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Synthesis and characterization of trimetallic complexes with a borazine core

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Abstract

Treatment of $[Cp^*Ru(dppe)]^+$ with B-triethynyl-*N*-trimethylborazine and piperidine produces the trimetallic complex $[Cp^*Ru(dppe)(C{\equiv}C)]_3B_3N_3Me_3$, the structure of which has been confirmed by X-ray diffraction. Reaction of $RuHCl(CO)(PPh_3)_3$ with B-triethynyl-*N*-trimethylborazine produces the trimetallic complex $[RuCl(CO)(PPh_3)_2(CH{=}CH)]_3B_3N_3Me_3$.

Keywords: Borazine; Ruthenium; Acetylide; Hydride

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1. Introduction

1,3,5-Triethynylbenzene has been used widely to construct trimetallic and polymetallic organometallic compounds [1–13]. These compounds are interesting because they show non-linear optical and luminescent properties. In this regard, it would be interesting to prepare trimetallic and polymetallic complexes based on related triethynyl substituted heterocycles such as borazine and triazine, in order to see if materials with improved properties could be obtained. The uses of these cores will create materials of different electronic structures, which will influence optical properties. However, such an approach has not been previously reported. In this work, we wish to report the first examples of trimetallic complexes based on B-triethynyl-*N*-trimethylborazine.

2. Results and discussion

2.1. Synthesis and characterization of $[Cp^*Ru(dppe)(C{\equiv}C)]_3B_3N_3Me_3$

A number of complexes of the type $[L_nM(C{\equiv}C)]_3$-C_6H_3 have been reported, where M = Fe [1], Ru [2], Rh [6], Ir [7], Pd [8,9], Pt [9–11] and Au [12]. We have tried to prepare analogous complexes containing a borazine core. The starting material B-triethynyl-*N*-trimethylborazine (**1**) was prepared from the reaction of B-trichloro-*N*-trimethylborazine with $HC{\equiv}CMgBr$ in THF [14]. Treatment of $[Cp^*Ru(dppe)]^+$ (generated in situ by reacting $Cp^*RuCl(dppe)$ (**2**) with $TlPF_6$) with **1**, followed by piperidine produced the trimetallic complex $[Cp^*Ru(dppe)(C{\equiv}C)]_3B_3N_3Me_3$ (**4**), which was isolated as a yellow solid (Scheme 1). Reactions of $[CpRu(PR_3)_2]^+$ with $HC{\equiv}CR'$ are known to give vinylidene complexes $[CpRu({=}C{=}CHR')(PR_3)_2]^+$ which can be deprotonated to give $CpRu(C{\equiv}CR')(PR_3)_2$ [15]. In our system, **4** could also be formed through the intermediate $\{[Cp^*Ru(dppe)({=}C{=}CH]_3B_3N_3Me_3\}^{3+}$, although we have not been able to isolate the intermediate in pure form.

Complex **4** has been characterized by NMR, MS and IR spectroscopy and elemental analysis. In particular,

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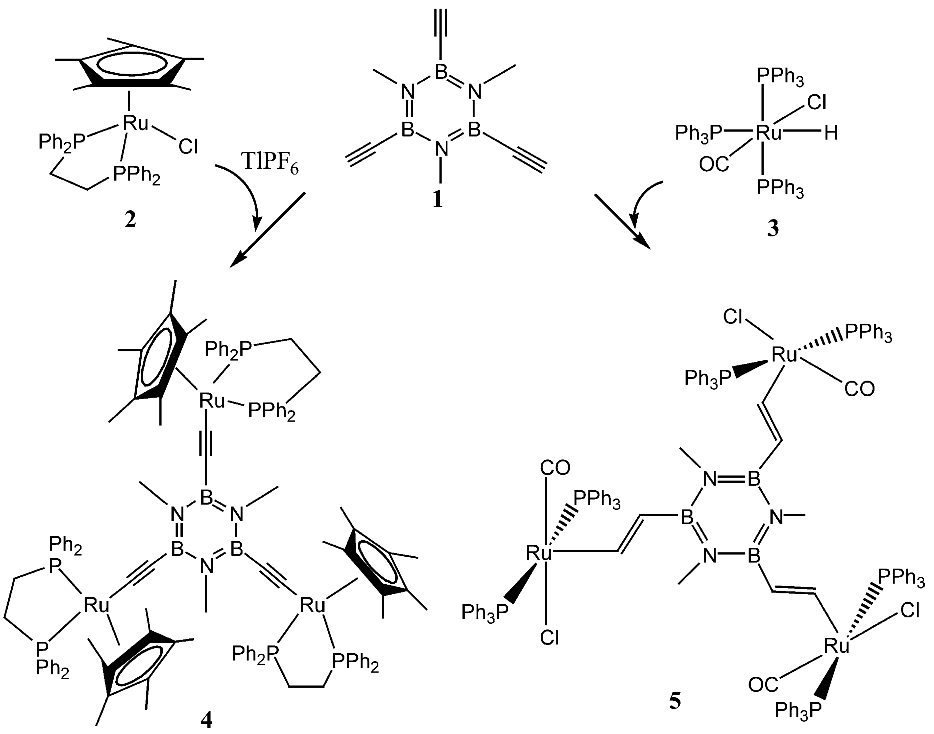

