### Title
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### Author(s)
Onishi, Masayoshi; Arikawa, Yasuhiro; Yamaguchi, Mamoru; Nagano, Tomoe; Inoue, Takayuki; Terasoba, Atsunobu; Matsuo, Suguru; Nakagawa, Maki; Kawano, Hiroyuki; Nagaoka, Junko; Umakoshi, Keisuke; Furukawa, Mutsuhisa

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Reactions of (polypyrazolylborato)(benzonitrile)rutheniums with terminal alkynes; Reactivity changeover by triethylamine toward arylalkyne polymerization or formation of (arylmethyl)(carbonyl) complexes

Masayoshi Onishi, a,* Yasuhiro Arikawa, b Mamoru Yamaguchi, b Tomoe Nagano, a Takayuki Inoue, a Atsunobu Terasoba, a Suguru Matsuo, b Maki Nakagawa, a Hiroyuki Kawano, c Junko Nagaoka, a Keisuke Umakoshi, a Mutsuhisa Furukawab

aDepartment of Applied Chemistry, Faculty of Engineering, Nagasaki University
Nagasaki 852-8521, JAPAN.

bGraduate School of Science and Technology, Nagasaki University
Nagasaki 852-8521, JAPAN.

cDivision of Liberal Arts, Kogakuin University
Hachioji, 192-0015, JAPAN

Corresponding author (M.O.);
fax: (+81) 95-819-2684 (Dept office); E-mail: onishi@nagasaki-u.ac.jp

Abstract
Reactions of (κ³-polypyrazolylborato)(benzonitrile)rutheniums [RuCl{B(4-Ypz)4}(PhCN)2] {4-Ypz; 4-bromo-1-pyrazolyl (Y= Br) and 1-pyrazolyl (Y= H) groups} with terminal alkynes were studied. For the reactions with arylalkynes HC≡C(aryl) in the presence of NEt3, (arylmethyl)(carbonyl)rutheniums [Ru{CH2(aryl)}{B(4-Ypz)4}(CO)(PhCN)] were yielded, indicating alkyne C≡C bond cleavage, whereas in the absence of NEt3, arylalkyne polymerization proceeded instead of the (arylmethyl)ruthenium formation. Reasonably attributed reaction mechanism shows significant role of the vinylidene intermediates “Ru=C=CH(aryl)”.

Keywords
ruthenium; vinylidene; polypyrazolylborato; 1-alkyne; polymerization.

Highlights
alkyne hydration > arylalkyne polymerization > (arylmethyl)(carbonyl) ruthenium > role of NEt₃ >
1. Introduction

Transition-metal mediated transformation of unsaturated hydrocarbon resources to afford more valuable organic compounds has been an active research field of organometallic and organosynthetic chemistry [1], and one representative focus is the study of organometallic vinylidene and further cumulenylidene species for environmentally friendly utilization of terminal alkynes with high chemoselectivity and efficient atom economy [2,3]. While water molecule addition to terminal alkynes assisted by protic acids, mercuric salt, NaAuCl₄, PtCl₄, and some other metal salts is well-known to follow Markovnikov’s rule and to give ketones as final organic products [4], anti-Markovnikov-type hydration proceeding has been also realized by use of some transition-metal, especially ruthenium complexes during the past few decades, where their vinylidene derivative species “M=Cα=CβHR” have been indicated as the key intermediates, bringing about nucleophilic addition of water molecules onto the α-carbon in the vinylidene moiety and release of the aldehydes RCH₂CαHO [2,3,5]. Ruthenium vinylidene species have been described to show diverse nucleophilic addition reactions normally on the α-carbon [3,5,6]. Actually, similar attacks on the α-carbon have been observed for other oxygen-nucleophiles, such as carboxylates, carbanates, and alcohols [2,7] and for nitrogen-nucleophiles [2,8]. Moreover, C-C coupling processes have been also demonstrated through migrations of alkyl, aryl, vinyl, and alkynyl groups onto the α-carbon of the vinylidenes [2,3,9].

On the other hand, in our recent research of (κ³-polypyrazolylborato)(nitrosyl)ruthenium(II) [RuCl₂{BH(pz)₃}(NO)] (pz; 1-pyrazolyl) with an electron-withdrawing nitrosyl ligand (NO⁺), treatments with terminal alkynes in the presence of NEt₃ afforded alkynyl derivatives [Ru(C=CR)Cl{BH(pz)₃}(NO)], and we have found a few interesting nucleophilic addition reactions on the η²-1-alkyne intermediates formed by protonation of these alkynyls [10] (scheme 1). Thus even within a class of six-coordinated (κ³-polypyrazolylborato)ruthenium(II) systems, their chemical reactivities with terminal alkynes have been fairly influenced by individually specific character of the coexisting ligands, and have led us to the present study on the reactions of (κ³-polypyrazolylborato)(benzonitrile)ruthenium(II) complexes [RuCl{B(4-Ypz)₄}(PhCN)₂]
Scheme 1. Typical reaction modes for ruthenium alkynyl species

Scheme 2. (Polypyrazolylborato)ruthenium(II) complexes
{4-Ypz; 4-bromo-1-pyrazolyl (Y= Br) and 1-pyrazolyl (Y= H) groups for (1a) and (1b), respectively} with terminal alkynes, where benzonitrile (PhCN) ligands are significantly dissociative [11,12] (scheme 2).

Polypyrazolylborate anions [BR(pz)$_3$]$^-$ and their versatilely substituted analogs have afforded a wide range of transition- and rare earth-metal complexes, but for half-sandwich-type mono($\kappa^3$-polypyrazolylborato) rutheniums, modification of their electronic and stereochemical properties by use of substituted pyrazoles seems to be a still-undeveloped subject [13].

2. Results and discussion

Two ($\kappa^3$-polypyrazolylborato)(benzonitrile)rutheniums, a complex with 4-bromo-1-pyrazolyl groups [RuCl{B(4-Brpz)$_4$}(PhCN)$_2$] (1a) and the non-substituted analog [RuCl{B(pz)$_4$}(PhCN)$_2$] (1b) [11] were prepared from the reactions of the benzonitrile compound [RuCl$_2$(PhCN)$_4$] [14] and potassium polypyrazolylborate salts in refluxing dichloromethane (CH$_2$Cl$_2$). These complexes, 1a and 1b with significantly dissociative PhCN ligands, were found to demonstrate interesting chemical reactivities with terminal alkynes.

