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Ruthenium-Catalyzed Dimerization of Terminal Alkynes Initiated by a Neutral Vinylidene Complex

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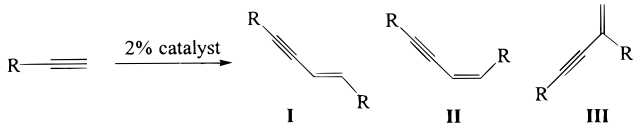
*Summary: The complexes RuTp(PPh$_3$)$_2$Cl (**1**) and RuTp(PPh$_3$)(py)Cl (**2**) catalyze the dimerization of HC≡CR, where R = Ph, SiMe$_3$, n-Bu, and t-Bu, to give 1,4- and 2,4-disubstituted butenynes with both conversion and selectivity strongly depending on the alkyne substituent, where the catalytic precursor is the neutral vinylidene complex RuTp(PPh$_3$)(Cl)(=C=CHR). The hydride complex RuTp(PPh$_3$)$_2$H (**3**) exhibits the same catalytic activity as **1** and **2**.*

Recently we have found that RuTp(py)$_2$Cl (Tp = trispyrazolylborate, py = pyridine) is an efficient catalyst for the selective coupling of HC≡CPh and allyl alcohol.[1] Interestingly, if a tertiary phosphine is substituted for py, the reaction takes quite another course in that C−C coupling between the alkynes is favored with the allyl alcohol ignored. Here we report on the catalytic coupling of HC≡CR (R = Ph, SiMe$_3$, *n*-Bu, and *t*-Bu) to 1,4- and 2,4-disubstituted butenynes with the aid of RuTp(PPh$_3$)$_2$Cl (**1**),[2] RuTp(PPh$_3$)(py)(Cl) (**2**),[3] and RuTp(PPh$_3$)$_2$H (**3**).[4]

Reaction of **1** with an excess of HC≡CPh in toluene at reflux for 20 h results in the formation of the head-to-head dimer (*E*)-1,4-diphenyl-1-buten-3-yne (**Ia**) and small amounts of the Z isomer (**IIa**) (Table 1).[3] The conversion is essentially quantitative. It should be mentioned that the coupling reactions take place only in nonprotic solvents such as toluene, benzene, or thf. While the product distribution is independent of these solvents, the conversion decreases from 98% (toluene) to benzene (80%) and thf (35%). Further, both conversion and selectivity vary drastically with the alkyne substituent as follows (with toluene taken as the solvent). For R = SiMe$_3$ the regioselectivity is reversed with respect to R = Ph giving no **Ib** but instead **IIb** (82%) together with the head-to-tail dimer 2,4-bis(trimethylsilyl)-1-buten-3-yne (**IIIb**) (15%) with slightly reduced conversion relative to R = Ph. For R = *n*-Bu the reaction is less selective giving all three isomers in a ratio of 42:25:33% (**Ic**:**IIc**:**IIIc**) and 70% conversion after a reaction time of 44 h in boiling toluene. For R = *t*-Bu, finally, only the formation of the head-to-head isomer **IId** is observed with the conversion dropped to about 10% even after a reaction time of 68 h. The reversal of reactivity suggests that the mechanism is not the same in all cases. It is worth noting that all of the reaction mixtures remain catalytically active.

Table 1. Conversion and Product Distribution of the Catalytic Dimerization of Terminal Alkynes



catal[a]	R	% **I**	% **II**	% **III**	% conversion
1	Ph	91	6		98
2	Ph	92	6		97
3	Ph	91	8		95
4	Ph	91	5		98
1	SiMe$_3$		82	15	94
1[b]	*n*-Bu	42	25	33	70
1[c]	*t*-Bu		98		10

[a] Reactions were performed in boiling toluene for 20 h. Yields are for isolated products. Product distribution has been determined by NMR spectroscopy. [b] Reaction was performed in boiling toluene for 44 h. [c] Reaction was performed in boiling toluene for 68 h.

