Heterodinuclear Complex $Cp^*Ru(CO)_2Co(CO)_4$ ($Cp^* = \eta^5$-C_5Me_5) Induced Selective Dimerization of Terminal Alkynes

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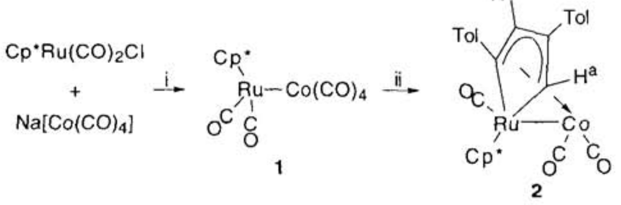
A heterobimetallic complex $Cp^*Ru(CO)_2Co(CO)_4$ **1** ($Cp^* = \eta^5$–C_5Me_5) and its selective reactions with alkynes are reported. Stoichiometric head-to-tail dimerization of tolylacetylene affords the dinuclear metallacyclopentadiene complex $Cp^*(CO)Ru\{\eta^2$:η^4–μ_2–C(Tol)CHC(Tol)CH$\}Co(CO)_2$ **2** whereas catalytic head-to-head coupling of methylpropiolate yields (*E*)-$(MeO_2C)CH{=}CH(C{\equiv}CCO_2Me)$ **3**. The structure of **2** has been determined by X-ray crystallography.

The chemistry of polynuclear transition metal complexes as a template for chemical transformations has been a major subject of current research interest.[1] Especially heteronuclear metal-metal bonded compounds are of particular interest since a result of cooperation between different metals at the adjacent position could lead to the development of unique activation and transformation of organic, inorganic, and organometallic substrates.[2] We report herein synthesis of a heterobimetallic complex $Cp^*Ru(CO)_2Co(CO)_4$ **1** which induces two types of selective dimerization of alkynes depending upon the nature of the alkynes.

A heterobimetallic complex **1** was prepared analogously as reported for its Cp analog $CpRu(CO)_2Co(CO)_4$.[3] Thus, a brown–yellow THF solution of $Cp^*Ru(CO)_2Cl$ was gradually turned to an orange suspension when treated with 1 equiv of $NaCo(CO)_4$ in THF at 60 °C for 4 days. Work up of the reaction mixture resulted in the isolation of **1** as an orange microcrystalline solid in 86% yield (Scheme 1). The metal-metal bonded structure of **1** was spectroscopiclly characterized.[4] In sharp contrast, the related Fe–Co complexes $Cp'Fe(CO)(\mu_2$–$CO)_2Co(CO)_3$ (Cp' = Cp[5, 6] or Cp^*[7]) were known to possess both terminal and bridging COs.



Scheme 1. i, THF, 60 °C, 96 h; ii, HC≡CTol (5equiv), Me_3NO (1 equiv), THF, reflux, 12 h.

Reaction of **1** with HC≡CTol (5 equiv) in the presence of Me_3NO yielded the dinuclear metallacyclopentadiene complex $Cp^*(CO)Ru\{\eta^2$:η^4-μ_2-C(Tol)CHC(Tol)CH$\}Co(CO)_2$ **2** in 95% yield (Scheme 1),[8] which was isolated as orange columnar crystals and has been fully defined by X-ray crystallography.[9] The ORTEP drawing of **2** is shown in Figure 1. Two HC≡CTol molecules are coupled in a head-to-tail manner on the bimetallic site to form the ruthenacyclopentadiene which coordinate to the $Co(CO)_2$ fragment. The four carbon atoms C(1)-C(4) are essentially coplanar. However, the metallacycle ring in **2** is not planar as commonly observed for the dinuclear metallacyclopentadiene systems but bent with a fold angle of 17.7° (angle between Ru(1)-C(1)-C(4) and C(1)-C(2)-C(3)-C(4) planes). The examples containing the folded five-membered ring are still limited.[10] The distance between the two metal atoms in **2** is 2.627(1) Å, indicating the existence of a Ru-Co single bond.[11]

On the other hand, reaction of **1** with $HC{\equiv}CCO_2Me$ occurred in a different manner. Thus, catalytic head-to-head dimerization of the alkyne readily proceeded at 50 °C in the presence of 5 mol% of **1** and Me_3NO to give (after 96 h) (*E*)-$(MeO_2C)CH{=}CH(C{\equiv}CCO_2Me)$ **3** (43%) together with (*E, E*)-$(MeO_2C)CH{=}CHOCH{=}CH(CO_2Me)$ **4** (7%), both of which