As attempts to prepare their alkynyl derivatives [10], in the presence of 10-fold moles of NEt$_3$, the complex 1a in THF was treated with 10-fold moles of $p$-tolylacetylene, and afforded air-stable yellow microcrystals (2a), which exhibited a strong IR $\nu$(CO) band at 1941 cm$^{-1}$, besides a medium $\nu$(CN) at 2242 cm$^{-1}$. In addition, its $^1$H NMR spectrum in chloroform-$d$ (CDCl$_3$) showed characteristic diastereotopic proton-signals of a geminal CH$^A$H$^B$ group at $\delta$ 2.95 and 2.52 coupled with each other ($J= 9.3$ Hz). As for the $\kappa^3$-B(4-Brpz)$_4$ moiety, each of all four 4-Brpz groups was spectroscopically unique and in different circumstances in the $^1$H and $^{13}$C NMR spectra. Complex 1a was also allowed to react with phenylacetylene, and gave yellow microcrystals (3a) with similar spectroscopic characteristics.

Moreover, good-quality single crystals of 2a·CHCl$_3$ were separated from CHCl$_3$ and hexane, and x-ray structural analysis was carried out (Table 1). Figure 1 shows the ortep
Figure 1. Ortep drawing of (p-tolylmethyl)(carbonyl)ruthenium 2a with 30% probability thermal ellipsoids and atom labels only for important atoms. Incorporated solvent CHCl₃ molecule is omitted for clarity.

Scheme 3. Treatments of the ruthenium complexes with terminal alkynes in the presence of NEt₃
drawing of 2a, which involves carbonyl (CO) and \( p \)-tolylmethyl (\( CH_2C_6H_4CH_3 \)) ligands. Accordingly, these yellow products were attributed to the (arylmethyl)(carbonyl)rutheniums \([Ru\{CH_2(aryl)\}\{B(4-Brpz)_4\}(CO)(PhCN)]\) (aryl; \( p \)-tolyl for 2a and phenyl for 3a) (scheme 3). Table 2 summarizes selected interatomic distances and bond angles of 2a, which are reasonable to the attributed structure. Elemental analyses and FAB MS data of these products also were well in accord with their attributed structures.

Formation of (arylmethyl)(carbonyl)rutheniums “Ru{CH\(_2\)(aryl)}(CO)” was accounted for by the following mechanism [2] (vide infra, as shown in Scheme 4); that is, replacement of one PhCN ligand with incoming terminal arylalkyne, formation of neutral vinylidene species “RuCl\{=C\( \alpha \)=C\( \beta \)=C\( \gamma \)H(aryl)\}”, addition of adventitious water molecule onto the \( \alpha \)-carbon of the vinylidene and concomitant 1,3-HCl elimination of the \( \alpha \)-OH group in the generated hydroxycarbene transient [2] to give acyl species “Ru\{C\( \alpha \)(=O)C\( \beta \)H\_2(aryl)\}”, and arylmethyl migration to yield the (arylmethyl)(carbonyl)rutheniums. Metal-mediated C≡C bond cleavage of terminal alkynes has been well-described in the literature [2b,3,5c,15], and thus the observed results were associated with intervention of vinylidene intermediates and with succeeding anti-Markovnikov-type addition of water molecules, in spite of our initial expectation to obtain the alkynyl derivatives “RuC≡C(aryl)” [2b,10,16].

As another terminal alkyne substrate, diphenylpropargyl alcohol HC≡CCPh\(_2\)OH was employed and its reaction with 1a in the presence of excess NEt\(_3\) gave the (diphenylethenyl)(carbonyl)ruthenium, \([Ru(CH=CCPh\_2)\{B(4-Brpz)_4\}\{CO\}(PhCN)]\) (4a) as pale orange powder with strong \( \nu \)(CO) band at 1956 cm\(^{-1}\). The structure of 4a was determined mainly by means of spectroscopic methods (\(^1\)H and \(^{13}\)C NMR, MS, IR etc.).

Through dehydration of the \( \gamma \)-OH group, allenylidene intermediate “Ru=\( C\alpha \)=\( C\beta \)=C\( \gamma \)Ph\(_2\)” would be probably generated [2,3], and subsequent nucleophilic attack of adventitious water molecule onto its \( \alpha \)-carbon gives diphenylethenylcarbonyl intermediate, “Ru=\( C\alpha \)(=O)C\( \beta \)H=C\( \gamma \)Ph\(_2\)”, to afford the final product 4a. Except formation of the allenylidene intermediate in place of the vinylidene, reaction mechanism with the propargyl alcohol was essentially the same to that with simple arylalkynes.

Reactions of the non-subsituted (\( \kappa^3 \)-polypyrazolyborato)ruthenium complex \([RuCl\{B(pz)_4\}\{PhCN\}_2]\) 1b with arylalkynes were conducted also. However, for example,
heating a THF mixture of 1b with 10-fold moles of p-tolylacetylene in the presence of excess NEt₃ gave only an unseparable mixture, and no identifiable product was isolated.

Then with the hope to examine the reaction proceeding on the basis of NMR spectroscopy under more strict anaerobic condition, benzene-d₆ (C₆D₆) solutions of 1a with 10-fold moles of p-tolylacetylene in the presence of excess NEt₃ in NMR tubes were heated gradually to 70 ºC. ¹H and ¹³C NMR signal patterns of 2a were really observed as a single major product, besides large amounts of the remaining unreacted p-tolylacetylene and NEt₃. While the complex 1a was disappeared, other conceivable intermediate species, such as η²-alkyne, vinylidene, alkyne, and aeyl (i.e. arylmethylcarbonyl) species were not detected [2e,17]. White precipitate in the tubes, which formed upon heating the solutions, was confirmed to be [NEt₃H]Cl.