Scheme 1.

the $^{31}P\{^1H\}$-NMR spectrum (in CD_2Cl_2) showed a singlet at 80.5 ppm. The IR spectrum showed a medium band at 2017.9 cm^{-1} assignable to $\upsilon(C\equiv C)$. In the $^{13}C\{^1H\}$-NMR spectrum (in CD_2Cl_2), the $RuC\equiv CB$ signals were observed at 148.0 ($Ru\mathit{C}\equiv CB$) and 117.8 ($RuC\equiv \mathit{C}B$) ppm. The chemical shift of $Ru\mathit{C}\equiv$ (148.0 ppm) is significantly down field compared with that of $H\mathit{C}\equiv$ in **1**. The appearance of the α carbons signals of ruthenium acetylides in such a down field region has been noted in other ruthenium complexes, for example, $[RuCl(dppe)_2(C\equiv CC_6H_4C\equiv C)]_3C_6H_3$ ($\delta(RuC) = 132.95$ ppm), $[Ru(C\equiv CSiMe_3)(dppe)_2(C\equiv CC_6H_4C\equiv C)]_3C_6H_3$ ($\delta(RuC) = 153.36$ and 140.98 ppm) [5].

The structure of **4** has been confirmed by X-ray diffraction. A view of the molecular structure is shown in Fig. 1 and selected bond distances and angles are given in Table 2. The structure can be described as three three-legged piano stools bridged with the ligand $B_3N_3Me_3(C\equiv C)_3$. As expected, the $RuC\equiv C$ units are essentially linear with RuCC angles in the range of 173.7(7)–176.2(7)°. The Ru–C (average at 2.007(7) Å) and C≡C (average 1.227(9) Å) bond distances are close or similar to the reported values of ruthenium acetylide complexes $CpRu(C\equiv CR)L_2$ [16–21]. For example, the Ru–C bond distances of $CpRu(C\equiv CPh)(dppe)$ [16], $CpRu(C\equiv CPh)(PPh_3)_2$ [16] and $CpRu(C\equiv CC_6H_4\text{-}4\text{-}NO_2)(PPh_3)_2$ [17] are 2.009(3), 2.017(5) and 1.989(7) Å, respectively; the C≡C bond distances of $CpRu(C\equiv CPh)(dppe)$ [16], $CpRu(C\equiv CPh)(PPh_3)_2$ [16], and $CpRu(C\equiv CC_6H_4\text{-}4\text{-}NO_2)(PPh_3)_2$ [17] are 1.204(5), 1.214(7) and 1.224(10) Å, respectively.

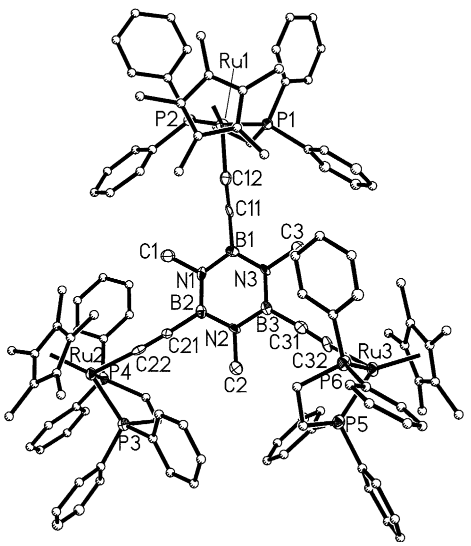

Fig. 1. The molecular structure of **4**. The solvents and hydrogen atoms are omitted for clarity.