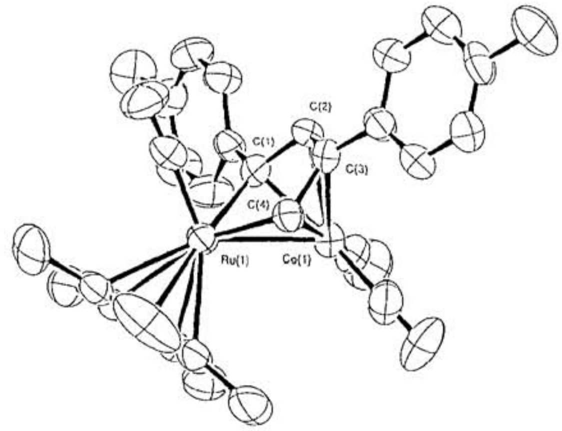
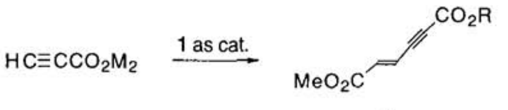


Figure 1. ORTEP diagram of **2**. Selected bond distances (Å) and angles (°); Ru(1)–Co(1) 2.627(1), Ru(1)–C(1) 2.101(7), Ru(1)–C(4) 2.049(7), Co(1)–C(1) 2.023(7), Co(1)–C(2) 2.084(7), Co(1)–C(3) 2.124(7), Co(1)–C(4) 2.045(7), C(1)–C(2) 1.438(9), C(2)–C(3) 1.40(1), C(3)–C(4) 1.421(9); Co(1)–Ru(1)–C(1) 49.1(2), Co(1)–Ru(1)–C(4) 50.0(2), C(1)–Ru(1)–C(4) 76.7(3), Ru(1)–Co(1)–C(1) 51.8(2), Ru(1)–Co(1)–C(2) 77.5(2), Ru(1)–Co(1)–C(3) 77.0(2), Ru(1)–Co(1)–C(4) 50.1(2), C(1)–Co(1)–C(2) 41.0(3), C(1)–Co(1)–C(3) 70.8(3), C(1)–Co(1)–C(4) 78.6(3), C(2)–Co(1)–C(3) 38.8(3), C(2)–Co(1)–C(4) 69.2(3), C(3)–Co(1)–C(4) 39.8(3), Ru(1)–C(1)–Co(1) 79.1(3), Ru(1)–C(1)–C(2) 113.3(5), Co(1)–C(1)–C(2) 71.8(4), Co(1)–C(2)–C(1) 67.2(4), Co(1)–C(2)–C(3) 72.2(4), C(1)–C(2)–C(3) 116.0(7), Co(1)–C(3)–C(2) 69.1(4), Co(1)–C(3)–C(4) 67.1(4), C(2)–C(3)–C(4) 112.7(6), Ru(1)–C(4)–Co(1) 79.8(3), Ru(1)–C(4)–C(3) 117.3(5), Co(1)–C(4)–C(3) 73.1(4).

were isolated as a white microcrystalline solid and spectroscopically characterized (Eq. 1).[12] It is of interest to note that the carbon–carbon bond formation between the alkyne molecules exclusively produces **3** and neither the corresponding (*Z*)-enyne nor the head-to-tail dimers were formed during this reaction.[13] Furthermore, cyclotrimerization of $HC\equiv CCO_2Me$ did not proceed under these conditions, which were most commonly observed in transition metal–catalyzed oligomerization of alkynes. Me_3NO is essential for this dimerization. Only a trace amount of cyclotrimerization products were detected when the reaction was carried out without Me_3NO. It is not certain at this stage whether a heterobimetallic complex **1** or a mononuclear species derived from **1** is the active catalyst.[14]



(1)

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Further studies are in progress on reactivities of **1** with various alkynes and a series of unsaturated organic molecules.

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4 After removal of the solvent, the residue was extracted with hexane and purified by chromatography on alumina with benzene/hexane(3/7). Evaporation of the solvent from a single orange band afforded **1** as an orange microcrystalline solid (86%). ^1H NMR ($CDCl_3$) δ 1.94 (Cp*). IR (hexane, cm^{-1}) ν_{CO} 2060, 2010, 1979. FAB–MS m/z = 464 {$(M+1)^+$}. Found: C, 41.67; H, 3.51%. Calcd for $C_{16}H_{15}CoO_6Ru$: C, 41.47; H, 3.26%.

