Triphenylphosphine Incorporation Reactions of Diynyl Complexes Containing a TpRu(NO) Fragment and Isomerization to Ruthenacyclobuta[*b*]naphthalene

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Nitrosylruthenium arylbutadiynyl complexes having a Tp ligand (Tp = BH(pyrazol-1-yl)$_3$) were prepared, and their reactivities toward PPh_3 incorporation in the presence of $HBF_4 \cdot Et_2O$ were described. The PPh_3 incorporation of mono(arylbutadiynyl) complex TpRuCl(C≡C−C≡C−C_6H_4Me)(NO) (**1**) resulted in the β-phosphonioalkenyl complex (*E*)-[TpRuCl(CH=C(PPh_3)−C≡C−C_6H_4Me)(NO)]BF_4 (**2**·BF_4), whereas when bis(arylbutadiynyl) TpRu(C≡C−C≡C−$C_6H_4Me)_2$(NO) (**3**) was treated, mono- and bis(β-phosphonioalkenyl) complexes (*E*)-[TpRu(C≡C−C≡C−C_6H_4Me)(CH=C(PPh_3)−C≡C−C_6H_4Me)(NO)]BF_4 (**4**·BF_4) and (*E, E*)-[TpRu(CH=C(PPh_3)−C≡C−$C_6H_4Me)_2$(NO)]$(BF_4)_2$ {**5**·$(BF_4)_2$} were obtained depending on the reaction conditions. On the other hand, an unsymmetrically mixed (arylbutadiynyl)(3-hydroxyalkynyl) complex, TpRu(C≡C−C≡C−C_6H_4Me){C≡CCPh_2(OH)}(NO) (**6**), was allowed to react with PPh_3 in the presence of the protic acid to give the α-phosphonioallenyl [TpRu(C≡C−C≡C−C_6H_4Me){C(PPh_3)=C=CPh_2}(NO)]BF_4 (**7**·BF_4). Interestingly, thermal isomerization of **7**·BF_4 to a ruthena-2-PPh_3-cyclobuta[*b*]naphthalene [TpRu{CH(PPh_3)[3-Ph-8-(MeC_6H_4−C≡C)−$C_{10}H_4$]}(NO)]BF_4 (**8**·BF_4) was observed.

Introduction

Transition-metal-mediated transformations of simple organic molecules to highly valuable products are of much interest in synthetic chemistry.[1] One candidate for the simple molecules is alkynes, which are useful and versatile organic resources.[2] In particular, terminal alkynes are attractive because of their relevance to vinylidene and allenylidene species on the transition metals.[3] Our research of alkynyl complexes derived from the terminal alkynes has focused on nitrosylruthenium having trispyrazolylborate (Tp),[4] which has led us to isolate a few unusual complexes. For example, the mutual coupling of two alkynyl groups with concomitant incorporation of H_2O has brought about the formation of unique five- or four-membered metallacycles.[4b,e] The latter metallacycles have shown their interesting ring-opening reactions upon HCl addition.[4e] Moreover, selective proton-assisted PPh_3 incorporations of the alkynyl complexes have been also observed.[4c]

We embarked upon a program to introduce arylbutadiyne chemistry with the TpRu(NO) fragment and, in this paper, deal with mono(arylbutadiynyl) TpRuCl(C≡C−C≡C−C_6H_4Me)(NO) (**1**), the bis(arylbutadiynyl) TpRu(C≡C−C≡C−$C_6H_4Me)_2$(NO) (**3**), and the unsymmetrically mixed (arylbutadiynyl)(3-hydroxyalkynyl) TpRu(C≡C−C≡C−C_6H_4Me){C≡CCPh_2(OH)}(NO) (**6**). Reactions of **1**, **3**, and **6** with PPh_3 in the presence of protic acid ($HBF_4 \cdot Et_2O$) were carried out to give β-addition products (from **1** and **3**) and α-addition product (from **6**). The latter product thermally isomerized to a novel naphthalene derivative-fused four-membered metallacycle (i.e., a ruthenacyclobuta[*b*]naphthalene). Although the obtained results, formation of β- and α-addition products themselves, are precedented,[4c,5,9] the reactivity of arylbutadiynyl complexes is worth investigating owing to the scarcity of their studies. Especially, the synthesis and reactivity of an unsymmetrically disubstituted complex such as **6**, which contains two different types of versatile alkynyl

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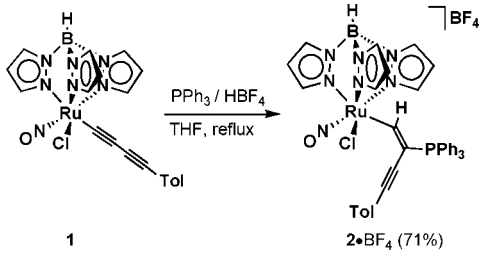
Scheme 1



groups, are interesting, in addition to the unprecedented thermal conversion to the ruthenacyclobuta[*b*]naphthalene.

Results and Discussion

Preparations of Arylbutadiynyl Complexes Containing a TpRu(NO) Fragment. Treatment of $TpRuCl_2(NO)$ with $HC{\equiv}C{-}C{\equiv}C{-}C_6H_4Me$ in the presence of Et_3N and catalytic amounts of CuI in refluxing CH_2Cl_2 afforded the mono(arylbutadiynyl) $TpRuCl(C{\equiv}C{-}C{\equiv}C{-}C_6H_4Me)(NO)$ (**1**) (35%) and the bis(arylbutadiynyl) $TpRu(C{\equiv}C{-}C{\equiv}C{-}C_6H_4Me)_2(NO)$ (**3**) (38%). The unsymmetrically mixed (arylbutadiynyl)(3-hydroxyalkynyl) $TpRu(C{\equiv}C{-}C{\equiv}C{-}C_6H_4Me)\{C{\equiv}C{-}CPh_2(OH)\}(NO)$ (**6**) was prepared from the mono(3-hydroxyalkynyl) $TpRuCl\{C{\equiv}CCPh_2(OH)\}(NO)$ with the arylbutadiyne under similar reaction conditions. The IR spectra of these complexes indicate the appearance of C≡C stretching bands in addition to ν(NO). Complexes **1**, **3**, and **6** were also characterized by ^{1}H NMR, MS spectra, and elemental analyses.

Proton-Assisted Reactions of 1 and 3 with PPh_3. Complex **1** was reacted with PPh_3 in the presence of $HBF_4\cdot Et_2O$ to give the β-phosphonioalkenyl complex (*E*)-$[TpRuCl(CH{=}C(PPh_3){-}C{\equiv}C{-}C_6H_4Me)(NO)]BF_4$ (**2**$\cdot BF_4$) in 71% yield (Scheme 1). The ^{1}H NMR spectrum of **2**$\cdot BF_4$ exhibits a characteristic vinylic proton as a doublet at δ 9.32 (J = 27 Hz) coupled with the ^{31}P nuclei. This coupling constant is comparable to those of (*E*)-$[TpRuCl(CH{=}C(PPh_3)Ph)(NO)]BF_4$[4c] and other related complexes,[5] indicating cis configuration of the vinylic proton to the phosphorus nuclei. In the $^{13}C\{^1H\}$ NMR spectrum, the ruthenium-linked α-carbon in the alkenyl moiety resonates at δ 198.5. Unfortunately, although single crystals of **2**$\cdot BF_4$ were not obtained, the phenylbutadiyne derivative (*E*)-$[TpRuCl(CH{=}C(PPh_3){-}C{\equiv}C{-}Ph)(NO)]BF_4$ (**2′**$\cdot BF_4$) crystallized satisfactorily and the molecular structure was determined by a single-crystal X-ray structural analysis.