Reported complexes closely related to **4** are $[CpRu(PPh_3)_2(C\equiv C)]_3C_6H_3$ [2] and $[Cp^*Fe(dppe)C\equiv C]_3C_6H_3$ [1], which were reported by groups of Long and Lapinte, respectively. More extended ruthenium acetylide complexes containing 1,3,5-$C_6H_3(C\equiv C)_3$ core have been recently reported by Dixneuf's group [5] and Humphrey's group [4].

2.2. Synthesis and characterization of $[RuCl(CO)(PPh_3)_2(CH{=}CH)]_3B_3N_3Me_3$

Reactions of $RuHCl(CO)(PPh_3)_3$ (**3**) with HC≡CR are known to give $RuCl((E){-}CH{=}CHR)(CO)(PPh_3)_2$ [22,23]. The reaction has been used to prepare bimetallic complexes such as $[RuCl(CO)(PPh_3)_2]_2$(μ-CH=CH–Ar–CH=CH) [24] and $[RuCl(CO)(PPh_3)_2]_2$(μ-CH=CH–CH=CH) [25]. Thus it is expected that reaction of **3** with B-triethynyl-*N*-trimethylborazine (**1**) will produce the trimetallic complex $[RuCl(CO)(PPh_3)_2(CH{=}CH)]_3B_3N_3Me_3$. The insertion reactions of **3** with simple terminal acetylenes usually occur rapidly at room temperature. However, it is found that it is necessary to reflux the mixture of **1** and excess **3** in CH_2Cl_2 for 60 h in order to ensure that all the three acetylenic groups are reacted. Pure sample of **5** can be obtained by repeated recrystallization of the product from CH_2Cl_2–hexane. When a mixture of **1** and three equivalents of **3** was stirred at room temperature for several hours or a day, a mixture of species showing ^{31}P signals around 30 ppm were produced. The chemical shifts are typical of $RuCl((E){-}CH{=}CHR)(CO)(PPh_3)_2$ [25]. Thus a mixture of mono, di- and tri-inserted products may be produced when the reaction was carried out at room temperature. Attempts to obtain pure products from the mixture were unsuccessful.

Compound **5** has been characterized by NMR, IR and elemental analysis. The $^{31}P\{^1H\}$-NMR spectrum in CD_2Cl_2 showed a singlet at 30.3 ppm, which is typical for $RuCl((E){-}CH{=}CHR)(CO)(PPh_3)_2$ [25] The ^1H-NMR spectrum in CD_2Cl_2 displayed the Ru–CH signal at 9.04 ppm and the β-CH signal at 6.28 ppm with $^2J(HH)$ coupling constant of 12.6 Hz. The magnitude of the coupling constant indicates that the two vinylic protons are in *trans* geometry and that the acetylene is *cis* inserted into the Ru–H bond. The N–CH_3 signal was observed at 2.89 ppm in the ^1H-NMR spectrum. Monomeric complexes $RuCl(RC{=}CHR')(CO)(PPh_3)_2$ are known to adopt a distorted trigonal-bipyramidal geometry around ruthenium with the two PPh_3 ligands in the apical positions [22]. Thus it is reasonable to assume that complex **5** has a similar geometry around ruthenium.

3. Experimental

All manipulations were carried out at room temperature (r.t.) under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane). The starting materials $RuHCl(CO)(PPh_3)_3$ [26], Cp*RuCl(dppe) [27] and B-triethynyl-*N*-trimethylborazine [14] were prepared according to literature methods. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ, USA). ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). $^{11}B\{^1H\}$-NMR spectra were collected on a JOEL-EX400 spectrometer (400 MHz). ^1H- and ^{13}C-NMR chemical shifts are relative to TMS, and ^{31}P-NMR chemical shifts are relative to 85% H_3PO_4. ^{11}B-NMR chemical shifts are relative to $BF_3 \cdot MeOH$.