NMR monitoring for the reaction of 1b with 10-fold moles of p-tolylacetylene and NEt₃ was performed similarly. In the NMR spectra observed after heating at 70 ºC, characteristic signal patterns of the (p-tolylmethyl)(carbonyl)ruthenium [Ru{CH₂(p-tolyl)}{B(pz)₄}(CO)(PhCN)] (2b), an analog of 2a were exhibited clearly, which include diastereotopic ¹H NMR signals of the geminal CHₐH₉ group at δ 3.01 and 3.61 with J= 9.4 Hz and further ¹³C NMR signals of CO and nitrile CN carbons at δ 206.4 and 118.7, respectively, and of RuCH₂C₆H₄CH₃ moiety, such as CH₂, CH₃, and CH₂-bonded ipso-C carbons at δ 19.9, 21.2, and 153.7, respectively, in spite of mixing with some unidentified compounds. In addition, precipitation of [NEt₃H]Cl was observed in the NMR tube also. However, upon exposure of the C₆D₆ solution to air, NMR signals of 2b, unambiguously those of the RuCH₂C₆H₄CH₃ moiety and the CO ligand disappeared shortly, indicating its facile decomposition and instability to air. Stability difference between 2a and 2b would be associated with large electron-withdrawing character of the bromo-substituted B(4-Brpz)₄ ligand [18] in the former. According to our initial view, NEt₃ addition to the reaction system would afford alkyne derivatives “Ru-C≡C(aryl)” [10], under support of literature descriptions [2b,9e,16] on the facile deprotonation of ruthenium vinylidene β-hydrogens, but it was disclosed that the (arylmethyl)(carbonyl) complexes were formed as major products, without deprotonation of the β-hydrogens.

One might ask a question on the role of NEt₃ in these reaction proceeding. In the
absence of NEt$_3$, the C$_6$D$_6$ solution of 1a with 10-fold moles of $p$-tolylacetylene was heated at 70 ºC for 3 h, of which NMR observation indicated that a small amount of 1a and some $p$-tolylacetylene were remained, whereas the ($p$-tolylmethyl)(carbonyl)ruthenium 2a was not detected. Similar results were also obtained for the reaction of 1b. Interestingly, each $^1$H NMR spectrum of the C$_6$D$_6$ solutions demonstrated two wide-spread hump-like signals overlapped by many spiky resonances in the ranges of δ 1.9 to 2.4 and δ 6.5 to 8.1, probably implying formation of the $p$-tolylacetylene polymeric compounds [2f,3c,19,20]. Actually, from the respective C$_6$D$_6$ solutions of 1a and 1b, small quantities of benzene-soluble, but acetone-insoluble organic compounds as slightly orange-tinged powder were separated. It was rightfully determined that in the absence of NEt$_3$, ($p$-tolylmethyl)(carbonyl)rutheniums were not produced, but significant quantities of the $p$-tolylacetylene were converted to its poly($p$-tolylacetylene), presumably in a mixture of various stereoisomeric configurations.

Thereupon, flask-contained acetone solutions of 1b with 50-fold moles of phenylacetylene were heated under reflux for 40 h in the absence of NEt$_3$, and slightly orange-tinged powder was collected. The powder was really characterized as poly(phenylacetylene) by use of Gel Permeation Chromatography (GPC) method to give 4,900 and 7,900 of a number-average molecular weight (Mn) and a weight-average molecular weight (Mw), respectively, with the polydispersity index (Mw/Mn, PDI) of 1.61. The collected acetone-insoluble poly(phenylacetylene) was in ca. 66 % yield based on the phenylacetylene charged, which corresponds to 33 turn-over-number (TON) relative to 1b. Similar experiment by using 500-fold moles of phenylacetylene increased moderately the TON to ca. 40.

As a whole, the most reasonable mechanism would be summarized in Scheme 4. Addition of excess NEt$_3$ would bring about basicity increase of water molecules to promote their nucleophilic addition onto the α-carbon in the vinylidene species, leading to efficient formation of the acyl species “Ru-C(=O)CH$_2$(aryl)” and of succeeding (arylmethyl)(carbonyl) products. For the reactions without NEt$_3$, vinylidene intermediates [RuCl{B(4-Ypz)$_4$} {$=C=CH$(aryl)}(PhCN)] with carbenic M=C reactive sites, probably
Scheme 4. Most reasonably attributed reaction mechanism for the ruthenium complexes with arylalkynes.

\[ \text{[Ru]; Ru(B(4-Ypz)4). (R; H, CH}_3 \text{).} \]
requisite for alkyne polymerization [20] [Footnote-1], would be the active initiator [Footnote-2], where one more remaining PhCN ligand would dissociate from ruthenium to give uncoordinated open site for the next incoming arylalkyne molecule, leading to the polymerization.

3. Concluding remarks

The \((\kappa^3\text{-polypyrrozolyborato})(benzonitrile)\text{rutheniums } [\text{RuCl}\{\text{B}(4\text{-Ypz})_4\}\text{(PhCN)}_2] \{4\text{-Ypz; 4-bromo-1-pyrazolyl } (Y=\text{Br}) \text{ for 1a and 1-pyrazolyl } (Y=\text{H}) \text{ for 1b} \} \) were treated with terminal arylalkynes in the presence of NEt₃ to afford the (aryl)methyl)\text{(carbonyl)\text{rutheniums } [\text{Ru}\{\text{CH}_2\text{(aryl)}\}\{\text{B}(4\text{-Ypz})_4\}\text{(CO)}\text{(PhCN)}], through nucleophilic addition of adventitious water molecules onto the \(\alpha\)-carbon in the vinylidene intermediates \(\text{“Ru=\text{C}^{\alpha}\equiv\text{C}^{\beta}\text{H(aryl)}”}\), although \(\beta\)-hydrogens in ruthenium vinylidene complexes have been frequently described to be deprotonated with nitrogen bases such as NEt₃ [2b,9e,16] to yield alkynyl species “M-\text{C}^{\alpha}\equiv\text{C}^{\beta}\text{R}” [10]. On the other hand, similar treatments in the absence of NEt₃ brought about arylalkyne polymerization in place of the (aryl)methyl)\text{(carbonyl)\text{ruthenium formation.}