Its ORTEP drawing and selected structural data are shown in Figure 1 and Table 1, respectively. The cis/trans C=C configuration of the moiety in the crystals is in accord with its ^{1}H NMR data in the solution state. The Ru−C10 bond distance (2.057(7) Å) is comparable to that of (*E*)-$[TpRuCl(CH{=}C(PPh_3)Ph)(NO)]BF_4$ (2.048(2) Å).[4c] The bond lengths of 1.33(1) Å (C10−C11) and 1.20(1) Å (C12−C13) are regarded to be typical C−C double and triple bonds, respectively.

Reaction of **3** with PPh_3 in the presence of HBF_4 in refluxing CH_2Cl_2 for 4 h gave the mono(β-phosphonioalkenyl) (*E*)-$[TpRu(C{\equiv}C{-}C{\equiv}C{-}C_6H_4Me)(CH{=}C(PPh_3){-}C{\equiv}C{-}C_6H_4Me)(NO)]BF_4$ (**4**$\cdot BF_4$) in 84% yield, along with a trace amount of the bis(β-phosphonioalkenyl) (*E,E*)-$[TpRu(CH{=}C(PPh_3){-}C{\equiv}C{-}C_6H_4Me)_2(NO)](BF_4)_2$ {**5**$\cdot (BF_4)_2$} (Scheme 2). Prolonged reaction time (3 days) led to enhanced formation of the latter species (34%). The ^{1}H NMR spectra of **4**$\cdot BF_4$ and **5**$\cdot (BF_4)_2$ show three and two sets of resonances for the pyrazolyl groups, respectively, and characteristic vinylic proton signals at δ 9.19 (d, J = 27 Hz) for **4**$\cdot BF_4$ and 9.05 (d, J = 28 Hz) for **5**$\cdot (BF_4)_2$. These

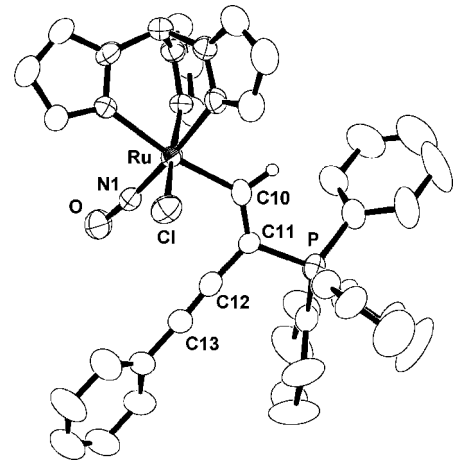
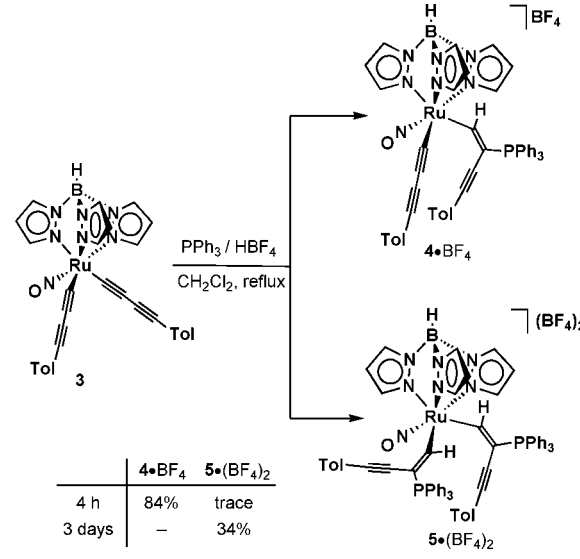


Figure 1. Molecular structure of **2′**, with thermal ellipsoids at the 40% probability level.

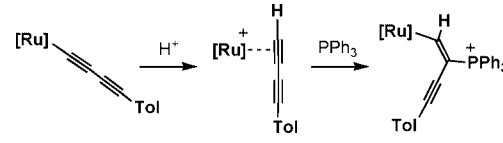
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 2′·BF$_4$

Ru−Cl	2.357(2)	O−N1	1.129(7)
Ru−N1	1.736(6)	C10−C11	1.33(1)
Ru−C10	2.057(7)	C11−C12	1.41(1)
P−C11	1.791(7)	C12−C13	1.20(1)
Ru−N1−O	171.6(6)	C10−C11−C12	125.4(7)
Ru−C10−C11	128.4(5)	C11−C12−C13	175.6(8)
P−C11−C10	121.7(6)		

Scheme 2



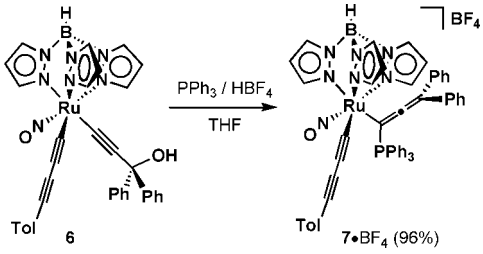
Scheme 3



coupling constants indicate the cis configuration of the protons to PPh_3, respectively.[4c] The FAB-MS spectra exhibit the parent molecular ion signals of $[\mathbf{4}]^+$ at *m/z* 886.3 and $[\mathbf{5} + BF_4]^+$ at *m/z* 1236.4.

Key intermediates in the formation of **2**$\cdot BF_4$, **4**$\cdot BF_4$, and **5**$\cdot (BF_4)_2$ would be π-alkyne species (Scheme 3). Protonation of the arylbutadiynyl group can lead to the vinylidene ($[Ru]{=}C{=}CH{-}C{\equiv}C{-}C_6H_4Me$) or butatrienylidene ($[Ru]{=}C{=}C{=}C{=}CH{-}C_6H_4Me$) intermediates.[6] But these species

Scheme 4



would rapidly isomerize to the π-alkynes, because of the presence of the strong π-accepter ligand NO^+. The electron-poor metal center tends to destabilize the vinylidene and butatrienylidene intermediates.[7] This propensity has been realized in H_2O or PPh_3 addition reactions to the alkynyl complexes TpRuCl(C≡CR)(NO).[4a,c] During the formation of these β-phosphonioalkenyl complexes, another C≡C part remains intact.