3.1. $[Cp^*Ru(dppe)(C{\equiv}C)]_3B_3N_3Me_3$ (**4**)

A mixture of Cp*RuCl(dppe) (435 mg, 0.649 mmol) and $TlPF_6$ (220 mg, 0.640 mmol) in THF (10 ml) was stirred at r.t. for 2 h to give an orange solution with white suspension. Then a solution of B-triethynyl-*N*-trimethylborazine (31.1 mg, 0.16 mmol) in THF (5 ml) was added to the reaction flask. After the reaction mixture was stirred for 3 h, piperidine (0.2 ml) was added. The mixture was stirred for further 30 min. The solvent was then removed under vacuum and the residue was washed with methanol until the filtrate was colorless. The solid was re-dissolved in CH_2Cl_2 (15 ml) and filtered through celite. The CH_2Cl_2 was removed under vacuum to give a yellow solid, which was washed with methanol and dried. Yield, 180 mg, 54%. Analytically pure sample of **4** was obtained by flash chromatograph on an Al_2O_3 column with benzene as the eluent (the first fraction was collected). $^{31}P\{^1H\}$-NMR (121.5 MHz, CD_2Cl_2): δ 80.5 (s). $^{11}B\{^1H\}$-NMR (128.15 MHz, CD_2Cl_2): δ 27 (br). ^1H-NMR (300.13 MHz, CD_2Cl_2): δ 7.07–7.74 (m, 60 H, Ph), 2.82 (m, 6 H, PC*H*H), 2.17 (m, 6 H, PCH*H*), 2.11 (s, 9 H, NCH_3), 1.53 (s, 45 H, C_5Me_5). $^{13}C\{^1H\}$-NMR (75.48 Hz, CD_2Cl_2): δ 148.0 (t, $J(PC) = 23.6$ Hz, RuC≡), 147.7–126.8 (m, Ph), 117.8 (br s, BC≡), 92.3 (d, $J(PC) = 2.1$ Hz, C_5Me_5), 35.9 (NCH_3), 28.9 (t, $J(PC) = 23.4$ Hz, PCH_2), 9.8 (C_5Me_5). IR (KBr, cm^{-1}): 2017.9 (m, υ(C≡C)). Anal. Calc. for $C_{117}H_{126}B_3N_3P_6Ru_3$: C, 67.05; H, 6.06; N, 2.00. Found: C, 66.84; H, 5.97; N, 2.01%. FABMS: *m*/*z* Calc. 2095.8. Found 2095.6.

3.2. $[RuCl(CO)(PPh_3)_2(CH{=}CH)]_3B_3N_3Me_3$ (**5**)

A mixture of B-triethynyl-*N*-trimethylborazine (72 mg, 0.37 mmol) and $RuHCl(CO)(PPh_3)_3$ (1.15 g, 1.21 mmol) in CH_2Cl_2 (15 ml) was refluxed under nitrogen for 60 h to give a brown solution. The mixture was filtered after the reaction mixture was cooled to r.t. and the residue was washed with CH_2Cl_2 (10 ml). The solvent of the filtrate was removed completely under vacuum. The crude product was recrystallized from CH_2Cl_2–hexane (1:4) four times and dried under vacuum to give an orange powder. Yield: 260 mg, 31%. $^{31}P\{^1H\}$-NMR (121.5 MHz, C_6D_6): δ 30.28 (s). ^1H-NMR (300.13 MHz, C_6D_6): δ 9.04 (d, $J(HH) = 12.6$ Hz, 3 H, Ru–CH), 7.60–8.40 (m, 90 H, Ph), 6.28 (d, $J(HH) = 12.6$ Hz, 3 H, B–CH), 2.89 (s, 9 H, NCH_3). IR (KBr, cm^{-1}): 1925.5 (s, υ(CO)). Anal. Calc. for $C_{120}H_{105}B_3Cl_3N_3O_3P_6Ru_3$: C, 63.63; H, 4.67; N, 1.85. Found: C, 63.36; H, 4.90; N, 1.80%.

3.3. *Crystallographic analysis for* **4**

Crystals suitable for X-ray diffraction were grown by layering methanol on a wet THF solution of **4**. During the process, 1.5 molecules of THF and 0.5 molecule of water co-crystallized with one molecule of **4**. A yellow single crystal with approximate dimensions of 0.12 × 0.08 × 0.05 mm^3 was mounted in a glass capillary for diffraction experiment. Intensity data were collected at 100 K on a Bruker Apex CCD Area Detector, by using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections (SADABS) were applied. The structure was solved by Patterson methods, expanded by difference Fourier syntheses and refined by full-matrix least-squares on F^2 using Bruker SHELXTL (Version 6.10) program package. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were introduced at calculated positions and refined via a riding model. The solvent water molecule was disordered over the crystallographic inversion center, and was refined with half site occupancy. The THF solvents displayed unstable anisotropic displacement parameters, which were refined with suitable restrains in the further refinement. Further crystal data and details of the data collection and refinement are summarized in Table 1 and selected bond distances and angles are given in Table 2.