Thus, the reaction system of 1a and 1b is an interesting example of ruthenium complexes with terminal arylalkynes, which demonstrated that reaction selectivities, whether they proceed to the arylalkyne polymerization or to the (aryl)methyl)(carbonyl)\text{ruthenium formation was determined by the absence or presence of NEt₃, respectively. Distinct feature of the present \((\kappa^3\text{-polypyrrozolyborato})(benzonitrile)\text{rutheniums is retention of three potential coordination sites available for these reaction proceedings; those are two sites realized by dissociation of PhCN ligands, and the remaining one site of chlorine ligand, of which facile dissociation as a chloride anion was exemplified by the above-mentioned 1,3-HCl liberation in the neutral hydroxycarbene transient species.}
4. Experimental section

4.1. Materials and physical measurements

The (benzonitrile)ruthenium [RuCl₂(PhCN)₄] [14] and potassium salt K[B(pz)₄] [13g] were prepared according to the literature, and all other reagents were commercially available. While reactions were run under dinitrogen atmosphere, work-up procedures after reaction completion were performed in air, involving column-chromatographic separations, unless noted specially.

Infrared (IR) spectra were recorded on a JASCO FT-IR-420 instrument. NMR spectra were obtained on a JEOL JNM-AL-400 and a Varian Gemini-300 spectrometers. For assignment of NMR resonances, ¹H-¹H COSY, ¹H-¹³C COSY, and ¹³C-DEPT were observed supplementarily. Elemental analyses (C, H, N) were performed on a Perkin Elmer 2400II elemental analyzer by the Centre for Instrumental Analyses of Nagasaki University.

4.2. Preparation of K[B(4-Brpz)₄]

A mixture of 4-bromopyrazole (4-BrpzH) (5.3 g, 36 mmol) and KBH₄ (325 mg, 6.0 mmol) was heated gradually to ca. 220 °C, and at this temperature heating was continued for 11 h. After cooling to room temperature, THF-soluble product was collected and the solvent was removed in vacuo. The resulting solid was dried under vacuum at 140 °C for 8 h to give K[B(4-Brpz)₄] (2.21 g, 3.49 mmol) as slightly brown-tinged microcrystals in 58 % yield.

K[B(4-Brpz)₄]
Mp.; 240~243 °C
¹H NMR (300 MHz, CD₃OD); δ 7.56 (4H, s, pz) and 7.30 (4H, s, pz).
Elemental analyses; Calcd for C₁₂H₈BBr₄K₈N₈, C 22.74, H 1.27, N 17.68. Found, C 22.50, H 1.54, N 17.45 %.

4.3. Preparations of (polypyrazolylborato)(benzonitrile)rutheniums
These ruthenium complexes were prepared as the following; The benzonitrile compound \([\text{RuCl}_2(\text{PhCN})_4]\) (718 mg, 1.23 mmol) and the potassium salt \(K[B(4-\text{Brpz})_4]\) (779 mg, 1.23 mmol) in CH\(_2\)Cl\(_2\) (300 ml) suspension were heated under reflux for 6 days. After solvent removal in vacuo., benzene extract was collected and subsequent column-chromatographic separation on alumina (activity II–III) was performed. Elution by a solvent mixture of CH\(_2\)Cl\(_2\) and diethyl ether (2/1) afforded yellowish green microcrystals of \([\text{RuCl}\{B(4-\text{Brpz})_4\}(\text{PhCN})_2]\) (1a) (646 mg, 0.689 mmol) in 56 % yield.

As briefly communicated earlier \[11a\], yellowish green complex of the non-substituted analog \([\text{RuCl}\{\text{B(pz)}_4\}(\text{PhCN})_2]\) (1b) was also obtained from \([\text{RuCl}_2(\text{PhCN})_4]\) (1.29 g, 2.21 mmol) and \(K[B(\text{pz})_4]\) (830 mg, 2.61 mmol) in refluxing CH\(_2\)Cl\(_2\) (500 ml) for 2 days. Column chromatographic separation with silica gel afforded \([\text{Ru}\{\kappa^3-\text{B(pz)}_4\}_2]\) (130 mg, 0.20 mmol) and 1b (1.01 g, 1.62 mmol) by elution with CH\(_2\)Cl\(_2\) and with a solvent mixture of CH\(_2\)Cl\(_2\) and acetone (5/1), respectively. Yield of 1b was 73 % (based on Ru) [Footnote-3].

\([\text{RuCl}\{B(4-\text{Brpz})_4\}(\text{PhCN})_2]\) 1a

Mp.; 180 ~ 183 °C
IR (KBr); \(\nu(\text{CN})\) 2233 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)); \(\delta\) 8.07 (2H, s, pz), 7.96 (1H, s, pz), 7.91 (1H, s, pz), 7.85 (1H, s, pz), 7.79 (2H, s, pz), 7.73 (4H, d, 7.3 Hz, Ph), 7.72 (1H, s, pz), 7.63 (2H, t, 7.4 Hz, Ph), 7.51 (4H, t, 7.4 Hz, Ph).

\(^{13}\)C NMR (75.3 MHz, CDCl\(_3\)); \(\delta\) 145.2 (2C, 3-pz), 144.3 (3-pz), 143.0 (3-pz), 136.7 (5-pz), 135.8 (2C, 5-pz), 135.3 (5-pz), 133.1 (2C, Ph), 133.0 (4C, Ph), 129.2 (4C, Ph), 124.3 (2C, CN), 111.9 (2C, CN-bonded ipso-C in Ph), 96.0 (4-pz), 93.8 (2C, 4-pz), 93.4 (4-pz).

FAB MS (m-NBA); 938 (M\(^+\)), 903 (M - Cl\(^+\)), 835 (M - PhCN\(^+\)).

Elemental analyses; Calcd for C\(_{26}\)H\(_{18}\)BB\(_4\)ClN\(_{10}\)Ru, C 33.31, H 1.94, N 14.94 %. Found, C 33.52, H 2.20, N 14.80 %.