While a detailed mechanism of the present reactions cannot yet be given, some major conclusions may be drawn from the following observations. The catalytic cycle is initiated by loss of a PPh$_3$ ligand and formation of a coordinatively unsaturated species as monitored by ^{31}P{^{1}H} NMR spectroscopy in benzene-*d*$_6$ at 80 °C (Scheme 1) by a resonance at 34.4 ppm (*cf.* **1** exhibits a signal at 43.0 ppm). On addition of HC≡CPh (10 equiv) the neutral vinylidene complex RuTp(PPh$_3$)(Cl)(=C=CHPh) (**4**) is formed intermediately. In the further course of reaction no other intermediate could be detected by NMR spectroscopy, but only the reaction products **Ia** and **IIa**. Valuable mechanistic information on the catalytic cycle is provided by the isolation of **4** from a mixture of the reaction run at room temperature. Stirring a solution of **1** in the presence of HC≡CPh in THF for 36 h afforded, on workup, dark red crystals of **4**[5] suitable for X-ray diffraction analysis (Figure 1).[6] Important bond lengths and angles are reported in the caption. The coordination geometry of ruthenium in **4** is approximately octahedral. The Ru(1)−P(1) and Ru(1)−Cl(1) bond lengths (2.365(1) and 2.401(1) Å) are very similar. The Ru(1)−C(28) bond distance is 1.801(4) Å comparable to other both cationic and neutral vinylidene ruthenium complexes.[7−9] The Ru=C=C group is essentially linear, the angle Ru(1)−C(28)−C(29) being 177.2(3)°. The C(28)−C(29) bond distance is 1.315(6) Å corresponding to a bond order between two and three.

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(1) Gemel, C.; Trimmel, G.; Slugovc, C.; Mereiter, K.; Kremel, S.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998.

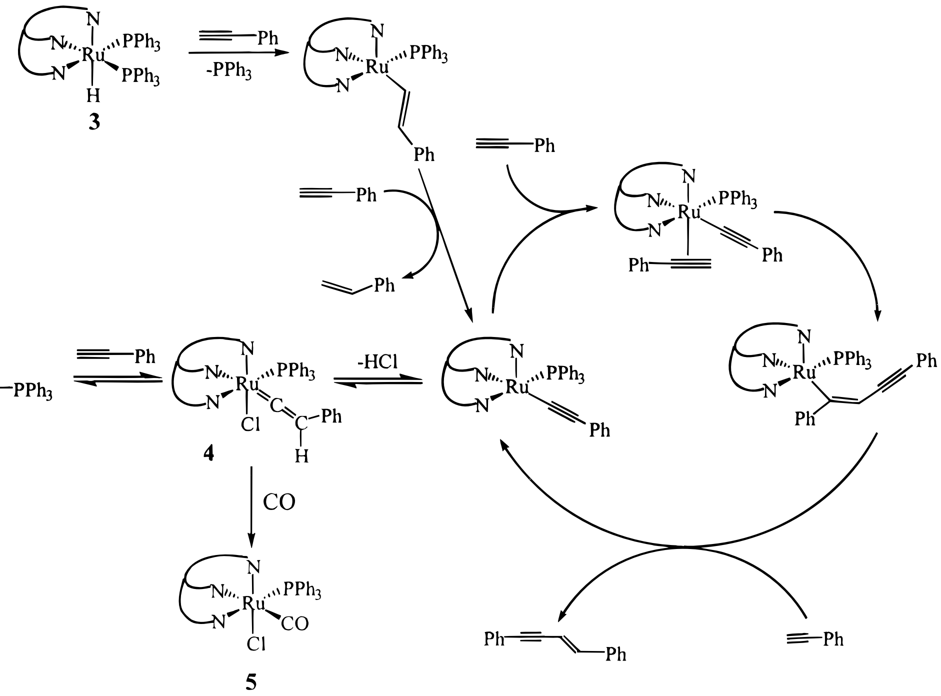
(2) Alcock, N. W.; Burns, I. D.; Claire, K.; S.; Hill, A. F. *Inorg. Chem.* **1992**, *31*, 2906.

(3) Compound **2** was characterized by elemental analysis and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. 1,4- and 2,4-Disubstituted butenynes were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. See the Supporting Information.

(4) Tenorio, M. J.; Tenorio, M. A. J.; Puerta, M. C.; Valerga, P. *Inorg. Chim. Acta,* in press.

