Synthesis, Structure, and Reactivities of the η^1:η^6-μ_2-Aryl Alkynyl Diruthenium Complex. X-Ray Structure of [Cp(PPh$_3$)$_2$Ru(η^1:η^6-μ_2-C≡CC$_6$H$_4$Me-*p*)RuCp*]PF$_6$ (Cp = η^5-C$_5$H$_5$, Cp* = η^5-C$_5$Me$_5$)

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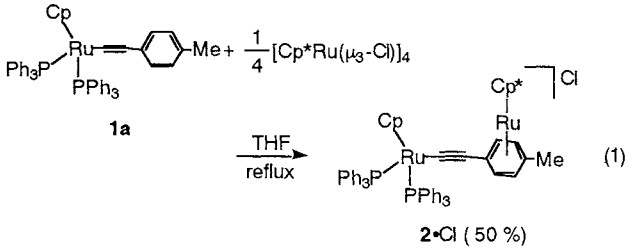
Preparation of a η^1:η^6-μ_2-aryl alkynyl diruthenium complex [Cp(PPh$_3$)$_2$Ru(η^1:η^6-μ_2-C≡CC$_6$H$_4$Me-*p*)RuCp*]Cl (**2**•Cl) [Cp = η^5-C$_5$H$_5$, Cp* = η^5-C$_5$Me$_5$] and its reactions with electrophile or CO are reported. The structure of **2**•PF$_6$ has been determined by X-ray crystallography.

Reactions of arenes with organometallic species to form η^6-arene complexes have found numerous application in organic synthesis.[1,2] Recently conversion of the mononuclear η^6–arene compounds to the dinuclear η^1:η^6-μ_2-structures offers a new set of polynuclear complexes with σ, π-bridging ligands.[3] This process proceeds via initial lithiation of the coordinated arene and subsequent reaction with organometallic compounds having halogen ligands. Another route involves treatment of η^6-haloarene complexes with anionic organometallic nucleophiles. Here we report alternative approach to the σ,π-bridging system containing a η^6-aryl group, which includes the reaction of an aryl alkynyl complex with a coordinatively unsaturated species to give a dinuclear η^1:η^6-μ_2-aryl alkynyl complex.

A dark red solution of a mixture of Cp(PPh$_3$)$_2$Ru-(C≡CC$_6$H$_4$Me-*p*) (**1a**) and [Cp*Ru(μ_3-Cl)]$_4$ (molar ratio, 4 : 1) in refluxing THF gradually turned to a yellow-brown suspension. Work up of the reaction mixture resulted in the isolation of the diruthenium η^1:η^6-μ_2-alkynyl complex [Cp(PPh$_3$)$_2$Ru(η^1:η^6-μ_2-C≡CC$_6$H$_4$Me-*p*)RuCp*]•Cl (**2**•Cl) in 50% yield, which was spectroscopically characterized (eq. 1).[4,5] The molecular structure of **2**•Cl was established by X-ray structural analysis of the anion-exchanged complex **2**•PF$_6$.[6]



(1)

The ^{1}H NMR spectrum of **2**•Cl exhibits two singlets at δ 4.36 and 1.95 ppm assigned to the Cp and Cp* protons, respectively, together with the signals of the PPh$_3$ ligands. The coordination of Cp*Ru$^+$ moiety to the tolyl part of **1a** caused the characteristic upfield shift; the tolyl protons are observed at δ 5.82 and 5.23 (2H each, J = 6.1 Hz) in an ABq pattern. Similar upfield shift was observed in the mononuclear η^6-coordinated arene complexes.[1] The IR spectrum of **2**•Cl shows a $\nu_{C\equiv C}$ absorption at 2071 cm^{-1}, which is well consistent with that observed for the parent alkynyl complex **1a**.

An ORTEP drawing of the **2**$^+$ cation is given in Figure 1, which clearly shows the dinuclear structure where two Ru atoms are bridged by the η^1:η^6-μ_2-C≡CC$_6$H$_4$Me-*p* group. Almost linear alkynyl moiety (Ru(1)-C(1)-C(2), 175.6(4)°; C(1)-C(2)-C(3), 174.8(5)°) terminally bound to the "Cp(PPh$_3$)$_2$Ru" unit coordinates to the "Cp*Ru" fragment in a η^6-manner through its tolyl ring. The distance of carbon-carbon triple bond (C(1)-C(2), 1.200(6) Å) is apparently shorter than that reported for Cp(PPh$_3$)$_2$Ru(η^1:η^2-μ_2-C≡CPh)CuCl (1.242(13) Å)[7] or CpRu(PMe$_3$)$_2$(η^1:η^2-μ_2-C≡CH)WCp(CO)(η^2-PhC≡CPh) (1.25(2) Å),[8] and compares well with the values observed for terminal alkynyl complexes such as Cp(PPh$_3$)$_2$Ru(C≡CPh) (**1b**) (1.214(7) Å).[9] The Ru-Ru distance of 6.36 Å clearly indicates the absence of bonding interaction between the two Ru atoms. The characteristic feature of the structure of **2** is that the aryl alkynyl ligand bridges two metal centers not in a common η^1:η^2-fashion but in a η^1:η^6-manner, presumably due to the steric