\([\text{RuCl}\{\text{B(pz)}_4\}(\text{PhCN})_2]\) 1b [11a]

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)); \(\delta\) 8.60 (2H, d, 1.5 Hz, pz), 8.11 (1H, d, 2.4 Hz, pz), 7.98 (1H, d,
1.5 Hz, pz), 7.93 (2H, d, 2.4 Hz, pz), 7.85 (1H, d, 1.5 Hz, pz), 7.76 (1H, d, 2.0 Hz, pz), 7.08 (4H, d, 7.8 Hz, Ph), 6.82 (2H, t, 7.8 Hz, Ph), 6.69 (4H, dd, 7.8 Hz, 7.8 Hz, Ph), 6.38 (1H, dd, 2.0 Hz, 1.5 Hz, pz), 6.12 (1H, dd, 2.4 Hz, 1.5 Hz, pz), 6.07 (2H, dd, 2.4 Hz, 1.5 Hz, pz).

$^{13}$C NMR (100 MHz, $C_6D_6$); $\delta$ 145.3 (2C, 3-pz), 143.9 (3-pz), 141.8 (3-pz), 136.3 (5-pz), 136.1 (5-pz), 135.4 (2C, 5-pz), 132.9 (4C, Ph), 131.9 (2C, Ph), 128.8 (4C, Ph), 123.5 (2C, CN), 112.9 (2C, CN-bonded ipso-C in Ph), 106.8 (4-pz), 106.5 (4-pz), 106.4 (2C, 4-pz).

4.4. Reactions of 1a with arylalkynes in the presence of NEt$_3$

To a THF solution (10 ml) of the bromo-substituted ruthenium 1a (100 mg, 0.107 mmol), NEt$_3$ (108 mg, 1.07 mmol) and $p$-tolylacetylene (124 mg, 1.07 mmol) were added successively and heated under reflux 4 h. Benzene-extracted solid was chromatographed on a silica-gel column, and elution with a solvent mixture of toluene and hexane (1/1) afforded yellow microcrystals of [Ru{CH$_2$(p-tolyl)}{B(4-Brpz)$_4$}(CO)(PhCN)] (2a) (67 mg, 0.072 mmol) in 67.3 % isolated yield.

Similar reaction with phenylacetylene was conducted to give yellow microcrystals of [Ru(CH$_2$Ph){B(4-Brpz)$_4$}(CO)(PhCN)] (3a) in 70.2 % isolated yield. Chromatographic separation was performed on a silica gel column by elution with a solvent mixture of $C_6H_6$ and CH$_2$Cl$_2$ (1/1).

[Ru{CH$_2$(p-tolyl)}{B(4-Brpz)$_4$}(CO)(PhCN)] 2a [Footnote-4]

Mp.; > 250 ºC.

IR (KBr); v(CN) 2242, v(CO) 1941 cm$^{-1}$.

$^1$H NMR (300 MHz, CDCl$_3$); $\delta$ 8.20 (1H, s, pz), 7.95 (1H, s, pz), 7.91 (1H, s, pz), 7.82 (1H, s, pz), 7.81 (1H, s, pz), 7.67 (1H, s, pz), 7.61 (1H, t, 7.5 Hz, Ph), 7.45 (1H, s, pz), 7.44 (2H, t, 7.7 Hz, Ph), 7.34 (2H, d, 7.2 Hz, Ph), 7.15 (2H, d, 7.8 Hz, tolyl), 7.03 (1H, s, pz), 6.93 (2H, d, 7.7 Hz, tolyl), 2.95 (1H, d, 9.3 Hz, CH$_2$), 2.52 (1H, d, 9.3 Hz, CH$_2$), 2.21 (3H, s, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$); $\delta$ 204.1 (CO), 151.2 (CH$_2$-bonded ipso-C in tolyl), 144.8 (3-pz), 143.5 (3-pz), 142.9 (3-pz), 141.8 (3-pz), 135.4 (2C, 5-pz), 135.2 (2C, 5-pz), 133.0 (Ph), 132.4 (2C, Ph), 130.7 (CH$_2$-bonded ipso-C in tolyl), 128.9 (2C, Ph), 128.5 (2C, tolyl),
127.2 (2C, tolyl), 124.1 (CN), 111.3 (CN-bonded ipso-C in Ph), 96.0 (4-pz), 93.9 (2C, 4-pz), 93.7 (4-pz), 21.1(CH3), 18.8 (CH2)

FAB MS (m-NBA); 933 (M)+, 828 (M - CH2(tolylnyl))+, 800 (M - CH2(tolylnyl) - CO)+

Elemental analyses; Calcd for C28H22BBr4N9ORu, C 36.08, H 2.38, N 13.53 %.  Found, C 35.69, H 2.35, N 13.32 %.

[Ru(CH2Ph){B(4-Brpz)4}(CO)(PhCN)] 3a

Mp.; ca. 165 ºC.

IR (KBr); ν(CN) 2242, ν(CO) 1942 cm⁻¹.

1H NMR (300 MHz, CDCl3); δ 8.22 (1H, bs, pz), 7.95 (1H, bs, pz), 7.91 (1H, bs, pz), 7.82 (2H, bs, pz), 7.67 (1H, bs, pz), 7.60 (1H, t, 7.6 Hz, Ph), 7.48 (1H, bs, pz), 7.45 (2H, t, 7.7 Hz, Ph), 7.35 (2H, d, 7.0 Hz, Ph), 7.25 (2H, d, 7.2 Hz, Ph), 7.14 (2H, t, 7.6 Hz, Ph), 7.03 (1H, bs, pz), 6.96 (1H, t, 7.2 Hz, Ph), 2.95 (1H, d, 9.3 Hz, CH2), 2.53 (1H, d, 9.3 Hz, CH2).