S0276-7333(96)00781-9 CCC: $12.00

Scheme 1



In the case of the other alkynes with R = SiMe$_3$, *n*-Bu, and *t*-Bu, the corresponding vinylidene complexes RuTp(PPh$_3$)(Cl)(=C=CHR) are detected as intermediates by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy but cannot be isolated. It is worth mentioning that the use of isolated **4** in an independent reaction catalyzes the coupling of HC≡CPh in a fashion nearly identical to **1** (Table 1). Furthermore, in the reaction of **4** no free PPh$_3$ can be observed. In the presence of a 100-fold excess of PPh$_3$ the same product distribution is maintained but a longer reaction time for quantitative conversion is required. This points to a competition between vinylidene and phosphine for coordination at the ruthenium center. In fact, treatment of **4** with L = CO and PPh$_3$ results in the quantitative formation of complexes RuTp(PPh$_3$)(Cl)(L) (**5, 1**)[10] and liberation of HC≡CPh, where **5** is no more catalytically active.

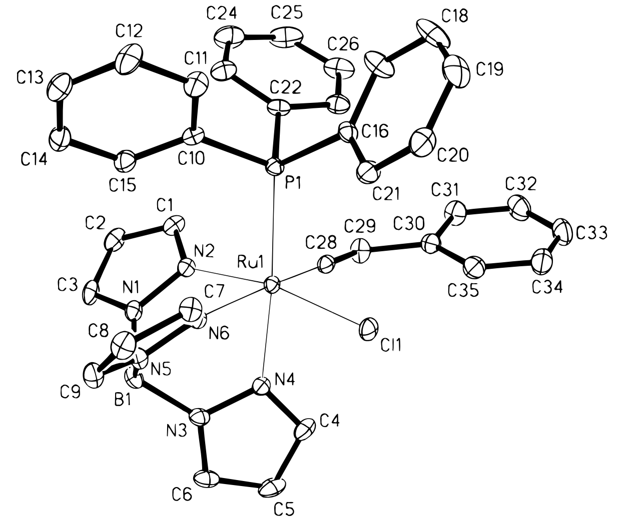


Figure 1. Structural view of one of the two independent complexes RuTp(PPh$_3$)(Cl)(=C=CHPh) (**4**). Selected bond lengths (Å) and angles (deg): Ru(1)−N(2) 2.092(3), Ru(1)−N(4) 2.116(3), Ru(1)−N(6) 2.199(3), Ru(1)−P(1) 2.365(1), Ru(1)−Cl(1) 2.401(1), Ru(1)−C(28) 1.801(4), C(28)−C(29) 1.315(6), N(6)−Ru(1)−C(28) 176.1(1), C(28)−Ru(1)−Cl(1) 93.9(1), P(1)−Ru(1)−Cl(1) 96.8(4).

Unfortunately, in all of the reactions analyzed no intermediate other than **4** could be detected in which the actual coupling reaction occurs. A possible reaction scheme could involve a coordinatively unsaturated alkyne complex formed by the liberation of HCl. This proposal, though difficult to be proven, is in accord with other work.[9] In this way the attack of a second alkyne molecule followed by a selectivity determining C−C coupling step becomes feasible as depicted in Scheme 1. Accordingly, the C$_4$ unsaturated product is eventually liberated from an intermediate σ-organyl metal species by σ-bond metathesis with an additional alkyne molecule.

