermal and metal-catalyzed conditions and generates novel, strained polycyclic compounds.[20–26] It is of interest to see if these ligands could also undergo mechanistically related organometallic reactions. Such a comparative study may help to develop the chemistry or reactions on organometallic compounds. We have studied the $[2+2+2]$ homo-Diels–Alder cycloaddition reaction of $[Cp^*Ru(H_2O)(NBD)]$ BF_4 with $RC{\equiv}CPh$ (R = Me, Ph).[27,28] In this work, we continue to study the coupling reactions of $PhC{\equiv}CR$ (R = H, COOEt) and $PhC{\equiv}C{-}C{\equiv}CPh$ with norbornadiene (NBD) mediated by $[Cp^*Ru]^+$.

RESULTS AND DISCUSSION

Reactions of $[Cp^*Ru(H_2O)(NBD)]$ BF_4 with $PhC{\equiv}CR$ (R = H, COOEt)

It was found that $[Cp^*Ru(H_2O)(NBD)]$ BF_4 in dichloromethane rapidly reacted with alkynes $PhC{\equiv}CR$ (R = H, COOEt) to give **1a** and **2a**, respectively. These complexes can be converted to **1b** and **2b** on treatment with $NaBPh_4$ *in situ*; **1b** and **2b** have been characterized by ^1H NMR elemental analysis. It is probably not surprising that formation of complexes **1a** and **2a,** as catalytic $[2+2+2]$ homo-Diels–Alder cycloadditions of $RC{\equiv}CR'$ to NBD has been achieved with complexes such as $[Co(acac)_3]/PR_3/Et_2AlCl$.[29] Homo-Diels–Alder cycloadditions of $RC{\equiv}CR'$ to COD could also be effected using ruthenium complexes such as $(\eta^6\text{-}C_9H_7)RuCl(COD)$ and CpRuCl(COD).[30–33] The reaction mechanism has been suggested and supported by theoretical calculations.[27,28] The structures of **1b** and **2b** have also been confirmed by X-ray diffraction. As indicated in Figs 1 and 2, a $PhC{\equiv}CR$ (R = H, COOEt) molecule is added to the NBD ligand and the aryl group is η^6-coordinated to ruthenium. The structure of **1b** and **2b** is similar to that of $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C_9H_8R)]BF_4$ (R = Me, Ph).[27,28] The molecule contains two fragments: $[Cp^*Ru(\eta^6\text{-arene})]$ and tetracyclic deltacyclenes.[25]

Reactions of $[Cp^*Ru(H_2O)(NBD)]$ with $PhC{\equiv}C{-}C{\equiv}CPh$

The above results prompted us to study the reaction of $[Cp^*Ru(H_2O)(NBD)]$ with bifunctional molecules 1,4-diphenylbutadiyne. It was interesting that $[Cp^*Ru(H_2O)$

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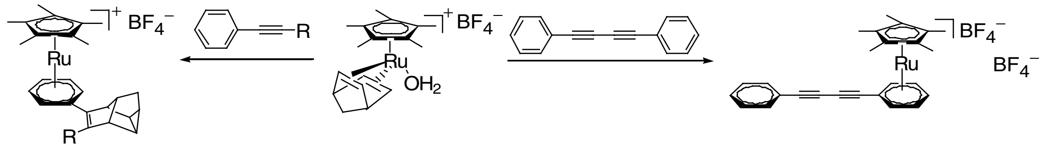

1a R=H
2a R=COOEt

3a

Scheme 1. Reaction of complex [Cp*Ru(H$_2$O)(NBD)]BF$_4$ with alkynes.

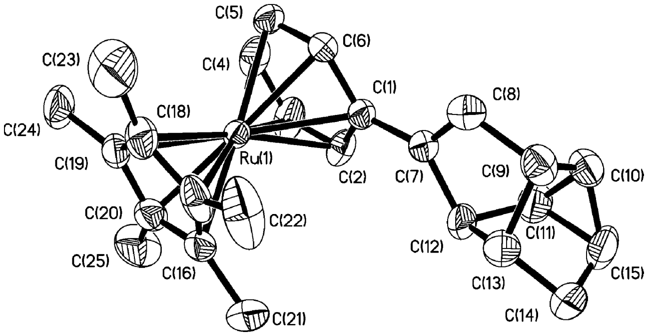

Figure 1. ORTEP diagram of **1b**. The hydrogen atoms and counteranion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) = 2.256(3); Ru(1)–C(4) = 2.217(4); Ru(1)–C(5) = 2.221(3); Ru(1)–C(6) = 2.220(3); Ru(1)–C(16) = 2.173(3); Ru(1)–C(17) = 2.161(3); Ru(1)–C(20) = 2.176(3); C(2)–C(3) = 1.409(5); C(7)–C(8) = 1.330(4); C(16)–C(17) = 1.416(6); C(16)–C(21) = 1.510(6); C(3)–Ru(1)–C(4) = 37.07(15); C(4)–Ru(1)–C(5) = 36.23(15); C(18)–Ru(1)–C(19) = 38.11(14); C(1)–C(7)–C(12) = 125.7(3); C(7)–C(8)–C(9) = 108.8(3).

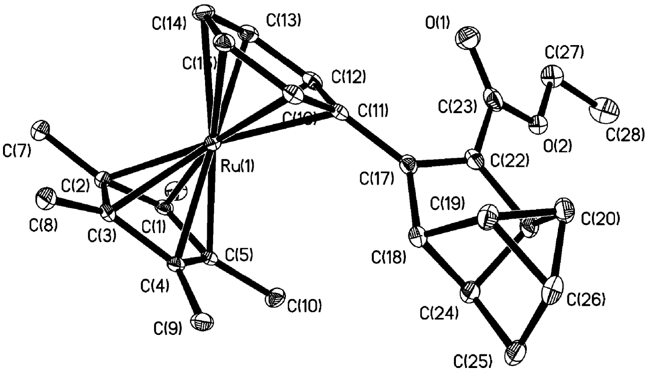

Figure 2. ORTEP diagram of **2b**. The hydrogen atoms and counteranion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) = 2.176(3); Ru(1)–C(11) = 2.248(2); Ru(1)–C(12) = 2.213(3); Ru(1)–C(16) = 2.205(3); C(1)–C(2) = 1.427(3); C(1)–C(6) = 1.489(4); C(11)–C(12) = 1.413(4); C(12)–C(13) = 1.411(4); C(13)–C(14) = 1.398(4); C(17)–C(18) = 1.509(4); C(17)–C(22) = 1.353(4); C(2)–Ru(1)–C(1) = 38.31(9); C(3)–Ru(1)–C(2) = 38.35(10); C(12)–Ru(1)–C(11) = 36.92(9); C(15)–Ru(1)–C(14) = 37.00(9); C(17)–C(22)–C(23) = 127.1(3); C(22)–C(17)–C(18) = 107.3(2).

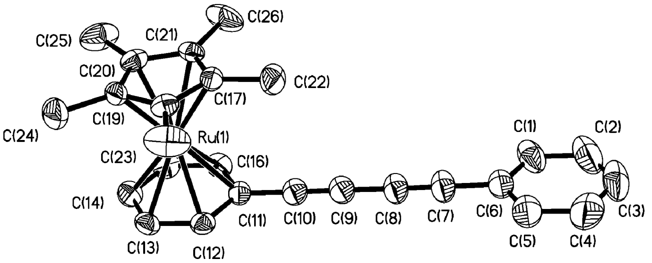

Figure 3. ORTEP diagram of **3b**. The hydrogen atoms and counteranion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–C(11) = 2.216(5); Ru(1)–C(17) = 2.187(4); C(1)–C(2) = 1.382(11); C(7)–C(8) = 1.176(7); C(9)–C(10) = 1.193(7); C(12)–C(13) = 1.396(7); C(17)–C(18) = 1.400(6); C(17)–C(22) = 1.511(7); C(12)–Ru(1)–C(11) = 37.4(2); C(19)–Ru(1)–C(18) = 37.83(18).

(NBD)] BF$_4$ reacted with PhC≡C–C≡CPh to give **3a; 3a** can be converted to **3b**. Unlike **1b** and **2b, 3b** contains no tetracyclic deltacyclenes, but only a [Cp*Ru(η^6-arene)]$^+$ fragment. Obviously, the product was not obtained by homo-Diels–Alder cycloadditions, although catalytic [2 + 2 + 2] homo-Diels–Alder cycloaddition of PhC≡C–C≡CPh to NBD has been achieved with cobalt complex.[20] The first [Cp*Ru(η^6-C$_6$H$_6$)] fragment was prepared as early as 1972,[34] and can be obtained from reactant [Cp*Ru(MeCN)$_3$]$^+$ and [Cp*Ru(OMe)]$_2$. [Cp*Ru(H$_2$O)(NBD)] can be considered as a new reactant to synthesize [Cp*Ru(η^6-arene)]$^+$ fragment. Compound **3b** was fully characterized by elemental analysis, ^{1}H NMR and X-ray diffraction analysis. The ^{1}H NMR spectrum showed multiple peaks from 7.40 to 7.60 ppm for the protons of the free phenyl ring and multiple peaks from 5.40 to 5.65 ppm for the protons of the phenyl ring π-coordination to the [Cp*Ru] fragment. The molecular structure of **3b** was unambiguously confirmed by single-crystal X-ray study. The molecular diagram of **3b** is shown in Fig. 3; **3b** consists of one [Cp*Ru] unit bound to one phenyl ring of 1,4-diphenylbutadiyne in an η^6-mode. The bonding is similar to the structure of [Cp*Ru(η^6-arene)]$^+$ derivatives **1b** and **2b**. The average C–C bond distance of the free phenyl ring is 1.368(11) Å. It is shorter than that of the bonded phenyl ring (the average C–C bond distance is 1.408Å). The C(7)≡C(8) bond distance is 1.176(7) Å. Clearly the most interesting feature of this structure is that the C(9)≡C(10) bond distance [1.193(7) Å] is longer than that of C(7)≡C(8) bond.

CONCLUSION

In summary, we have demonstrated that reactions of $[Cp^*Ru(H_2O)(NBD)]^+$ with PhC≡CR(R = H, COOEt) lead to formal [2 + 2 + 2] cycloaddition between the substrates and the coordinated NBD. While a similar reaction is not observed for the reaction with PhC≡C–C≡CPh, the $[Cp^*Ru(\eta^6\text{-arene})]^+$ fragment was obtained without the [2 + 2 + 2] cycloaddition reaction of NBD with C≡C bond.

EXPERMENTAL SECTION

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques. The starting materials $[Cp^*Ru(H_2O)(NBD)]BF_4$[35] and 1,4-diphenylbutadiyne[36] were prepared according to literature methods. All other chemicals were obtained from commercial sources. ^1H NMR were collected on an American Varian Mercury Plus 400 spectrometer (400 MHz). ^1H NMR chemical shifts are relative to TMS. Elemental analyses (C–H–N) were performed on an Elementar Vario EL analyzer.

Reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with PhC≡CH; preparation of $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C_9H_9)]\ BF_4$ (1a) and $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C_9H_9)]\ BPh_4$ (1b)

A mixture of $[Cp^*(H_2O)(NBD)]\ BF_4$ (0.5 g, 1.15 mmol) and phenylacetylene (0.204 g, 2.0 mmol) in acetone (40 ml) was stirred at room temperature for 30 min. The volume of reaction mixture was reduced to 5 ml under vaccum, and diethyl ether was added to give an off-white solid. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum; **1a** was obtained. The mixture of **1a** and $NaBPh_4$ (0.5 g, 1.46 mmol) in methanol (30 ml) was stirred for 30 min to give a gray solid. The solid was collected by filtration, washed with methanol and diethyl ether, and dried under vacuum; 0.29 g (34%) of **1b** was produced. **1b** ^1H NMR (400 MHz, $CDCl_3$): δ 1.30–1.60 (m, 4H, CH), 1.70 (s, 15H, Cp*), 1.80 (m, 1H, CH), 2.01 (m, 1H, CH), 2.59 (m, 1H, CH), 2.73 (m, 1H, CH), 4.99–5.29(m, 5H, Ph), 6.38 (d, $J = 2.8$ Hz, 1H, C=CH), 6.86 (m, 4H, BPh), 7.00 (m, 8H, BPh), 7.38 (m, 8H, BPh). Anal. calcd for $C_{49}H_{49}BRu$: C, 78.49; H, 6.59. Found: C, 78.30; H, 6.60.

Reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with $PhC{\equiv}CCOOC_2H_5$; Preparation of $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C_9H_8COOC_2H_5)]\ BF_4$ (2a) and $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C_9H_8\ COOC_2H_5)]\ BPh_4$ (2b)

Similar to the preparation of **1a** and **1b**, when 0.348 g (2.0 mmol) of ethyl phenylpropiolate was used instead of

Table 1. Crystal data and structure refinements for **1b, 2b** and **3b**

	1b	**2b**	**3b**
Empirical formula	$C_{49}\ H_{49}\ B\ Ru$	$C_{52}\ H_{53}\ B\ O_2\ Ru$	$C_{51}\ H_{47}\ B\ Cl_2\ Ru$
Formula mass	686	821.82	842.67
Temperature (K)	293(2)	100(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c	C2/c
a (Å)	11.0605(7)	11.2733(9)	10.6612(6)
b (Å)	18.4876(12)	9.7925(8)	21.1970(13)
c (Å)	19.0938(13)	36.921(3)	20.0278(12)
α (deg)	90	90	90
β (deg)	90	93.652	104.99
γ (deg)	90	90	90
V (Å^3)	3904.3(4)	4067.5(6)	4372.0(4)
Z	4	4	4
D_{calcd} (mg/mm^3)	1.276	1.342	1.28
μ (mm^{-1})	0.434	0.427	0.514
F(000)	1568	1720	1744
Refections collected	20955	20900	28429
Independent reflection	7576	7059	9956
R_{int}	0.0302	0.0441	0.0644
R	0.0491	0.0349	0.0668
R_w	0.1096	0.0722	0.1502
Goodness-of-fit on F^2	1.124	1.001	1.007

phenylacetylene, 0.652 g (69%) of **2b** was obtained. **2b** ^1H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, $J = 5.4$ Hz, 3H, CH_3), 1.60–1.96 (m, 5H, CH), 1.88 (s, 15H, Cp*), 2.07 (m, 1H, CH), 2.87 (m, 1H, CH), 3.14 (m, 1H, CH), 4.12–4.16 (m, 2H, CH_2), 5.72–6.43 (m, 5H, Ph). Anal. calcd for $C_{52}H_{53}BO_2Ru$: C, 75.99; H, 6.50. Found: C, 75.86; H, 6.60.

Reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with $PhC{\equiv}C{-}C{\equiv}CPh$; Preparation of $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C{\equiv}C{-}C{\equiv}CPh)]\ BF_4$ (3a) and $[Cp^*Ru(\eta^6\text{-}C_6H_5{-}C{\equiv}C{-}C{\equiv}CPh)]\ BPh_4$ (3b)

Similar to the preparation of **1a** and **1b**, when 0.202 g (1.0 mmol) of 1,4-diphenylbutadiyne was used instead of phenylacetylene, 0.270 g (31%) of **3b** was obtained. **3b** ^1H NMR (400 MHz, CD_2Cl_2): δ 1.86 (s, 15H, Cp*), 5.40–5.65(m, 5H, Ph), 6.90 (m, 4H, BPh), 7.03 (m, 8H, BPh), 7.34 (m, 8H, BPh), 7.40–7.60 (m, 5H, Ph). Anal. calcd for $C_{50}H_{45}BRu$: C, 79.25; H, 5.99. Found: C, 79.10; H, 5.74.

X-ray structure determination

Crystals of **1b, 2b** and **3b** for X-ray diffraction were grown by the slow diffusion of hexane into a solution of **1b, 2b** or **3b** in CH_2Cl_2 at room temperature. A crystal was mounted on a glass fiber, and the diffraction intensity data were collected on a Bruker CCD 4 K diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption corrections were performed using SAINT version 6.45 and SADABS version 2.03. Structure solution and refinement were performed using the SHELXTL version 6.14 software package. The space group $P_4(2)/m$ was determined base on systematic absences and intensity statistics. All non-hydrogen atoms were refined anisotropic. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Further crystallographic details were summarized in Table 1.

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