4. Supplementary materials

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 194349. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 1
Crystallographic details for **4**

Empirical formula	$C_{123}H_{139}B_3N_3O_2P_6Ru_3$ (**4**·1.5THF·0.5H_2O)
Formula weight	2212.83
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	14.5261(10)
b (Å)	18.3745(13)
c (Å)	21.8408(15)
α (°)	84.308(2)
β (°)	86.021(2)
γ (°)	74.799(2)
V ($Å^3$)	5592.1(7)
Z	2
D_{calc} (g cm^{-3})	1.314
Absorption coefficient (mm^{-1})	0.537
F(000)	2302
θ Range (°)	1.45–25.01
Index ranges	$-16 \leq h \leq 17$, $-7 \leq k \leq 21$, $-22 \leq l \leq 25$
Reflections collected	25 552
Independent reflections	18 969 [$R_{int} = 0.0647$]
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	18 969/20/1288
Goodness-of-fit on F^2	0.927
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0620$, $wR_2 = 0.1190$
Largest difference peak and hole (e $Å^{-3}$)	1.372 and −0.959

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
Ru(1)–C(12)	2.020(7)	Ru(1)–P(1)	2.255(2)
Ru(1)–P(2)	2.274(2)	Ru(2)–C(22)	2.000(8)
Ru(2)–P(4)	2.249(2)	Ru(2)–P(3)	2.250(2)
Ru(3)–C(32)	1.999(7)	Ru(3)–P(6)	2.254(2)
Ru(3)–P(5)	2.259(2)	B(1)–N(3)	1.432(10)
B(1)–N(1)	1.440(10)	B(1)–C(11)	1.531(11)
B(2)–N(1)	1.439(10)	B(2)–N(2)	1.440(9)
B(2)–C(21)	1.519(11)	B(3)–N(3)	1.434(10)
B(3)–N(2)	1.441(9)	B(3)–C(31)	1.522(10)
C(11)–C(12)	1.210(9)	C(21)–C(22)	1.243(9)
C(31)–C(32)	1.229(9)		
Bond angles			
C(12)–Ru(1)–P(1)	89.3(2)	C(12)–Ru(1)–P(2)	81.8(2)
P(1)–Ru(1)–P(2)	82.33(7)	C(22)–Ru(2)–P(4)	85.4(2)
C(22)–Ru(2)–P(3)	83.1(2)	P(4)–Ru(2)–P(3)	81.73(8)
C(32)–Ru(3)–P(6)	83.6(2)	C(32)–Ru(3)–P(5)	85.0(2)
P(6)–Ru(3)–P(5)	83.87(8)	N(3)–B(1)–N(1)	117.0(7)
N(3)–B(1)–C(11)	122.4(7)	N(1)–B(1)–C(11)	120.6(7)
N(1)–B(2)–N(2)	116.8(7)	N(1)–B(2)–C(21)	121.6(7)
N(2)–B(2)–C(21)	121.6(7)	N(3)–B(3)–N(2)	118.2(7)
N(3)–B(3)–C(31)	122.0(7)	N(2)–B(3)–C(31)	119.6(7)
B(2)–N(1)–B(1)	123.3(6)	B(2)–N(1)–C(1)	117.7(6)
B(1)–N(1)–C(1)	118.7(6)	B(2)–N(2)–B(3)	122.1(6)
B(2)–N(2)–C(3)	119.8(6)	B(3)–N(2)–C(3)	118.1(6)
B(1)–N(3)–B(3)	122.3(6)	B(1)–N(3)–C(2)	118.5(6)
B(3)–N(3)–C(2)	119.1(6)	C(12)–C(11)–B(1)	171.0(8)
C(11)–C(12)–Ru(1)	173.7(7)	C(22)–C(21)–B(2)	175.5(8)
C(21)–C(22)–Ru(2)	174.3(6)	C(31)–C(32)–Ru(2)	176.2(7)

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