13C NMR (100 MHz, CDCl3); δ 204.5 (CO), 155.0 (CH2-bonded ipso-C in Ph), 145.1 (3-pz), 143.8 (3-pz), 143.2 (3-pz), 142.1 (3-pz), 135.6 (2C, 5-pz), 135.4 (2C, 5-pz), 133.3 (Ph), 132.7 (2C, Ph), 129.1 (2C, Ph), 128.0 (2C, Ph), 127.5 (2C, Ph), 124.3 (CN), 121.8 (Ph), 111.4 (CN-bonded ipso-C in Ph), 96.1 (4-pz), 94.0 (2C, 4-pz), 93.8 (4-pz), 19.2 (CH2).

FAB MS (m-NBA); 918 (M - H)+, 828 (M - CH2Ph)+, 800 (M - CH2Ph - CO)+.

Elemental analyses; Calcd for C27H26BBr4N9ORu, C 35.33, H 2.20, N 13.73 %.  Found, C 35.52, H 2.32, N 13.62 %.

4.5. Reaction of 1a with diphenylpropargyl alcohol in the presence of NEt3

To a THF solution (20 ml) of [RuCl{B(4-Brpz)4}(PhCN)]2 1a (440 mg, 0.469 mmol) under dinitrogen atmosphere, NEt3 (475 mg, 4.69 mmol) and diphenylpropargyl alcohol HC≡CCPh2OH (977 mg, 4.69 mmol) were added and the mixture was heated at 45 ºC overnight.  Volatile materials were removed under vacuum, and the resulting residue was column-chromatographed on silica gel.  Elution with a solvent mixture of C6H6 and hexane (5/1) gave a brown band.  The material obtained from the band was dissolved in hexane and its solution was kept at – 40 ºC.  After overnight standing, pale orange powder precipitated
was collected and assigned to \([\text{Ru}\{\text{CH}=\text{CPh}_2\}\{\text{B}(4-\text{Brpz})_4\}(\text{CO})(\text{PhCN})]\) (4a) (39 mg, 38.8 \(\mu\)mol) in about 8.3 % yield [Footnote-5], however which was contaminated with 1,1-diphenylethylene (\(\text{CH}_2=\text{CPh}_2\)) in ca. 15 % molar ratio to 4a. The compound, 1,1-diphenylethylene was generated probably through the Ru-C(vinyl) bond cleavage of 4a.

\([\text{Ru}\{\text{CH}=\text{CPh}_2\}\{\text{B}(4-\text{Brpz})_4\}(\text{CO})(\text{PhCN})]\) 4a

IR (KBr); \(\nu(\text{CN})\) 2247, \(\nu(\text{CO})\) 1956 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)); \(\delta\) 8.08 (1H, bs, pz), 7.97 (1H, bs, pz), 7.94 (1H, bs, Ru-CH=), 7.91 (2H, bs, pz), 7.82 (1H, bs, pz), 7.65 (1H, bs, pz), 7.64 ~ 7.0 (17H, complicatedly overlapping, Ph). Representative resonance of \(\text{CH}_2=\text{CPh}_2\) impurity; \(\delta\) 5.46 (2H, s, \(\text{CH}_2\)).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) [Footnote-6]; 4a; \(\delta\) 202.9 (CO), 153.2 (Ru-CH=), 150.4 (Ru-CH=), 147.1 (ipso-C(Ph) in RuCH=CPh\(_2\)), 145.8 (ipso-C(Ph) in RuCH=CPh\(_2\)), 145.7 (3-pz), 143.5 (3-pz), 143.1 (3-pz), 142.5 (3-pz), 135.4 (4C, 5-pz), 133.3 (Ph), 132.3 (2C, Ph), 131.1 (2C, Ph), 129.0 (2C, Ph), 127.6 (2C, Ph), 127.5 (2C, Ph), 126.4 (2C, Ph), 125.6 (Ph), 124.7 (Ph), 124.7 (CN), 111.2 (CN-bonded ipso-C in Ph), 96.1 (4-pz), 94.1 (4-pz), 94.0 (4-pz), 93.9 (4-pz). Representative resonances of \(\text{CH}_2=\text{CPh}_2\) impurity; \(\delta\) 149.9 (CH\(_2=\)), 141.4 (2C, ipso-C(Ph) in CH\(_2=\)), 128.1 (4C, Ph), 128.0 (4C, Ph), 127.5 (2C, Ph), 114.1 (CH\(_2=\)).

FAB MS (\(m\)-NBA); 1007 (M\(^+\)), 904 (M - PhCN\(^+\)), 875 (M – PhCN – CO – H\(^+\)).

4.6. NMR monitoring for the reactions of \((\text{polypyrazolylborato})(\text{benzonitrile})\) rutheniums with arylalkynes

4.6.1. Reaction of 1a, p-tolylacetylene, and NEt\(_3\)

In a 5 mm\(^6\) NMR tube, p-tolylacetylene (12.8 mg, 0.11 mmol) and NEt\(_3\) (11.1 mg, 0.11 mmol) were added successively to the C\(_6\)D\(_6\) solution (0.7 ml) of the complex 1a (10.0 mg, 10.7 \(\mu\)mol), and the mixture was deaerated by several freeze-pump-thaw cycles, followed by sealing of the tube in vacuo. Then, the mixture was heated at 70 \(^\circ\)C for 3 h, and \(^1\)H and \(^{13}\)C NMR observations were performed. While large amount of p-tolyacetylene was remained unreacted, the complex 1a charged was disappeared and formation of the
(p-tolylmethyl)(carbonyl)ruthenium 2a was confirmed [Footnote-4].

4.6.2. Reaction of 1b, p-tolylacetylene, and NEt3

NMR monitoring was performed for the reaction of 1b similarly. Although some unidentified materials were mixed, analogous NMR results were obtained. Following resonances observed were unambiguously attributed to the signals of [Ru{CH2(p-tolyl)}{B(pz)4}(CO)(PhCN)] (2b).

1H NMR of 2b (300 MHz, C6D6); δ 3.61 (1H, d, 9.4 Hz, CH2), 3.01 (1H, d, 9.4 Hz, CH2), 2.23 (3H, s, CH3).

13C NMR of 2b (100 MHz, C6D6); δ 206.4 (CO), 153.7 (CH2-bonded ipso-C in tolyl), 118.7 (CN), 112.2 (CN-bonded ipso-C in Ph), 21.2 (CH3), 19.9 (CH2).