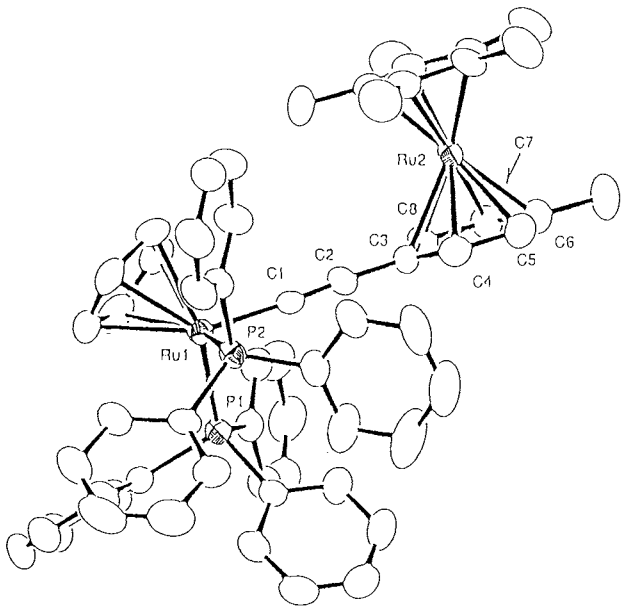


Figure 1. An ORTEP drawing of the **2**$^+$ cation. Selected bond distances (Å) and angles (°); Ru(1)-C(1) 1.997(4), Ru(1)-P(1) 2.297(1), Ru(1)-P(2) 2.311(1), Ru(2)-C(3) 2.272(4), Ru(2)-C(4) 2.212(5), Ru(2)-C(5) 2.203(5), Ru(2)-C(6) 2.232(5), Ru(2)-C(7) 2.206(5), Ru(2)-C(8) 2.197(4), C(1)-C(2) 1.200(6), C(2)-C(3) 1.428(6); P(1)-Ru(1)-C(1) 89.9(1), P(2)-Ru(1)-C(1) 86.6(1), Ru(1)-C(1)-C(2) 175.6(4), C(1)-C(2)-C(3) 174.8(5).

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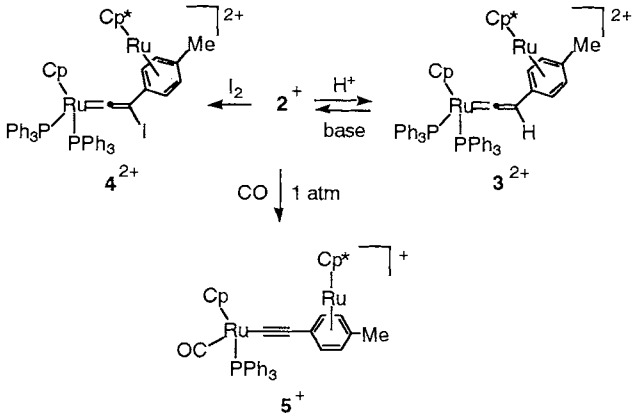
hinderance around the Ru atom in **1a**. The related η^1:η^5-μ_2-alkynyl complex $Cp(PPh_3)_2Ru(\eta^1{:}\eta^5\text{-}\mu_2\text{-}C{\equiv}CC_5H_4)MCp$ (M = Fe, Ru) was recently prepared by treatment of $Cp(PPh_3)_2RuCl$ with ferrocenyl- or ruthenocenylacetylene.[10]

Addition of electrophiles to $\mathbf{2}^+$ produced the corresponding dinuclear vinylidene complexes (Scheme 1). Thus, protonation of **2**•OTf (OTf = OSO_2CF_3)[12] with HOTf gave $[Cp(PPh_3)_2Ru(\eta^1{:}\eta^6\text{-}\mu_2\text{-}C{=}CHC_6H_4Me\text{-}p)RuCp^*]$•$[OTf]_2$ (**3**•$[OTf]_2$), which was isolated as orange plates in 93% yield and spectroscopically characterized (Scheme 1).[12,13] The ^1H NMR spectrum of **3**•$[OTf]_2$ shows a singlet at δ 5.02 due to the proton attached to the C^β of the vinylidene ligand whereas its ^{13}C NMR spectrum exhibits a characteristic resonance at δ 346 assigned to the C^α of the vinylidene moiety. Addition of $LiBHEt_3$ to a CH_2Cl_2 solution of **3**•$[OTf]_2$ did not yield the corresponding dinuclear alkenyl complex $[Cp(PPh_3)_2Ru(\eta^1{:}\eta^6\text{-}\mu_2\text{–}CH{=}CHC_6H_4Me\text{-}p)RuCp^*]$•[OTf], but reproduced **2**•[OTf] quantitatively. Similar treatment of **2**•Cl with I_2 and subsequent anion metathesis with $AgBF_4$[12] yielded the iodovinylidene complex $[Cp(PPh_3)_2Ru(\eta^1{:}\eta^6\text{-}\mu_2\text{-}C{=}CIC_6H_4Me\text{-}p)RuCp^*][BF_4]_2$ (**4**•$[BF_4]_2$).[14]



Scheme 1. Anions are omitted for clarity.

On the other hand, substitution of the PPh_3 ligand in **2**•OTf with CO readily proceeded under 1 atm of CO at room temperature to give $[Cp(PPh_3)(CO)Ru(\eta^1{:}\eta^6\text{-}\mu_2\text{-}C{\equiv}CC_6H_4Me\text{-}p)]$•OTf (**5**•OTf), which was isolated as yellow needles and spectroscopically characterized (Scheme 1).[15] The IR spectrum of **5**•OTf shows a ν_{CO} absorption at 1952 cm^{-1} together with a $\nu_{C\equiv C}$ absorption at 2095 cm^{-1}. The ^{1}HNMR spectrum of **5**•OTf exhibits characteristic four sets of doublet at δ 5.86, 5.42, 5.24 and 4.80 ppm assigned to the tolyl protons. Similar substitution reaction in **1b** to give $Cp(PPh_3)(CO)Ru(C{\equiv}CPh)$ was reported to proceed under 100 atm of CO at 105°C for 3 days.[16] Note that the present ligand substitution readily proceeds under extremely mild reaction conditions, which strongly suggests that the Cp*Ru fragment in **2**•OTf attached to the aromatic ring in the alkynyl unit would play an important role to facilitate this transformation.

Further studies are in progress on preparation and properties of homo- and heterodinuclear η^1:η^6-μ_2-alkynyl complexes.

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References and Notes

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1 M. F. Semmelhack, S. G. Davies, T. D. McCarthy in "Comprehensive Organometallic Chemistry II", ed by E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon, Oxford (1995), Vol. 12, Chap. 9, p 979; M. Uemura in "Advances in Metal-Organic Chemistry", ed by L. S. Liebeskind, JPI Press, Greenwich (1991), Vol. 2, p 195; H. L. Bozec, D. Touchard, and P. H. Dixneuf, *Adv. Organomet. Chem.*, **29**, 163 (1989); L. A. P. Kane-Maguire, E. D. Honig, and D. A. Sweigart, *Chem. Rev.*, **84**, 525 (1984).

2 N. Taniguchi, N. Kaneta, and M. Uemura, *J. Org. Chem.*, **61**, 6088 (1996); D. R. Robertson, W. Robertson, and T. A. Stepehnson, *J. Organomet. Chem.*, **202**, 309 (1980).

3 S. Lotz, P. H. Van Rooyen, and R. Meyer, *Adv. Organomet. Chem.*, **37**, 219 (1995) and references cited therein.

4 After filtration, the residue was extracted with CH_2Cl_2 and chromatographed on alumina first with CH_2Cl_2 to remove a yellow band of **1a** then with MeOH/THF (3/7) to elute a yellow band of **2**•Cl. Evaporation of the solvent from the second band afforded a yellow solid which was recrystalllized from CH_2Cl_2/hexane to give **2**•Cl as yellow columnar crystals (50%). ^1H NMR ($CDCl_3$) δ 7.36 - 7.09(m, 30H, Ph), 5.82, 5.23(d, 2H each, J = 6.1 Hz, C_6H_4Me), 4.36(s, 5H, Cp), 2.25(s, 3H, C_6H_4Me), 1.95(s, 15H, Cp*). IR (KBr, cm^{-1}) $\nu_{C\equiv C}$ 2071. Found: C, 62.73; H, 5.18%. Calcd for $C_{60}H_{57}ClP_2Ru_2{\cdot}CH_2Cl_2$: C, 63.01; H, 5.11%.

5 Formation of the $[Cp^*Ru(arene)]^+$ cation from $[Cp^*RuCl]_4$ and arenes; P. J. Fagan, M. D. Ward, and J. C. Calabrese, *J. Am. Chem. Soc.*, **111**, 1698 (1989).

6 *Crystal data for* **2**•PF_6: $C_{60}H_{57}F_3P_3Ru_2$, M = 1187.16, monoclinic, space group $P2_1/n$ (no. 14), a = 14.7239(2), b = 18.5463(2), c = 20.0903(4) Å, β = 104.9924(9)°, U = 5299.3901 $Å^3$, Z = 4, D_c = 1.488 $g{\cdot}cm^{-3}$, μ(Mo–Kα) = 7.21 cm^{-1}, F_{000} = 2416, R = 0.042, Rw = 0.047 [$w = 1/\sigma^2(Fo)$] for 6978 reflections with $I > 3\sigma(I)$ (5° < 2θ < 50°, 640 parameters). The structure was solved and refined with teXsan program package.

7 N. V. Ragjavan and R. E. Davis, *J. Cryst. Mol. Struct.*, **6**, 73 (1976).

8 K. G. Frank and J. P. Selegue, *J. Am. Chem. Soc.*, **112**, 6414 (1990).

9 J. M. Wisner, T. J. Bartczak, and J. A. Ibers, *Inorg. Chim. Acta*, **100**, 115 (1985).

10 M. Sato, H. Shintate, Y. Kawata, M. Sekino, M. Katada, and S. Kawata, *Organometallics*, **13**, 1956 (1994).

11 The Cl^- anion in **2**•Cl was exchanged to OTf^- since the protonation of **2**•Cl with HOTf and subsequent recrystallization produced a mixture of **2**•$[OTf]_2$, **2**•Cl[OTf], and **2**•Cl_2, which are difficult to separate. To avoid the similar situation, all anions were exchanged to BF_4^- before isolation of the dicationic dinuclear iodovinylidene complex **4**•$[BF_4]_2$.

12 A yellow CH_2Cl_2 solution of **2**•OTf prepared in situ by reaction of **2**•Cl with AgOTf (1 equiv) immediately turned to red when added 1.5 equiv of HOTf. After removal of the solvent, the resultant solid was washed with ether and recrystallized from THF/hexane to give **3**•$[OTf]_2$ as orange plates (93%). ^1H NMR ($CDCl_3$) δ 7.42 - 6.96(m, 30H, Ph), 5.95, 5.76(d, 2H each, J = 6.1 Hz, C_6H_4Me), 5.42(s, 5H, Cp), 5.02(s, 1H, C=C*H*Tol), 2.08(s, 3H, C_6H_4Me), 1.98(s, 15H, Cp*). ^{13}C NMR ($CDCl_3$) δ 346.0(Ru=*C*=CHC_6H_4Me). IR (KBr, cm^{-1}) $\nu_{C=C}$ 1631. Found: C, 54.97; H, 4.49%. Calcd for $C_{62}H_{58}F_6O_6P_2Ru_2S_2$: C, 55.51; H, 4.36%.

13 Formation of vinylidene complexes from **1b** and related σ-alkynyl complexes; M. I. Bruce, *Chem. Rev.*, **91**, 197 (1991).

14 Yield, 91%. ^1H NMR ($CDCl_3$) δ 7.52 - 6.91(m, 30H, Ph), 5.79, 5.70(d, 2H each, J = 6.3 Hz, C_6H_4Me), 5.40(s, 5H, Cp), 2.11(s, 3H, C_6H_4Me), 2.00(s, 15H, Cp*). ^{13}C NMR ($CDCl_3$) δ 345.8(Ru=*C*=ClC_6H_4Me). IR (CH_2Cl_2, cm^{-1}) $\nu_{C=C}$ 1617. Found: C, 54.36; H, 4.38%. Calcd for $C_{60}H_{57}B_2F_8IP_2Ru_2$: C, 53.66; H, 4.28%.

15 To a CH_2Cl_2 solution of **2**•OTf prepared in situ, was bubbled CO for 15min and the mixture was stirred for 1 week at room temperature. After removal of the solvent, the resultant solid was recrystallized from CH_2Cl_2/Et_2O to give **5**•OTf as yellow needles (70%). ^1H NMR ($CDCl_3$) δ 7.95 - 7.10(m, 15H, Ph), 5.86, 5.42, 5.24, 4.80(d, 1H each, J = 6.0 Hz, C_6H_4Me), 5.00(s, 5H, Cp), 2.10(s, 3H, C_6H_4Me), 1.83(s, 15H, Cp*). IR (KBr, cm^{-1}) $\nu_{C\equiv C}$ 2095, ν_{CO} 1952. Found: C, 61.21; H, 5.14%. Calcd for $C_{43}H_{42}ClOPRu_2$: C, 61.22; H, 5.02%.

16 M. I. Bruce and A. G. Swincer, *Aust. J. Chem.*, **33**, 1471 (1980).