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8 Complex **1** reacted with a mixture of HC≡CTol (5 equiv) and Me_3NO (1 equiv) in THF at 60 °C for 12 h. After removal of the solvent, the residue was purified by chromatography on alumina with hexane. Evaporation of the solvent from a single orange band afforded **2** as an orange microcrystalline solid (95%). Single crystals for structural analysis were obtained by recrystallization from hexane. ^1H NMR ($CDCl_3$) δ 8.00 (d, 1H, *J* = 2.5 Hz, H^a), 7.47, 7.37 (d, 2H each, *J* = 8.2 Hz, aryl), 7.14 – 7.12 (m, 4H, aryl), 6.90 (d, 1H, *J* = 2.5 Hz, H^b), 2.37, 2.34 (s, 3H each, $C_6H_4\mathit{Me}$), 2.02 (s, 15H, Cp*). IR (hexane, cm^{-1}) ν_{CO} 2010 (vs), 1970 (vs), 1956 (vs). Found: C, 61.31; H, 5.24%. Calcd for $C_{31}H_{31}CoO_3Ru$: C, 60.87; H, 5.11%. The ^1H NMR analysis of the crude reaction mixture indicates the absence of free oligomers derived from the alkyne such as (*E*)-TolCH=CHC≡CTol.

9 *Crystal data for* **2**: $C_{31}H_{31}O_3CoRu$, *M* = 611.69, triclinic, space group $P\bar{1}$ (no. 2), a = 10.681(3), b = 14.722(4), c = 9.443(2) Å, α = 100.18(2), β = 99.42(2), γ = 105.06(2)°, U = 1376.5(8) $Å^3$, Z = 2, D_c = 1.475 $g\cdot cm^{-3}$, $\mu(Mo\text{–}K\alpha) = 11.81\ cm^{-1}$, F_{000} = 624, R = 0.044, Rw = 0.036 [$w = 1/\sigma^2(Fo)$] for 2683 reflections with $I > 3\sigma(I)$ ($5° < 2\theta < 55°$, 325 parameters). The structure was solved and refined with teXsan program package.

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12 $HC\equiv CCO_2Me$ (0.40 mmol), **1** (0.021 mmol), Me_3NO (0.021 mmol), THF (14 ml), 50 °C, 96 h. **4**: ^1H NMR ($CDCl_3$) δ 7.58, 5.66 (d, 2H each, *J* = 12.2 Hz, alkenyl), 3.74 (s, 6H, OMe). ^{13}C NMR ($CDCl_3$) δ 166.4 (CO), 157.3 (-O-*C*=C), 104.0 (-O-C=*C*), 51.6 (OMe). IR (KBr: cm^{-1}) ν_{CO} 1717. MS (EI), 186 (M^+). Found: C, 51.81; H, 5.26%. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41%. The dialkenyl ether **4** was formally produced by combination of two alkyne molecules and H_2O, however we must await further investigation on the mechanism of its formation.

13 Selective head-to-head coupling of terminal alkynes to form *trans*-enynes has been reported. See: M. Ishikawa, J. Ohshita, K. Furumori, A. Matsuguchi, and M. Ishikawa, *J. Org. Chem.*, **55**, 3277 (1990); C.-H. Jun, Z. Lu, and R. H. Crabtree, *Tetrahedron Lett.*, **1992**, 33, 7119; M. A. Esteruelas, L. A. Oro, and N. Ruiz, *Organometallics*, **13**, 1507 (1994); C. Bianchini, P. Frediani, M. Peruzzini, and F. Zanobini, *Organoemetallics*, **13**, 4616 (1994); T. Rappert and A. Yamamoto, *Organometallics*, **13**, 4984 (1994); C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, and K. Kirchner, *Organometallics*, **15**, 5275 (1996); C. S. Yi and N. Liu, *Organometallics*, **15**, 3968 (1996); M. D. Fryzuk, M. J. Jonker, and S. J. S. Rettig, *J. Chem. Soc., Chem. Commun.*, **1997**, 377; C. Gemel, G. Kickelbick, R. Schmid, and K. Kirchner, *J. Chem. Soc., Dalton Trans.*, **1997**, 2113.

14 The ^1H NMR analysis indicates the absence of **1** in the crude reaction mixture but instead several Cp* resonances were observed around δ 2 ppm.