4.6.3. Reactions of the ruthenium complexes (1a and 1b) and p-tolylacetylene without NEt3

Reaction of 1a with p-tolylacetylene in the deaerated NMR tube was conducted, but in the absence of NEt3. 1H NMR spectra observed were found to show two wide-spread hump-like signals overlapped by many spiky resonances in the ranges of δ 1.9 to 2.4 and δ 6.5 to 8.1, attributable to p-tolylacetylene polymeric compounds. The spectra confirmed the lack of (p-tolylmethyl)(carbonyl) ruthenium (2a) and also the survival of a small amount of 1a. Moreover, from the NMR C6D6 solution, benzene-soluble, but acetone-insoluble slightly orange-tinged powder (ca. 3 mg) was collected by reprecipitation of the reaction mixture from toluene and methanol, and was associated with poly(p-tolylacetylene).

Elemental analyses; Calcd for (C9H8)n, C 93.06, H 6.94 %.  Found; C 92.78, H 7.10 %.

Analogous results were obtained also for the reaction of 1b and p-tolylacetylene without NEt3 in the NMR tube.

4.7. Reactions of 1b and phenylacetylene in refluxing acetone without NEt3

Mixture of the complex [RuCl{B(pz)4}(PhCN)2] 1b (25.2 mg, 0.041 mmol) and phenylacetylene (204.3 mg, 2.0 mmol) in acetone (10 ml) was heated under reflux for 40 h. Acetone-insoluble material was collected and reprecipitation from its toluene solution by
methanol addition gave slightly orange-tinged powder of poly(phenylacetylene) (135 mg) in 66 % yield based on the phenylacetylene charged.

Elemental analyses; Calcd for (C₈H₆)n; C 94.08, H 5.92 %.  Found; C 94.34, H 6.19 %.

Polymer characterization with Gel Permeation Chromatography (GPC) method was conducted with the following conditions; in THF by use of Shimadzu HPLC LC-6A and UV/VIS Detector SPD-6A, and of several polystyrene standards. The number-average molecular weight (Mn), the weight-average molecular weight (Mw), and polydispersity index (Mw/Mn, PDI) were evaluated to be 4,900, 7,900, and 1.61, respectively. Similar reactions in refluxing C₆H₆ for 10 h afforded poly(phenylacetylene) in 58 % yield, with Mn 3,400, Mw 5,700, and PDI 1.68.

4.8. Crystallography

Single-crystal x-ray structural analysis of 2a was carried out for its CHCl₃-solvated crystals obtained by serene built-up of two solvent layers, i.e. hexane and 2a-containing CHCl₃ layers in test tubes.

Crystallographic and structural refinement data are summarized in Table 1. Diffraction intensity data were collected at room temperature on a Rigaku/MSC Mercury CCD diffractometer, by using graphite-monochromated Mo Kα radiation. The intensity images were obtained at the exposure rate of 53.3 sec/deg. The frame data were integrated using the Rigaku CrystalClear program package, and were corrected for Lorentz and polarization effects.

All calculations were conducted with CrystalStructure software package. The crystal structure was solved by direct methods (SIR-97), and refined on F² by full-matrix least-squares method. Concerning the incorporated CHCl₃ molecule, disorder in two configurations was observed with occupancy factors of 0.6/0.4, while the hydrogen atom in the CHCl₃ molecule was not located. All non-hydrogen atoms except for the disordered CHCl₃ molecule were refined anisotropically, and the hydrogen atoms were put at calculated positions with C-H distances of 0.97 Å.

Crystallographic data of 2a has been deposited at the Cambridge Crystallographic Data
Centre, with the reference number, CCDC 811806, and can be obtained free of charge from the Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We wish to acknowledge Yusuke Ito, Motoshi Miyahira, Naotaka Izumi, and Hitomi Miyazaki for their technical assistance. Special thanks are due to Professor Ken Kojio and the late Professor Katsuma Hiraki of Nagasaki University for their valuable suggestion.
Footnote list

[Footnote-1] Alkyne polymerization with \([M(=CR^A R^B)(CO)_5]\) (M; Cr, W) [20] has been described to proceed through formation of “\(M(\eta^2\text{-alkyne})(=CR^A R^B)\)” intermediate species, in other words, metallocyclobutene transients. Moreover, (vinylidene)rutheniums \([\text{RuCl}_2(=\text{C} \equiv \text{CHR}')(\text{PR}_3)_2]\) have been reported to show high efficiencies for ring-opening metathesis polymerization of cyclic olefins, via metallocyclobutane transients [2i].

[Footnote-2] While potential catalytic activity of the hydroxycarbene transient species \([\text{RuCl}\{\text{B}(4-\text{Ypz})_4\}{=\text{C(OH)}\text{CH}_2(\text{aryl})}\}{(\text{PhCN})}\) can not be ruled out in terminal alkyne polymerization because of their retention of carbenic Ru=\(\text{C}\) sites (Scheme 4), facile 1,3-HCl elimination from neutral hydroxycarbenes has been well-known to proceed. The authors would suggest only small, or negligible contribution by the hydroxycarbenes to alkyne polymerization, although certain informations on real structures of poly(arylalkyne) end moieties are not available at this stage. To our knowledge, several hydroxycarbene species have been isolable by the treatments of acyl metal complexes (without anionic dissociative coexistent ligands) with strong protic acids HX (X; non-coordinative bulky anions, such as \(\text{CF}_3\text{SO}_3^-\)). See (a) D. S. Barratt, C. Glidewell, D. J. Cole-Hamilton, J. Chem. Soc., Dalton Trans. (1988) 1079-1081; (b) M. A. Esteruelas, A. V. Gómez, F. J. Lahoz, A. M. López, E. Oñate, L. A. Oro, Organometallics 15 (1996) 3423-3435.