Proton-Assisted Reaction of 6 with PPh_3. The unsymmetrically mixed complex TpRu(C≡C−C≡C−C_6H_4Me){C≡C−CPh_2(OH)}(NO) (**6**) was allowed to react with PPh_3 and $HBF_4 \cdot Et_2O$ in THF at room temperature to afford the α-phosphonioallenyl [TpRu(C≡C−C≡C−C_6H_4Me){C(PPh_3)═C═CPh_2}(NO)]BF_4 (**7**·BF_4) in 96% yield (Scheme 4). When the reaction proceeded in CH_2Cl_2, column chromatographic separation gave **7**·BF_4 (63%) and a brown minor byproduct, which is unfortunately uncharacterized. The ^{1}H NMR spectrum of **7**·BF_4 exhibits the absence of a vinylic proton, which is observed for **2**·BF_4, **4**·BF_4, and **5**·$(BF_4)_2$. Furthermore, in the ^{13}C{^{1}H} NMR spectrum, characteristic signals at δ 215.7 (d, J_{CP} = 3.3 Hz, Cβ), 107.5 (d, J_{CP} = 21 Hz, Cγ), and 86.6 (d, J_{CP} = 36 Hz, Cα) are observed, indicating the allenyl skeleton. These NMR data are comparable to those of the previous α-phosphonioallenyl complex [TpRuCl{C(PPh_3)═C═CPh_2}(NO)]BF_4.[4c]

The structure of **7**·BF_4 was confirmed by a single-crystal X-ray structural analysis, and the ORTEP view of its cationic part **7** is shown in Figure 2. Selected bond lengths and angles are summarized in Table 2. Structural analysis of **7**·BF_4 determines the bond lengths of Ru1−C10, C10−C11, and C11−C12 in the allenyl group to be 2.124(2), 1.312(4), and 1.318(4) Å, respectively. Further, the C10−C11−C12 angle is 176.8(3)°.

In the formation of **7**·BF_4, protonation of the 3-hydroxyalkynyl group would induce dehydration to give the allenylidene intermediate ([Ru]═C═C═$C(Ph)_2$), and finally, addition of PPh_3 on the α carbon of the intermediate would give rise to **7**·BF_4.[8] This preference in the addition position can be attributed to the steric hindrance between PPh_3 and two phenyl groups at the γ-carbon of the allenylidene moiety.[9] A similar situation has been demonstrated in the formation of the previous α-phosphonioallenyl [TpRuCl{C(PPh_3)═C═CPh_2}(NO)]BF_4.[4c] In these reaction conditions, the arylbutadiynyl group remains intact.

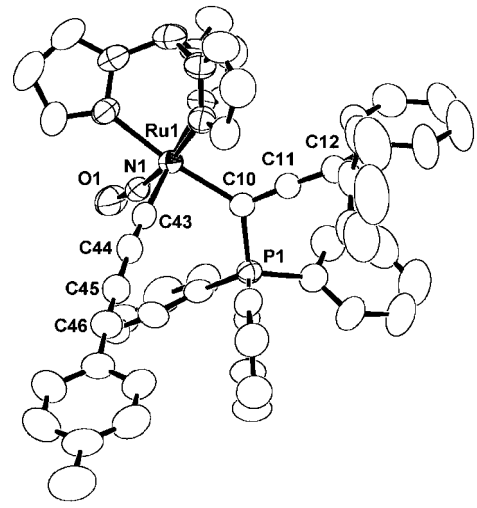
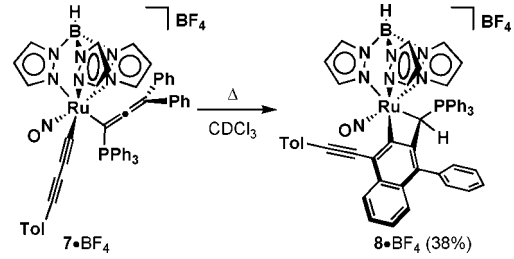


Figure 2. Molecular structure of **7**, with thermal ellipsoids at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 7·BF_4

Ru1−N1	1.735(2)	C10−C11	1.312(4)
Ru1−C10	2.124(2)	C11−C12	1.318(4)
Ru1−C43	2.013(3)	C43−C44	1.203(4)
P1−C10	1.796(3)	C44−C45	1.385(4)
O1−N1	1.154(3)	C45−C46	1.188(4)
Ru1−N1−O1	169.3(2)	P1−C10−C11	110.7(2)
Ru1−C10−P1	125.97(15)	C10−C11−C12	176.8(3)
Ru1−C10−C11	123.3(2)	C43−C44−C45	175.5(3)
Ru1−C43−C44	178.1(2)	C44−C45−C46	177.5(3)

Scheme 5



Thermal Isomerization of 7·BF_4. It is noteworthy that **7**·BF_4 thermally isomerized to an unusual four-membered metallacycle of **8**·BF_4, as shown in Scheme 5. When a $CDCl_3$ solution of **7**·BF_4 was heated for 48 h, new ^{1}H NMR signals came out, which include a conspicuous resonance at δ 4.52 (d, J = 1.7 Hz). The FAB-MS spectral observation supports an unaltered mass value (m/z) for the detected parent ion peak. The structural assignment of **8**·BF_4 was performed by an X-ray diffraction study of single crystals grown from MeOH/Et_2O (Figure 3 and Table 3). The isomerized product was determined to be the ruthena-2-PPh_3-cyclobuta[*b*]naphthalene [TpRu{CH(PPh_3)[3-Ph-8-(MeC_6H_4−C≡C)$C_{10}H_4$]}(NO)]BF_4 (**8**·BF_4).

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(8) The reaction mechanism would be that after the formation of the allenylidene intermediate, PPh_3 was initially added on the γ-carbon, followed by migration to the α-carbon. This reaction scheme has been verified in the TpRuCl{C≡C$C(Ph)_2$OH}(NO) system. See ref 4c.

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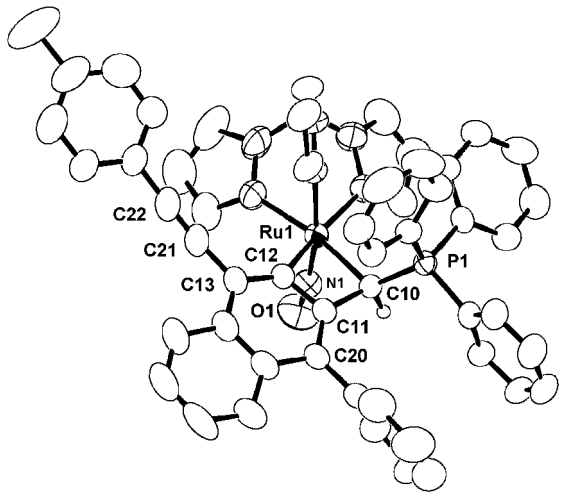
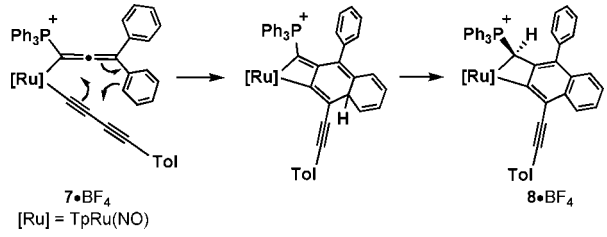


Figure 3. Molecular structure of **8**, with thermal ellipsoids at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 8·BF$_4$

Ru1−N1	1.731(4)	C10−C11	1.520(6)
Ru1−C10	2.208(4)	C11−C12	1.419(6)
Ru1−C12	2.045(4)	C11−C20	1.387(6)
P1−C10	1.786(4)	C12−C13	1.375(6)
O1−N1	1.153(6)	C21−C22	1.200(8)
Ru1−N1−O1	171.4(4)	P1−C10−C11	120.1(3)
Ru1−C10−P1	123.5(2)	C10−C11−C12	103.4(3)
Ru1−C10−C11	89.5(2)	C11−C12−C13	121.5(4)
Ru1−C12−C11	99.2(3)	C13−C21−C22	173.4(6)

Scheme 6



The molecule consists of the substituted naphthalene-fused four-membered metallacycle with Tp and NO ligands. The naphthalene possesses phenyl and arylalkynyl substituents at the 3- and 8-positions, respectively, and is fused with the metallacycle at the [*b*] position. The phosphine PPh_3 is bound to the four-membered ring at the 2-position. The bond length of Ru1−C10 (2.208(4) Å) is longer than that of Ru1−C12 (2.045(4) Å), and the C10−C11 and C11−C12 bond distances are 1.520(6) and 1.419(6) Å, respectively. The mean deviation from the least-squares plane (Ru1, C10, C11, and C12) is 0.0738 Å, and stereochemical dimensions of the naphthalic skeleton are similar to those of the free naphthalene molecule.

The formation of **8**·BF_4 would be rationalized according to Scheme 6. Thermal stimulation would lead to the [4+2] cycloaddition of two C=C bonds (the allenyl ligand and one of Ph substituents) and one C≡C bond (the arylbutadiynyl ligand), affording the intermediate, which is transformed into **8**·BF_4 via a 1,5-hydrogen shift with concomitant aromatization. Although two diastereomeric conformations are conceivable from the presence of the chiral carbon center C10, only one isomer, where PPh_3 is directed toward the Tp ligand, was obtained. The reason for its selective formation is unclear, but it is probable that the nitrogen atom of the NO ligand would assist the migration to the Cα in the transition state during the 1,5-hydrogen shift. Similar assistant behavior has been observed in our TpRu(NO) chemistry.[4e]

Conclusions

In conclusion, we carried out the PPh_3 incorporation reactions of mono(arylbutadiynyl) TpRuCl(C≡C−C≡C−C_6H_4Me)(NO) (**1**), bis(arylbutadiynyl) TpRu(C≡C−C≡C−C_6H_4Me)$_2$(NO) (**3**), and unsymmetrically mixed (arylbutadiynyl)(3-hydroxyalkynyl) TpRu(C≡C−C≡C−C_6H_4Me){C≡CCPh_2(OH)}(NO) (**6**) in the presence of HBF_4·Et_2O. For **1** and **3**, the generation of π-alkyne intermediates would lead to the β-addition products (*E*)-[TpRuCl(CH=C(PPh_3)−C≡C−C_6H_4Me)(NO)]BF_4 (**2**·BF_4), (*E*)-[TpRu(C≡C−C≡C−C_6H_4Me)(CH=C(PPh_3)−C≡C−C_6H_4Me)(NO)]BF_4 (**4**·BF_4), and (*E,E*)-[TpRu(CH=C(PPh_3)−C≡C−C_6H_4Me)$_2$(NO)]$(BF_4)_2$ {**5**·$(BF_4)_2$}. On the other hand, for **6**, α-phosphonioallenyl [TpRu(C≡C−C≡C−C_6H_4Me){C(PPh_3)=C=CPh_2}(NO)]BF_4 (**7**·BF_4) was obtained through the allenylidene intermediate. A facile dehydration process to the allenylidene has been previously shown in the similar (arylalkynyl)(3-hydroxyalkynyl) complex.[4e] Intriguingly, the substituted naphthalene-fused metallacycle [TpRu{CH(PPh_3)[3-Ph-8-(MeC_6H_4−C≡C)−$C_{10}H_4$]}(NO)]BF_4 (**8**·BF_4) was obtained by thermal isomerization of **7**·BF_4. Isolation of **8**·BF_4 would indicate a 6π-electrocyclization process and subsequent aromatization.

Experimental Section

Reactions were carried out under an atmosphere of dry dinitrogen, whereas subsequent workup was performed in air. Solvents were distilled from sodium/benzophenone ketyl (THF) or from CaH_2 (CH_2Cl_2). The starting material $TpRuCl_2(NO)$[10] and arylbutadiynes (HC≡C−C≡C−R; R = C_6H_4Me, Ph)[11] were prepared by previously reported methods. All other organic solvents and reagents were commercially available and used without further purification.

NMR spectra in $CDCl_3$ were recorded with a Varian Gemini-300 and a JEOL JNM-AL-400 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are quoted with respect to TMS and the solvent signals, respectively. ^{31}P{^{1}H} NMR spectra are referenced to an external standard of 85% H_3PO_4. Infrared spectra in KBr pellets were obtained on a JASCO FT-IR-420 spectrometer. Electron ionization mass spectra (EI-MS) and fast atom bombardment mass spectra (FAB-MS) were recorded on a JEOL JMS-700N spectrometer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400II elemental analyzer.

TpRuCl(C≡C−C≡C−C_6H_4Me)(NO) (1) and TpRu(C≡C−C≡C−C_6H_4Me)$_2$(NO) (3). To a solution of $TpRuCl_2(NO)$ (423 mg, 1.02 mmol) dissolved in CH_2Cl_2 (15 mL) were added HC≡C−C≡C−C_6H_4Me (421 mg, 3.0 mmol/CH_2Cl_2 5 mL), CuI (21.2 mg, 0.111 mmol), and Et_3N (1020 mg, 10.1 mmol), and then the mixture was refluxed for 3 h. After removal of the volatiles, the residue was separated on column chromatography of a silica gel by use of CH_2Cl_2 as an eluent to give TpRuCl(C≡C−C≡C−C_6H_4Me)(NO) (**1**) (183 mg, 35%) and TpRu(C≡C−C≡C−C_6H_4Me)$_2$(NO) (**3**) (241 mg, 38%). Complex **1**: IR: ν(BH) 2513 (w), ν(C≡C) 2193 (w), 2078 (w), ν(N≡O) 1874 (s) cm^{-1}. ^{1}H NMR: δ 8.14 (d, *J* = 2.0 Hz, 1H of pz), 7.98 (d, *J* = 1.7 Hz, 1H of pz), 7.87 (d, *J* = 1.7 Hz, 1H of pz), 7.78 (d, *J* = 2.3 Hz, 1H of pz), 7.76 (d, *J* = 2.2 Hz, 1H of pz), 7.54 (d, *J* = 2.1 Hz, 1H

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(11) (a) Dabdoub, M. J.; Baroni, A. C. M.; Lenardão, E. J.; Gianeti, T. R.; Hurtado, G. R. *Tetrahedron* **2001**, *57*, 4271–4276. (b) Brandsma, L., *Synthesis of Acetylenes, Allenes and Cumulenes, Methods and Techniques*; Elsevier, Ltd.: Oxford, 2004.

of pz), 7.33 (d, J = 8.0 Hz, 2H of C_6H_4Me), 7.08 (d, J = 8.0 Hz, 2H of C_6H_4Me), 6.41 (t, J = 2.6 Hz, 1H of pz), 6.40 (t, J = 2.4 Hz, 1H of pz), 6.22 (t, J = 2.2 Hz, 1H of pz), 2.33 (s, 3H of Me). $^{13}C\{^1H\}$ NMR: δ 145.1 (s, pz), 143.9 (s, pz), 142.3 (s, pz), 138.3 (s, C_6H_4Me), 136.8 (s, pz), 136.0 (s, pz), 135.0 (s, pz), 132.4 (s, C_6H_4Me), 128.9 (s, C_6H_4Me), 119.9 (s, C_6H_4Me), 107.7 (s, pz), 107.2 (s, pz), 106.4 (s, pz), 97.8 (s, C≡C), 92.9 (s, C≡C), 75.2 (s, C≡C), 74.0 (s, C≡C), 21.5 (s, C_6H_4*Me*). EI-MS (*m*/*z*): 519 ($[M]^+$), 489 ($[M - (NO)]^+$), 385 ($[M - (pz)_2]^+$). Anal. Calcd for $C_{20}H_{17}N_7BClORu$: C, 46.31; H, 3.30; N, 18.90. Found: C, 46.63; H, 3.19; N, 18.44. Complex **3**: IR: ν(BH) 2512 (w), ν(C≡C) 2193 (w), 2075 (w), ν(N≡O) 1875 (s) cm^{-1}. ^1H NMR: δ 8.15 (d, J = 2.2 Hz, 1H of pz), 7.95 (d, J = 2.0 Hz, 2H of pz), 7.74 (d, J = 2.4 Hz, 2H of pz), 7.50 (d, J = 2.2 Hz, 1H of pz), 7.34 (d, J = 8.1 Hz, 4H of C_6H_4Me), 7.07 (d, J = 8.2 Hz, 4H of C_6H_4Me), 6.38 (t, J = 2.2 Hz, 2H of pz), 6.19 (t, J = 2.3 Hz, 1H of pz), 2.33 (s, 6H of Me). $^{13}C\{^1H\}$ NMR: δ 145.8 (s, pz), 143.1 (s, pz), 138.1 (s, C_6H_4Me), 135.9 (s, pz), 135.0 (s, pz), 132.3 (s, C_6H_4Me), 128.9 (s, C_6H_4Me), 120.1 (s, C_6H_4Me), 107.0 (s, pz), 106.2 (s, pz), 99.5 (s, C≡C), 93.2 (s, C≡C), 75.6 (s, C≡C), 73.6 (s, C≡C), 21.5 (s, C_6H_4*Me*). EI-MS (*m*/*z*): 623 ($[M]^+$), 593 ($[M - (NO)]^+$). Anal. Calcd for $C_{31}H_{24}N_7BORu$: C, 59.82; H, 3.89; N, 15.75. Found: C, 59.33; H, 3.72; N, 15.53.

(*E*)-[TpRuCl(CH═C(PPh$_3$)−C≡C−C$_6$H$_4$Me)(NO)]BF$_4$ (2·BF$_4$). To a THF solution (5 mL) of TpRuCl(C≡C−C≡C−C_6H_4Me)(NO) (**1**) (50.3 mg, 0.097 mmol) and PPh_3 (130 mg, 0.496 mmol) was added $HBF_4 \cdot Et_2O$ (65.8 μL, 0.48 mmol), and the mixture was refluxed overnight. After the protic acid remaining in the solution was quenched by a solid powder of $NaHCO_3$, the mixture was filtered and the filtrate was evaporated to dryness. The residue was chromatographed on a silica gel column using CH_2Cl_2/acetone (10:1) as an eluent to give (*E*)-[TpRuCl(CH═C(PPh$_3$)−C≡C−C_6H_4Me)(NO)]BF_4 (**2**·BF_4) (60.2 mg, 71%). IR: ν(BH) 2529 (w), ν(C≡C) 2197 (m), ν(N≡O) 1855 (s) cm^{-1}. ^1H NMR: δ 9.32 (d, J_{PH} = 27 Hz, 1H of RuC*H*), 7.96 (d, J = 2.1 Hz, 1H of pz), 7.89−7.63 (m, 4H of pz and 15H of Ph), 7.32 (d, J = 2.2 Hz, 1H of pz), 7.08 (d, J = 8.1 Hz, 2H of C_6H_4Me), 6.98 (d, J = 8.1 Hz, 2H of C_6H_4Me), 6.57 (t, J = 2.3 Hz, 1H of pz), 6.36 (t, J = 2.2 Hz, 1H of pz), 6.15 (t, J = 2.3 Hz, 1H of pz), 2.32 (s, 3H of Me). $^{13}C\{^1H\}$ NMR: δ 198.5 (s, Ru*C*H), 143.8 (s, pz), 141.7 (s, pz), 141.5 (s, pz), 140.2 (s, C_6H_4Me), 137.7 (s, pz), 136.4 (s, pz), 136.3 (s, pz), 135.3 (d, J = 3.3 Hz, P*Ph$_3$*), 134.3 (d, J = 10 Hz, P*Ph$_3$*), 131.2 (d, J = 2.0 Hz, C_6H_4Me), 130.3 (d, J = 13 Hz, P*Ph$_3$*), 129.3 (s, C_6H_4Me), 118.1 (d, J = 88 Hz, P*Ph$_3$*), 117.7 (d, J = 3.4 Hz, C_6H_4Me), 109.5 (d, J = 80 Hz, RuCH═*C*), 108.6 (s, pz), 107.1 (s, pz), 106.6 (s, pz), 97.4 (d, J = 8.1 Hz, C≡C), 85.4 (d, J = 17 Hz, C≡C), 21.5 (s, C_6H_4*Me*). $^{31}P\{^1H\}$ NMR: δ 20.6 (s). FAB-MS (*m*/*z*): 782.2 ($[M]^+$), 380.0 ($[TpRuCl(NO)]^+$). Anal. Calcd for $C_{38}H_{33}N_7B_2ClF_4OPRu$: C, 52.53; H, 3.83; N, 11.29. Found: C, 52.59; H, 3.81; N, 11.44.

(*E*)-[TpRu(C≡C−C≡C−C$_6$H$_4$Me)(CH═C(PPh$_3$)−C≡C−C$_6$H$_4$Me)(NO)]BF$_4$ (4·BF$_4$) and (*E,E*)-[TpRu(CH═C(PPh$_3$)−C≡C−C$_6$H$_4$Me)$_2$(NO)](BF$_4$)$_2$ {5·(BF$_4$)$_2$}. Bis(arylbutadiynyl) TpRu(C≡C−C≡C−C_6H_4Me)$_2$(NO) (**3**) (30.4 mg, 0.0488 mmol) in CH_2Cl_2 (5 mL) was treated with PPh_3 (255 mg, 0.972 mmol) and $HBF_4 \cdot Et_2O$ (131.5 μL, 0.96 mmol), and the mixture was refluxed for 4 h. After addition of $NaHCO_3$ powder, filtration, and evaporation of the filtrate, the residue was chromatographed on silica gel with CH_2Cl_2/acetone (50:1) to yield (*E*)-[TpRu(C≡C−C≡C−C_6H_4Me)(CH═C(PPh$_3$)−C≡C−C_6H_4Me)(NO)]BF_4 (**4**·BF_4) (40 mg, 84%) and a trace amount of (*E,E*)-[TpRu(CH═C(PPh$_3$)−C≡C−C_6H_4Me)$_2$(NO)](BF$_4$)$_2$ {**5**·(BF$_4$)$_2$}. In analogous procedures to the above-mentioned reaction, the reaction mixture, containing **3** (69 mg, 0.111 mmol), PPh_3 (585 mg, 2.23 mmol), and $HBF_4 \cdot Et_2O$ (304 μl, 2.22 mmol), was refluxed for 3 days to give **5**·(BF$_4$)$_2$ (49.6 mg, 34%). Complex **4**·BF_4: IR: ν(BH) 2497 (w), ν(C≡C) 2193 (w), 1957 (w), ν(N≡O) 1868 (s) cm^{-1}. ^1H NMR: δ 9.19 (d, J_{PH} = 27 Hz, 1H of RuC*H*), 7.96 (d, J = 1.9 Hz, 1H of pz), 7.86 (d, J = 1.9 Hz, 2H of pz), 7.84−7.72 (m, 1H of pz and 15H of Ph), 7.58 (d, J = 2.2 Hz, 1H of pz), 7.37 (d, J = 8.1 Hz, 2H of C_6H_4Me), 7.34 (d, J = 2.1 Hz, 1H of pz), 7.13 (d, J = 8.0 Hz, 2H of C_6H_4Me), 7.08 (d, J = 2.0 Hz, 4H of C_6H_4Me), 6.52 (t, J = 2.3 Hz, 1H of pz), 6.35 (t, J = 2.2 Hz, 1H of pz), 6.11 (t, J = 2.3 Hz, 1H of pz), 2.36 (s, 3H of Me), 2.33 (s, 3H of Me). $^{13}C\{^1H\}$ NMR: δ 198.5 (s, Ru*C*H), 143.0 (s, pz), 142.5 (s, pz), 142.2 (s, pz), 140.0 (s, C_6H_4Me), 138.4 (s, C_6H_4Me), 136.8 (s, pz), 136.2 (s, pz), 136.1 (s, pz), 135.2 (d, J = 3.1 Hz, P*Ph$_3$*), 134.3 (d, J = 9.4 Hz, P*Ph$_3$*), 132.1 (s, C_6H_4Me), 131.2 (d, J = 2.5 Hz, C_6H_4Me), 130.3 (d, J = 13 Hz, P*Ph$_3$*), 129.3 (s, C_6H_4Me), 129.0 (s, C_6H_4Me), 119.7 (s, C_6H_4Me), 118.4 (d, J = 88 Hz, P*Ph$_3$*), 118.0 (d, J = 2.5 Hz, C_6H_4Me), 108.8 (d, J = 80 Hz, RuCH═*C*), 107.8 (s, pz), 107.0 (s, pz), 106.5 (s, pz), 100.3 (s, C≡C), 97.3 (d, J = 8.1 Hz, C≡C), 93.9 (s, C≡C), 86.4 (d, J = 18 Hz, C≡C), 75.3 (s, C≡C), 73.7 (s, C≡C), 21.7 (s, C_6H_4*Me*), 21.6 (s, C_6H_4*Me*). $^{31}P\{^1H\}$ NMR: δ 20.3 (s). FAB-MS (*m*/*z*): 886.3 ($[M]^+$). Anal. Calcd for $C_{49}H_{40}N_7B_2F_4OPRu$: C, 60.51; H, 4.15; N, 10.08. Found: C, 60.34; H, 4.06; N, 9.88. Complex **5**·(BF$_4$)$_2$: IR: ν(BH) 2513 (w), ν(C≡C) 2193 (w), ν(N≡O) 1862 (s) cm^{-1}. ^1H NMR: δ 9.05 (d, J_{PH} = 28 Hz, 2H of RuC*H*), 7.91 (d, J = 1.6 Hz, 2H of pz), 7.82−7.77 (m, 2H of pz and 6H of Ph), 7.69−7.59 (m, 24H of Ph), 7.53 (d, J = 2.0 Hz, 1H of pz), 6.94−6.90 (m, 1H of pz and 4H of C_6H_4Me), 6.78 (d, J = 8.0 Hz, 4H of C_6H_4Me), 6.43 (t, J = 2.0 Hz, 2H of pz), 6.30 (t, J = 2.1 Hz, 1H of pz), 2.28 (s, 6H of Me). $^{13}C\{^1H\}$ NMR: δ 196.3 (s, Ru*C*H), 142.3 (s, pz), 140.8 (s, pz), 140.0 (s, C_6H_4Me), 136.9 (s, pz), 136.6 (s, pz), 135.3 (d, J = 2.5 Hz, P*Ph$_3$*), 134.0 (d, J = 9.4 Hz, P*Ph$_3$*), 131.0 (d, J = 2.5 Hz, C_6H_4Me), 130.3 (d, J = 13 Hz, P*Ph$_3$*), 129.2 (s, C_6H_4Me), 118.0 (d, J = 87 Hz, P*Ph$_3$*), 117.6 (d, J = 2.9 Hz, C_6H_4Me), 110.3 (d, J = 78 Hz, RuCH═*C*), 107.7 (s, pz), 107.6 (s, pz), 98.3 (d, J = 8.2 Hz, C≡C), 86.4 (d, J = 18 Hz, C≡C), 21.6 (s, C_6H_4*Me*). $^{31}P\{^1H\}$ NMR: δ 21.1 (s). FAB-MS (*m*/*z*): 1236.4 ($[M^{2+} + BF_4^-]^+$), 1149.4 ($[M]^+$), 886.3 ($[M - (PPh_3) - 1]^+$), 747.2 ($[M - (CH═C(PPh_3)−C≡C−C_6H_4Me)]^+$). Anal. Calcd for $C_{67}H_{56}N_7B_3F_8OP_2Ru$: C, 60.84; H, 4.27; N, 7.41. Found: C, 60.61; H, 4.27; N, 7.03.

TpRu(C≡C−C≡C−C$_6$H$_4$Me){C≡CCPh$_2$(OH)}(NO) (6). Arylbutadiyne HC≡C−C≡C−C_6H_4Me (430 mg, 3.07 mmol), CuI (8.20 mg, 0.043 mmol), and Et_3N (316 mg, 3.12 mmol) were added to a CH_2Cl_2 solution (15 mL) of TpRuCl{C≡CC(Ph)$_2$OH}(NO) (232 mg, 0.395 mmol). The solution was refluxed for 3 h and was concentrated to dryness. The residue was chromatographed on a silica gel column using CH_2Cl_2 as an eluent to give TpRu(C≡C−C≡C−C_6H_4Me){C≡CCPh$_2$(OH)}(NO) (**6**) (176 mg, 65%). IR: ν(BH) 2496 (w), ν(C≡C) 2191 (w), 2137 (w), 2075 (w), ν(N≡O) 1872 (s) cm^{-1}. ^1H NMR: δ 8.00 (d, J = 2.0 Hz, 1H of pz), 7.94 (d, J = 1.9 Hz, 1H of pz), 7.80 (d, J = 1.9 Hz, 1H of pz), 7.78−7.71 (m, 6H of Ph), 7.46 (d, J = 2.3 Hz, 1H of pz), 7.35 (d, J = 8.1 Hz, 2H of C_6H_4Me), 7.30−7.14 (m, 2H of pz and 4H of Ph), 7.07 (d, J = 8.0 Hz, 2H of C_6H_4Me), 6.34 (t, J = 2.2 Hz, 1H of pz), 6.29 (t, J = 2.1 Hz, 1H of pz), 6.05 (t, J = 2.2 Hz, 1H of pz), 2.95 (s, 1H of OH), 2.32 (s, 3H of Me). $^{13}C\{^1H\}$ NMR: δ 147.1 (s, Ph), 147.0 (s, Ph), 145.6 (s, pz), 142.9 (s, pz), 142.9 (s, pz), 137.9 (s, C_6H_4Me), 135.7 (s, pz), 135.7 (s, pz), 134.7 (s, pz), 132.2 (s, C_6H_4Me), 128.8 (s, C_6H_4Me), 127.7 (s, Ph), 127.7 (s, Ph), 126.7 (s, Ph), 126.6 (s, Ph), 126.2 (s, Ph), 126.2 (s, Ph), 120.2 (s, C_6H_4Me), 112.5 (s, C≡C), 106.9 (s, pz), 106.7 (s, pz), 105.7 (s, pz), 100.7 (s, C≡C), 96.1 (s, C≡C), 93.2 (s, C≡C), 75.7 (s, C≡C), 75.2 (s, *C*Ph$_2$(OH)), 73.4 (s, C≡C), 21.6 (s, C_6H_4*Me*). FAB-MS (*m*/*z*): 692.2 ($[M + 1]^+$), 674.2 ($[M - (OH)]^+$). Anal. Calcd for $C_{35}H_{28}N_7BO_2Ru$: C, 60.88; H, 4.09; N, 14.20. Found: C, 61.19; H, 3.93; N, 13.79.

[TpRu(C≡C−C≡C−C$_6$H$_4$Me){C(PPh$_3$)═C═CPh$_2$}(NO)]BF$_4$ (7·BF$_4$). A mixture of TpRu(C≡C−C≡C−C_6H_4Me){C≡CCPh$_2$-(OH)}(NO) (**6**) (52.8 mg, 0.0765 mmol) and PPh_3 (99.3 mg, 0.379 mmol) in THF (5 mL) was treated with $HBF_4 \cdot Et_2O$ (49.6 μL, 0.362

Table 4. Crystal Data for 2′·BF_4, 7·BF_4·EtOH, and 8·BF_4·0.5MeOH

	2′·BF_4	7·BF_4·EtOH	8·BF_4·0.5MeOH
formula	$C_{37}H_{31}N_7OB_2ClF_4PRu$	$C_{53}H_{42}N_7OB_2F_4PRu$·EtOH	$C_{53}H_{42}N_7OB_2F_4PRu$·0.5MeOH
molecular wt	854.81	1068.69	1038.64
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pbcn* (No. 60)	$P2_1/n$ (No. 14)	*Pbcn* (No. 60)
color	pink	red	red
a (Å)	14.667(2)	19.968(4)	28.9973(14)
b (Å)	20.8516(9)	12.346(2)	16.8723(9)
c (Å)	25.4182(6)	21.254(4)	21.1493(11)
α (deg)			
β (deg)		95.1910(5)	
γ (deg)			
V (Å^3)	7773.8(9)	5218.0(17)	10347.3(9)
Z	8	4	8
ρ_{calcd} (g cm^{-3})	1.461	1.360	1.333
μ (cm^{-1})	5.72	3.936	3.942
$2\theta_{max}$ (deg)	55.0	55.0	55.0
no. of unique rflns	8665	11 879	11 847
R_{int}	0.073	0.030	0.060
no. of params	467	683	681
R_1[a] [$I > 2\sigma(I)$]	0.072	0.0516	0.0601
R[b] (all data)	0.151	0.0732	0.1201
R_w[c]	0.202	0.1509	0.1883
GOF[d]	0.93	1.002	1.005

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R = \sum|F_o^2 - F_c^2|/\sum F_o^2$. [c] $R_w = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [d] GOF $= [\{\sum w(|F_o| - |F_c|)^2\}/(N_o - N_p)]^{1/2}$, where N_o and N_p denote the number of observations and parameters.

mmol). After stirring for 10 min, followed by addition of $NaHCO_3$ powder, the mixture was filtered and evaporated to dryness. The residue was separated on column chromatography (SiO_2) to give [TpRu(C≡C−C≡C−C_6H_4Me){C(PPh_3)=C=CPh_2}(NO)]BF_4(**7**·BF_4) (75.5 mg, 96%) from a CH_2Cl_2/acetone (20:1) eluent. The use of CH_2Cl_2 reaction solvent under the same reaction conditions (**6** (30.1 mg, 0.0436 mmol), PPh_3 (117 mg, 0.446 mmol), and HBF_4·Et_2O (60 μL, 0.438 mmol)) gave rise to **7**·BF_4 (28.1 mg, 63%) and an uncharacterized brown powder (13.6 mg). IR: ν(BH) 2513 (w), ν(C≡C) 2189 (w), 2071 (w), ν(N≡O) 1866 (s) cm^{-1}. ^{1}H NMR: δ 7.98 (d, J = 2.0 Hz, 1H of pz), 7.94−7.89 (m, 6H of aryl), 7.83 (d, J = 2.2 Hz, 1H of pz), 7.69−7.65 (m, 3H of aryl), 7.63 (d, J = 2.3 Hz, 1H of pz), 7.60 (d, J = 1.8 Hz, 1H of pz), 7.59−7.55 (m, 1H of pz and 6H of aryl), 7.50 (d, J = 2.0 Hz, 1H of pz), 7.28−7.13 (m, 10H of aryl), 6.53 (t, J = 2.3 Hz, 1H of pz), 6.49−6.47 (m, 2H of aryl), 6.40 (d, J = 7.9 Hz, 2H of C_6H_4Me), 6.23 (t, J = 2.3 Hz, 1H of pz), 5.86 (t, J = 2.3 Hz, 1H of pz), 2.38 (s, 3H of Me). ^{13}C{^{1}H} NMR: δ 215.7 (d, J = 3.3 Hz, Ru−C=*Cβ*=C), 145.4 (s, pz), 144.6 (s, pz), 142.2 (s, pz), 138.5 (s, aryl), 136.5 (s, pz), 136.0 (s, pz), 135.8 (s, pz), 134.7 (d, J = 9.8 Hz, P*Ph*$_3$), 134.1 (d, J = 3.2 Hz, P*Ph*$_3$), 132.0 (s, *C*$_6$H$_4$Me), 129.6 (d, J = 12 Hz, P*Ph*$_3$), 129.0 (s, aryl), 128.9 (d, J = 4.6 Hz, P*Ph*$_3$), 128.4 (s, aryl), 128.3 (s, aryl), 128.0 (s, aryl), 128.0 (s, aryl), 128.0 (s, aryl), 127.9 (s, aryl), 122.0 (s, aryl), 121.2 (s, aryl), 119.6 (s, aryl), 108.4 (s, pz), 107.5 (d, J = 21 Hz, Ru−C=C=*Cγ*), 107.0 (s, pz), 106.5 (s, pz), 101.9 (d, J = 2.5 Hz, C≡C), 98.4 (s, C≡C), 86.6 (d, J = 36 Hz, Ru-*C*α=C=C), 74.8 (s, C≡C), 74.6 (s, C≡C), 21.7 (s, C$_6$H$_4$*Me*). ^{31}P{^{1}H} NMR: δ 27.7 (s). FAB-MS (*m*/*z*): 936.3 ([M]$^+$), 674.2 ([M − (PPh_3)]$^+$). Anal. Calcd for $C_{53}H_{42}N_7B_2F_4OPRu$: C, 62.25; H, 4.14; N, 9.59. Found: C, 61.83; H, 4.34; N, 9.44.

[TpRu{CH(PPh_3)[3-Ph-8-(MeC_6H_4−C≡C)−$C_{10}H_4$]}(NO)]BF_4 (8·BF_4). A solution of [TpRu(C≡C−C≡C−C_6H_4Me){C(PPh_3)=C=CPh_2}(NO)]BF_4 (**7**·BF_4) (30.8 mg, 0.0301 mmol) in $CDCl_3$ was heated at 55 °C for 48 h and then was evaporated. The residue was crystallized from MeOH/ether to afford [TpRu{CH(PPh_3)[3-Ph-8-(MeC_6H_4−C≡C)−$C_{10}H_4$]}(NO)]BF_4 (**8**·BF_4) (11.8 mg, 38%). IR: ν(BH) 2516 (m), ν(C≡C) 2197 (w), 2071 (w), ν(N≡O) 1850 (s) cm^{-1}. ^{1}H NMR: δ 8.06 (d, J = 1.9 Hz, 1H of pz), 7.96 (d, J = 2.1 Hz, 1H of pz), 7.82 (d, J = 1.1 Hz, 1H of aryl), 7.78 (d, J = 2.2 Hz, 2H of pz), 7.73 (d, J = 2.6 Hz, 1H of pz), 7.72−7.69 (m, 3H of aryl), 7.43−7.37 (m, 6H of aryl), 7.23−7.18 (m, 4H of aryl), 7.13−7.06 (m, 5H of aryl), 7.01−6.94 (m, 6H of aryl), 6.86 (d, J = 7.2 Hz, 1H of aryl), 6.71 (d, J = 8.0 Hz, 2H of C_6H_4Me), 6.27 (t, J = 2.3 Hz, 1H of pz), 6.09 (t, J = 2.2 Hz, 1H of pz), 6.06 (d, J = 1.9 Hz, 1H of pz), 5.92 (t, J = 2.2 Hz, 1H of pz), 4.52 (d, J = 1.7 Hz, 1H of RuC*H*), 2.36 (s, 3H of Me). ^{13}C{^{1}H} NMR: δ 187.3 (d, J = 3.1 Hz, aryl), 144.5 (d, J = 3.1 Hz, aryl), 144.2 (s, pz), 142.2 (s, pz), 142.2 (s, pz), 138.8 (s, aryl), 138.6 (d, J = 21 Hz, P*Ph*$_3$), 137.2 (s, pz), 136.1 (s, pz), 135.5 (s, pz), 134.4 (d, J = 3.1 Hz, P*Ph*$_3$), 133.4 (d, J = 10 Hz, P*Ph*$_3$), 131.4 (s, aryl), 129.9 (s, aryl), 129.8 (d, J = 13 Hz, P*Ph*$_3$), 129.1 (s, aryl), 128.7 (s, aryl), 128.6 (s, aryl), 128.0 (s, aryl), 127.6 (s, aryl), 127.2 (s, aryl), 126.8 (s, *C*$_6$H$_4$Me), 125.9 (s, aryl), 122.7 (d, J = 1.7 Hz, aryl), 122.0 (s, aryl), 121.1 (s, aryl), 119.5 (s, aryl), 110.8 (d, J = 42 Hz, aryl), 107.1 (s, pz), 107.0 (s, pz), 106.4 (s, pz), 98.0 (s, C≡C), 87.8 (d, J = 4.2 Hz, C≡C), 50.4 (d, J = 4.2 Hz, Ru-*C*αH), 21.6 (s, C$_6$H$_4$*Me*). ^{31}P{^{1}H} NMR: δ 12.6 (s). FAB-MS (*m*/*z*): 936.3 ([M]$^+$). Anal. Calcd for $C_{53}H_{42}B_2F_4N_7OPRu$·0.5(MeOH): C, 61.87; H, 4.27; N, 9.44. Found: C, 61.45; H, 4.11; N, 9.51.

X-ray Crystal Structure Determinations. Crystal data and refinement parameters for the structurally characterized complexes are summarized in Table 4. Single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/AcOEt for 2′·BF_4, EtOH/ether for **7**·BF_4·EtOH, and MeOH/ether for **8**·BF_4·0.5MeOH. Diffraction data were collected at room temperature on a Rigaku AFC7 diffractometer equipped with a MSC/ADSC Quantum CCD (2′·BF_4) or Rigaku Mercury CCD area detector (**7**·BF_4·EtOH and **8**·BF_4·0.5MeOH) by using graphite-monochromated Mo Kα radiation. Seven (2′·BF_4) or six (**7**·BF_4·EtOH and **8**·BF_4·0.5MeOH) preliminary data frames were measured at 0.5° increments of ω, in order to assess the crystal quality and preliminary unit cell parameters. The intensity images were obtained at the exposure rate of 70 s/deg (2′·BF_4) and 53.3 s/deg (**7**·BF_4·EtOH and **8**·BF_4·0.5MeOH). The frame data were integrated using the MSC d*TREK program package (Quantum CCD) or the Rigaku CrystalClear program package (Mercury CCD), and the data sets were corrected for absorption using the REQAB program.

The calculations were performed with the TEXSAN (2′·BF_4) or the CrystalStructure (**7**·BF_4·EtOH and **8**·BF_4·0.5MeOH) software package. The structures were solved by direct methods (SIR92 or SIR97) and refined on F^2 by full-matrix least-squares methods. For 2′·BF_4, each asymmetric unit carries one entire molecule (2′) along with two halves of BF_4. All non-hydrogen atoms

except for one-half of BF_4 were refined anisotropically. For the BF_4 anion, the boron atom was isotropically refined and the florine atoms were fixed. In the case of **7**·BF_4·EtOH, the oxygen atom of the EtOH solvent molecule was disordered with occupancy factors of 0.7/0.3. All non-hydrogen atoms except for the EtOH solvent molecule were refined anisotropically. On the other hand, the structure of **8**·BF_4 contains a half of MeOH solvent molecule in each asymmetric unit, whose carbon atom was disordered with occupancy factors of 0.5/0.5. All non-hydrogen atoms were refined anisotropically. For all the structures, the hydrogen atoms were put at calculated positions with C−H distances of 0.97 Å, except for those of B−H, while the solvent molecules of **7**·BF_4·EtOH and **8**·BF_4·0.5MeOH were not included in the calculations.

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Supporting Information Available: CIF files for **2′**·BF_4, **7**·BF_4·EtOH, and **8**·BF_4·0.5MeOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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