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(5) Procedure and data for **4**: A solution of **1** (600 mg, 0.686 mmol) in dry THF (5 mL) was treated with HC≡CPh (300 μL, excess) and stirred for 36 h at room temperature. After removal of the solvent the residue was dissolved in 0.5 mL of CH$_2$Cl$_2$ and the product was precipitated with diethyl ether. Yield: 423 mg (92%). Anal. Calcd for C$_{35}$H$_{31}$BClN$_6$PRu: C, 58.88; H, 4.38; N, 11.77. Found: C, 58.99; H, 4.54; N, 11.47. ^{1}H NMR (δ, CDCl$_3$, 20 °C): 7.94 (d, 1H, J = 2.1 Hz), 7.73 (d, 1H, J = 2.5 Hz), 7.70 (d, 1H, J = 2.5 Hz), 7.64−7.56 (m, 7H), 7.44−7.37 (m, 3H), 7.31−7.24 (m, 8H), 7.18−7.04 (m, 3H), 6.80 (d, 1H, J = 2.1 Hz), 6.16 (dd, 1H, J = 2.1 Hz, J = 1.8 Hz), 6.01 (d, 1H, J = 2.1 Hz), 5.98 (dd, 1H, J = 2.5 Hz, J = 2.5 Hz), 5.82 (dd, 1H, J = 2.1 Hz, J = 2.1 Hz), 4.98 (d, 1H, $^4J_{PH}$ = 3.9 Hz). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 368.9 (d, 1C, C$_\alpha$, $^2J_{CP}$ = 18.8 Hz), 145.5, 144.1, 144.0 (d, $^3J_{CP}$ = 1.7 Hz), 137.1, 135.3 (d, $^2J_{CP}$ = 10.2 Hz), 134.8 (d, $^3J_{CP}$ = 2.5 Hz), 132.6 (d, $^1J_{CP}$ = 44.9 Hz), 130.9 (d, 1C, Ph, $^3J_{CP}$ = 1.7 Hz), 130.5 (d, 1C, Ph, $^4J_{CP}$ = 2.5 Hz), 129.3 (2C Ph), 128.5 (d, $^3J_{CP}$ = 10.2 Hz), 126.6 (2C, Ph), 125.6 (1C, Ph), 112.7 (d, 1C, C$_\beta$, $^3J_{CP}$ = 1.7 Hz), 106.5 (d, $^4J_{CP}$ = 2.5 Hz), 106.4, 106.2. ^{31}P{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 37.5. IR (diffuse reflectance, cm^{-1}): 2483 (m, B−H), 1647 (s, C=C).

(6) Crystal data of **4**: triclinic space group $C\bar{1}$ (nonstandard setting of space group $P\bar{1}$, No. 2), a = 11.352(2) Å, b = 16.184(2) Å, c = 35.518(6) Å, α = 90.01(1)°, β = 93.39(1)°, γ = 89.98(1)°, V = 6514(2) Å^3, Z = 8 for RuTp(PPh$_3$)(Cl)(=C=CHPh), R_1 = 0.044 (all data), wR_2 = 0.0837 (all data), no. of reflections 11 161, no. of refined parameters 813.

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The present catalytic C−C coupling reactions initiated by a neutral vinylidene complex catalyst precursor appear to be novel mechanistically. It is worth noting that our neutral vinylidene complex does not differ much either structurally or spectroscopically from the cationic analogs of which many data are available.[7] The actual difference, however, lies in the kinetic behavior, in that the cationic examples are rather inert, whereas the neutral one is labile giving rise to the catalytic activity. The majority of all hitherto known catalytic dimerizations of terminal alkynes to C_4 units are migratory insertions of acetylenes into σ metal−carbon bonds proceeding, for instance, via alkynyl−vinylidene or alkynyl−vinyl coupling.[11−15] In the case of late transition metals, enynyl intermediates could be isolated occasionally giving predominantly (*Z*) head-to-head coupling products.[11] A somewhat other mechanism appears to operate in the case of early transition metals, lanthanides, and actinides where preferentially (*E*) head-to-head and head-to-tail dimers together with trimeric and even oligomeric coupling products are obtained. The catalytically active species in all these cases is a metal alkynyl complex generated by the intervention of a strongly basic ligand such as hydride and alkyl groups.

In order to establish the role of ligated base in the present reactions we also tested RuTp(PPh_3)(py)(Cl) (**2**)[3] and RuTp(PPh_3)$_2$H (**3**)[4] bearing the basic coligands py and H^- as catalyst precursors for the dimerization of HC≡CPh finding as the first steps the release of py from **2** and PPh_3 from **3**. As is further judged from the unchanged degree in conversion and unchanged selectivity (Table 1), the catalytically active species should be the same alkynyl complex as that arising from **1** but in the case of **3** presumably arrived at by the usual insertion of the alkyne into the Ru−H bond giving a vinyl intermediate also depicted in Scheme 1.[11a,15]

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Supporting Information Available: Text giving full experimental details and spectroscopic analytical data for complexes **2** and **3** and all 1,4- and 2,4-disubstituted butenynes and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles, and ORTEP diagrams for complex **4** (15 pages). Ordering information is given on any current masthead page.

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