[Footnote-3] The BH(pz)_3 analog, \([\text{RuCl}\{\text{BH}(\text{pz})_3\}\{(\text{PhCN})\}_2]\) is obtainable similarly in ca. 30 % yield by using K[BH(pz)_3] [11a]. Chromatographic separation afforded \([\text{Ru}\{\kappa^3\text{-BH}(\text{pz})_3\}_2]\) and the BH(pz)_3 analog by elution with C_6H_6 and with a solvent mixture of CH_2Cl_2 and diethyl ether (ca. 8/1), respectively. ^1H NMR of the BH(pz)_3 analog (400 MHz, CDCl_3); \(\delta\) 8.00 (2H, pz), 7.73 (pz), 7.71 (2H, pz), 7.68 (4H, Ph), 7.64 (pz), 7.54 (2H, Ph), 7.44 (4H, Ph), 6.24 (2H, pz), 6.23 (pz). ^13C NMR (100 MHz, CDCl_3); \(\delta\) 143.4 (2C, 3-pz), 142.8 (3-pz), 135.5 (5-pz), 135.0 (2C, 5-pz), 132.9 (4C, Ph), 132.4 (2C, Ph), 129.0 (4C, Ph), 123.1 (2C, CN), 113.0 (2C, CN-bonded ipso-C in Ph), 105.9 (3C, 4-pz). J. Zagermann, M. Molon, N. Metzler-Nolte, Dalton Trans. (2011) 1011-1015.
[Footnote-4] NMR data of 2a in C₆D₆

¹H NMR (300 MHz); δ 8.23 (1H, s, pz), 7.99 (1H, s, pz), 7.66 (1H, s, pz), 7.59 (1H, s, pz), 3.32 (1H, d, 9.3 Hz, CH₂), 2.86 (1H, d, 9.3 Hz, CH₂), 2.22 (3H, s, CH₃). ¹³C NMR (100 MHz); δ 205.1 (CO), 152.0 (CH₂-bonded ipso-C in tolyl), 145.3 (3-pz), 143.8 (3-pz), 143.1 (3-pz), 142.2 (3-pz), 136.2 (5-pz), 135.9 (5-pz), 135.7 (2C, 5-pz), 132.7 (2C, Ph or phenylene in tolyl), 132.4 (4C, Ph and/or phenylene in tolyl), 131.0 (CH₃-bonded ipso-C in tolyl), 124.4 (CN), 111.3 (CN-bonded ipso-C in Ph), 96.3 (4-pz), 94.4 (2C, 4-pz), 94.2 (4-pz), 21.2 (CH₃), 19.4 (CH₂). Assignments of ¹H resonances at δ 6.50 to 7.55 and ¹³C resonances at δ 125 to 130 were not undergone.

[Footnote-5] Proper experimental optimization in the preparative and separative procedures for 4a has not been completed, and its noted yield value is tentative.

[Footnote-6] These three ¹³C resonances of quaternary carbons at δ 150.4, 147.1, and 145.8 were most plausibly assigned, but possibility of mutual interchange among them can not be ruled out.
References


Captions for Figure and Schemes

Figure 1. Ortep drawing of ($p$-tolylmethyl)(carbonyl)ruthenium 2a with 30% probability thermal ellipsoids and atom labels only for important atoms. Incorporated solvent CHCl₃ molecule is omitted for clarity.

Scheme 1. Typical reaction modes for ruthenium alkynyl species.

Scheme 2. (Polypyrazolylborato)ruthenium(II) complexes.

Scheme 3. Treatments of the ruthenium complexes with terminal alkynes in the presence of NEt₃.

Scheme 4. Most reasonably attributed reaction mechanism for the ruthenium complexes with arylalkynes.
Table 1. Crystallographic and structural refinement data for 2a-CHCl₃.

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<td>(b) (Å)</td>
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<td>(V) (Å³)</td>
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</tr>
<tr>
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<td>(wR2)(^d)</td>
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<td>goodness of fit (S)(^e)</td>
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\(^a\) All reflections.

\(^b\) \(I > 2.0\sigma(I); \ R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo||. 

\(^c\) \(R = \Sigma(Fo^2-Fc^2)\SigmaFo^2.\)

\(^d\) \(wR2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}.\)

\(^e\) \(S = [\Sigma w(Fo^2-Fc^2)^2/(No-Nv)]^{1/2}, \) where \(No\) and \(Nv\) denote the number of observations and
variables.
Table 2. Selected interatomic distances (Å) and bond angles (°) of 2a·CHCl₃.

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</table>

| Bond angles                 | N(1)-Ru(1)-N(9) | Ru(1)-C(14)-C(15) | N(3)-Ru(1)-C(13) | Ru(1)-N(1)-N(2) | N(5)-Ru(1)-C(14) | Ru(1)-N(3)-N(4) | Ru(1)-C(13)-O(1) | Ru(1)-N(5)-N(6) |
|-----------------------------| 173.77(17)     | 115.7(4)      | 176.6(2)     | 119.5(3)     | 171.25(17)    | 121.5(3)      | 175.7(5)     | 120.8(3)     |

Received: August 2011.
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Graphical Abstract (Table of Contents)

Title:
Reactions of (polypyrazolylborato)(benzonitrile)rutheniums with terminal alkynes;
Reactivity changeover by triethylamine toward arylalkyne polymerization or formation of
(arylmethyl)(carbonyl) complexes

Authors:
Masayoshi Onishi,* Yasuhiro Arikawa, Mamoru Yamaguchi, Tomoe Nagano, Takayuki
Inoue, Atsunobu Terasoba, Suguru Matsuo, Maki Nakagawa, Hiroyuki Kawano, Junko
Nagaoka, Keisuke Umakoshi, Mutsuhisa Furukawa

Text:
(Polypyrazolylborato)(benzonitrile)rutheniums [RuCl{B(4-Ypz)4}(PhCN)2] {4-Ypz; 4-bromo-1-pyrazolyl and 1-pyrazolyl groups} were allowed to react with arylalkynes HCC=CH(aryl) in the presence of NEt3 to afford (arylmethyl)(carbonyl)rutheniums [Ru{CH2(aryl)}{B(4-Ypz)4}(CO)(PhCN)], whereas in the absence of NEt3, arylalkyne polymerization proceeded instead. Reasonably attributed reaction mechanism shows significant role of the vinylidene intermediates “Ru=C=CH(aryl)”.

Image: