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Oxidatively Induced Carbonylation and Cyclization of Ruthenium(II) Vinyl−Olefin Complexes Prepared via Allyl/Alkyne Coupling

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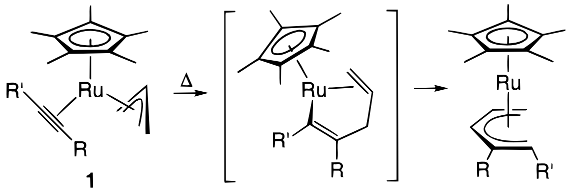
Summary: One-electron oxidation of otherwise unreactive ((1:4,5-η)-1,4-pentadien-1-yl)ruthenium carbonyl complexes in acetonitrile under carbon monoxide leads to the formation of 5-methylene-2-cyclopenten-1-ones via carbonylation, migratory cyclization, and β-hydride elimination. Oxidation in dichloromethane produces an acyclic 1,4-pentadiene, even under a carbon monoxide atmosphere.

The rate enhancement of fundamental transition-metal-mediated reactions upon oxidation to the odd-electron manifold is well-established, a phenomenon that includes processes such as ligand substitution, reductive elimination, structural isomerization, and migratory insertion.[1] In particular, alkyl-to-acyl conversion by migratory insertion of transition-metal alkyl carbonyl complexes is known to be dramatically accelerated upon single-electron oxidation, relative to even-electron analogues.[2] In this communication, we report the synthesis of stable $(C_5Me_5)Ru((1{:}4,5\text{-}\eta)\text{-}1,4\text{-pentadien-1-yl})(CO)$ complexes via allyl/alkyne coupling and describe the oxidatively induced reactivity of these σ,π-vinyl−olefin complexes. Single-electron oxidation initiates a cascade of reactions that ultimately leads to the *selective* formation of either cyclic or acyclic organic products, as determined by the choice of solvent and added carbon monoxide.



(1)

We recently isolated a range of reactive Ru(II) η^3-allyl η^2-alkyne complexes (**1**) that undergo allyl/alkyne coupling upon warming to form open-chain η^5-pentadienyl complexes, presumably via an unsaturated σ,π-vinyl−olefin intermediate (eq 1).[3] We now report that heating diphenylacetylene complex **1a** under carbon monoxide suppresses the formation of the η^5-pentadienyl complex, trapping the intermediate formed from initial allyl/alkyne coupling and providing the (1:4,5-η)-1,4-pentadien-1-yl carbonyl complex **2a** in very good yield (Scheme 1).[4] This reaction confirms the competency of such σ,π-vinyl−olefin complexes as intermediates in the thermal reactions of allyl alkyne complexes. The corresponding reaction of the 2-butyne derivative $(C_5Me_5)Ru(\eta^3\text{-allyl})(\eta^2\text{-MeC}{\equiv}\text{CMe})$ (**1b**) proceeds under milder conditions but requires the presence of added 2-butyne to inhibit the displacement of the labile alkyne ligand by carbon monoxide. Decomposition of the 2-butyne complex **1b** during the reaction remains a problem, however, resulting in a yield significantly lower than that obtained from diphenylacetylene complex **1a**. Both complexes are isolated as air-stable yellow solids and analytically pure crystals are readily obtained by recrystallization from diethyl ether/methanol. The ^1H and ^{13}C NMR spectroscopic data for complexes **2** are fully consistent with the presence of a σ,π-vinyl−olefin moiety,[5] on the basis of comparisons to known complexes in related systems.[6] The presence of the carbonyl ligand in complexes **2a** and **2b** is supported by the infrared spectra, which exhibit strong absorptions at 1933 and 1938 cm^{-1}, respectively.

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(1) Reviews: (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (c) Astruc, D. *Chem. Rev.* **1988**, *88*, 1216. (d) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153. (e) Trogler, W. C., ed. *Organometallic Radical Processes*; Elsevier Science: Amsterdam, 1990. (f) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36. (g) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (h) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. Recent and lead references: (i) Legzdins, P.; McNeil, W. S.; Rettig, S. J.; Smith, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 3513. (j) Fooladi, E.; Tilset, M. *Inorg. Chem.* **1997**, *36*, 6021 and references therein. (k) Shaw, M. J.; Geiger, W. E.; Hyde, J.; White, C. *Organometallics* **1998**, *17*, 5486. (l) Bartlett, I. A.; Connelly, N. G.; Martin, A. J.; Orpen, A. G.; Paget, T. J.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1999**, 691. (m) Wolfbauer, G.; Bond, A. M.; MacFarlane, D. R. *Inorg. Chem.* **1999**, *38*, 3836.

(2) Lead references to CO insertion in the 17e/19e manifold: (a) Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* **1985**, *4*, 374. (b) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5127 and references therein. (c) Golovin, M. N.; Meirowitz, R. E.; Rahman, M. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 2285. (d) Donovan, B. T.; Geiger, W. E. *Organometallics* **1990**, *9*, 865. (e) Tracey, A. A.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1399. (f) Prock, A.; Giering, W. P.; Greene, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. C.; Wilson, M.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* **1991**, *10*, 3479.

(3) (a) Older, C. M.; Stryker, J. M. *Organometallics* **2000**, *19*, 2166. (b) This intermediate could in principle be further stabilized by solvent or η^2-vinyl coordination, although the latter may be geometrically untenable.

(4) Complete experimental and characterization data are provided as Supporting Information.

(5) Selected NMR spectroscopic data are as follows (room temperature). **2a**: ^1H NMR (300 MHz, C_6D_6) δ 7.27 (dd, $J = 8.1, 1.2$ Hz, 2H, H_{Ph}), 7.13 (dd, $J = 9.5, 1.2$ Hz, 2H, H_{Ph}), 7.06 (t, $J = 7.6$ Hz, 2H, H_{Ph}), 6.97 (t, $J = 7.6$ Hz, 2H, H_{Ph}), 6.92−6.84 (m, 2H, H_{Ph}), 3.88 (dd, $J = 16.4, 6.4$ Hz, 1H, H_{3a}), 3.61 (dddd, $J = 12.0, 8.0, 7.5, 6.2$ Hz, 1H, H_4), 3.03 (d, $J = 11.7$ Hz, 1H, H_{5anti}), 2.59 (d, $J = 16.4, 7.3$ Hz, 1H, H_{3b}), 2.11 (d, $J = 8.0$ Hz, 1H, H_{5syn}), 1.22 (s, 15H, C_5Me_5); ^{13}C NMR (75 MHz, C_6D_6) δ 211.0 (CO), 152.0 (C_1), 151.7 (C_2), 151.4 (C_{ipso}), 142.4 (C_{ipso}), 130.0 (C_{Ph}), 129.2 (C_{Ph}), 128.3 (C_{Ph}), 127.5 (C_{Ph}), 125.0 (C_{Ph}), 123.9 (C_{Ph}), 98.3 (C_5Me_5), 72.7 (C_4), 48.8 (C_5), 47.8 (C_3), 8.9 ($C_5\mathit{Me}_5$). **2b**: ^1H NMR (300 MHz, CD_2Cl_2) δ 3.36 (dddd, $J = 12.0, 8.3, 6.7, 6.0$ Hz, 1H, H_4), 2.87 (br dd, $J = 16.0, 6.7$ Hz, 1H, H_{3a}), 2.61 (d, $J = 11.9$ Hz, 1H, H_{5anti}), 2.15 (d, $J = 8.3$ Hz, 1H, H_{5syn}), 2.04 (br dd, $J = 15.9, 7.5$ Hz, 1H, H_{3b}), 1.88 (s, 3H, CH_3), 1.75 (s, 15H, C_5Me_5), 1.53 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 211.5 (CO), 142.1 (C_1), 142.0 (C_2), 98.0 (C_5Me_5), 72.7 (C_4), 47.5 (C_5), 46.0 (C_3), 27.3 ($\mathit{C}H_3$), 15.8 ($\mathit{C}H_3$), 9.9 ($C_5\mathit{Me}_5$).

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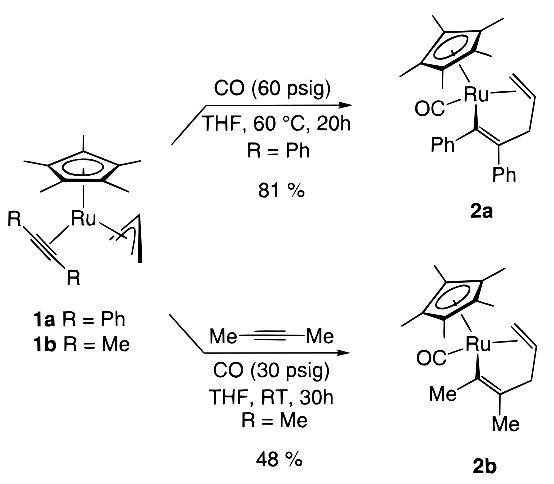
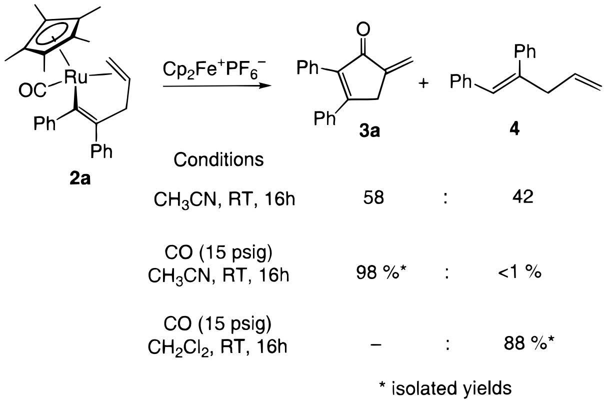
Scheme 1



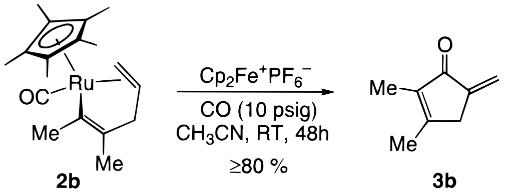
Scheme 2



The σ,π-vinyl−olefin complexes **2** are remarkably stable: prolonged heating at 110 °C results only in the recovery of clean starting material, even in the presence of Lewis acids. Extensive photolysis (450 W Hanovia Hg lamp, Pyrex filter) of complex **2a** at room temperature leads only to minimal decomposition.

Although the diphenylacetylene-derived complex **2a** is thermally unreactive at temperatures up to the onset of decomposition, carbonyl insertion can be induced at room temperature upon treatment with a chemical oxidant.[2] Thus, addition of ferrocenium hexafluorophosphate (1.2 equiv) to complex **2a** in acetonitrile at room temperature yields the known organic compounds 2,3-diphenyl-5-methylene-2-cyclopenten-1-one[7] (**3a**) and (*Z*)-1,2-diphenyl-1,4-pentadiene[8,9] (**4**) in a 58:42 ratio, respectively (Scheme 2). The cyclization to cyclopentenone **3a** can be optimized (98% isolated yield) by performing the same reaction under an atmosphere of carbon monoxide in a sealed vessel; only a trace (<1%) of the acyclic diene **4** is formed under these conditions. The use of substoichiometric ferrocenium (0.25 equiv) results in the recovery of starting material in addition to a proportional amount of the organic product, indicating that the induced cyclization reaction is not catalytic in oxidant. Remarkably, the use of the less coordinating dichloromethane as the solvent promotes the formation of diene **4** as the exclusive organic product, even in the presence of carbon monoxide. The same oxidation carried out in tetrahydrofuran yields no identifiable products, while the use of methanol as solvent leads only to the recovery of starting material.[10]

Treatment of the 2-butyne-derived complex **2b** with excess ferrocenium under the optimized cyclization conditions (CH_3CN, low-pressure CO) results in the isolation of the corresponding 5-methylene-2-cyclopenten-1-one **3b** in approximately 80% yield (eq 2).[11] The organic product **3b** is the natural cyclopentanoid antibiotic methylenomycin B, which has been synthesized previously by a multitude of methods, many of which are less direct than the procedure reported here.[12]



(2)

The disposition of the ruthenium component is also dependent on the reaction conditions. Oxidation of (1:4,5-η)-1,4-pentadien-1-yl complexes **2** in dichloromethane in the absence of carbon monoxide results in a complex mixture of unidentifiable, possibly paramagnetic, complexes containing the $(C_5Me_5)Ru$ fragment. However, when the oxidation of **2b** is conducted in acetonitrile under a carbon monoxide atmosphere, yellow crystals can be isolated from the crude product mixture.[4] Spectroscopic data and elemental analysis of this material are consistent with the isolation of a mixture of two complexes, tentatively identified as $[(C_5Me_5)Ru(CH_3CN)_2CO]^+PF_6^-$ and the known $[(C_5Me_5)Ru(CH_3CN)(CO)_2]^+PF_6^-$.[13]

A preliminary mechanistic rationale consistent with the observed effects of solvent and carbon monoxide can be constructed (Scheme 3). Outer-sphere, one-electron oxidation by ferric ion presumably initiates the reaction,[1h] providing the cationic Ru(III) intermediate **I**. The origin of the rate acceleration for migratory insertion in the odd-electron manifold has been extensively discussed;[2]

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(6) Other (1:4,5-η)-1,4-pentadien-1-yl complexes prepared by allyl/alkyne coupling: (a) Appleton, T. G.; Clark, H. C.; Poller, R. C.; Puddephatt, R. J. *J. Organomet. Chem.* **1972**, *39*, C13. (b) Green, M.; Taylor, S. J. *J. Chem. Soc., Dalton Trans.* **1975**, *1142*. (c) Bottrill, M.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 292. (d) Betz, P.; Jolly, P. W.; Kruger, C.; Zakrzewski, U. *Organometallics* **1991**, *10*, 3520. (e) Schwiebert, K. E. Ph.D. Dissertation, Indiana University, 1993.

(7) Siwapinyoyos, T.; Thebtaranonth, Y. *J. Org. Chem.* **1982**, *47*, 598.

(8) Suzuki, N.; Kondakov, D. Y.; Kageyama, M.; Kotora, M.; Hara, R.; Takahashi, T. *Tetrahedron* **1995**, *51*, 4519.

(9) Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11570.

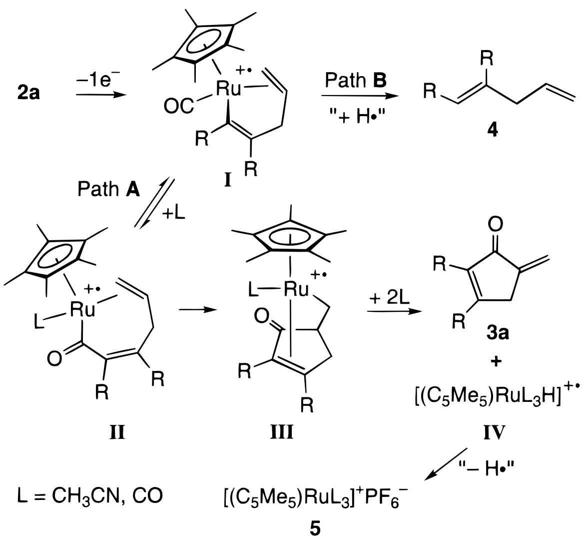
(10) The oxidation reaction in acetonitrile (no added carbon monoxide) was also carried out in the presence of excess alkyne or under an atmosphere of ethylene. No significant difference in the products or the product ratios was observed in these experiments compared to the products obtained from the reaction in acetonitrile alone.

(11) The reported yield of **3b** is considered to be a lower limit due to the volatility of this compound.

(12) For recent and leading references to the total synthesis of methylenomycin B (**3b**), see ref 7 and the following: (a) Jernow, J.; Tautz, W.; Rosen, P.; Williams, T. H. *J. Org. Chem.* **1979**, *44*, 4212. (b) Camps, F.; Coll, J.; Moretó, J. M.; Torras, J. *Tetrahedron Lett.* **1985**, *26*, 6397. (c) Mikolajczyk, M.; Zatorski, A. *J. Org. Chem.* **1991**, *56*, 1217 and references therein. (d) Mathew, J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2039. (e) Jacobi, P.; Brielmann, H. L.; Cann, R. O. *J. Org. Chem.* **1994**, *59*, 5305. (f) Negishi, E. I.; Ma, S.; Amanfu, J.; Copéret, C.; Miller, J. A.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5919. (g) Balczewski, P. *Tetrahedron* **1997**, *53*, 2199.

(13) $[(C_5Me_5)Ru(CH_3CN)(CO)_2]^+$: Kulawiec, R. J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **1990**, *9*, 745.

Scheme 3



the high reactivity is generally attributed to the rapid coordination of an additional ligand to the electron-deficient 17e$^-$ complex, producing a 19e$^-$ species which undergoes facile migratory insertion in order to reduce the electron count at the metal. In this case, it is likely that coordination of the donor acetonitrile is responsible for inducing the alkyl migration, yielding acyl intermediate **II** (path **A**). The acyl complex thus formed then undergoes migratory cyclization to generate complex **III**, containing the cyclopentenone ring. Subsequent β-hydride elimination, presumably preceded by displacement of the olefinic residue,[14] releases the organic product and produces the Ru(III) hydride complex **IV**, from which hydrogen radical must be abstracted to form the observed divalent ruthenium byproducts **5**. The carbon monoxide overpressure required for selective cyclization probably acts to inhibit CO dissociation from intermediate **I**. Although the initial alkyl migration is unambiguously induced by oxidation, it is uncertain whether the subsequent cascade of reactions is also accelerated in the odd-electron manifold. The overall reaction sequence that produces the cyclopentenones—allyl/alkyne coupling, carbonyl insertion, and migratory cyclization—closely parallels the postulated mechanism of the Chiusoli reaction, a nickel-mediated cycloaddition of allyl halides, alkynes, and carbon monoxide.[15]

Replacement of the donor acetonitrile with a noncoordinating solvent diverts the reaction pathway away from carbon monoxide insertion; instead, the organic moiety abstracts hydrogen radical to form 1,4-pentadiene **4**, even under carbon monoxide pressure (path **B**). Without a strong donor ligand capable of trapping the Ru(III) acyl intermediate **II**, it is plausible that the initial carbonylation step is reversible. The hydrogen abstraction process is not well understood but presumably does not involve homolytic cleavage of the Ru−vinyl bond, which would lead to loss of alkene stereochemistry from inversion of the vinyl free radical. Abstraction of a hydrogen radical by the odd-electron Ru(III) center, however, would provide a diamagnetic Ru(IV) hydride complex; stereochemically pure (*Z*)-diene **4** is anticipated from a subsequent reductive elimination. A third possibility involves σ-bond metathesis of one pentamethylcyclopentadienyl methyl group, resulting in a "tuck-in" fulvene complex and the organic pentadiene.[16] Further investigation is required to determine the mechanistic details of this unusual reaction.

In conclusion, the one-electron oxidation of the otherwise unreactive ruthenium (1:4,5-η)-1,4-pentadien-1-yl complexes **2** provides a rich reactivity manifold in which the distribution of products is determined by the partitioning between coordination of a donor ligand and hydrogen atom abstraction. In the presence of carbon monoxide, either pathway can be accessed selectively by the simple choice of solvent. Although the mechanism of the oxidatively induced carbonyl insertion process has been subject to intensive investigation,[2] little is as yet known about controlling the downstream reactivity in such reactions.[9] The complex cascade of carbonylation, cyclization, and demetalation triggered by the one-electron oxidation of $(C_5Me_5)Ru((1:4,5\text{-}\eta)\text{-}1,4\text{-pentadien-}1\text{-yl})(CO)$ complexes demonstrates the potential synthetic utility of such methodology.

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Supporting Information Available: Text giving experimental procedures and complete spectroscopic and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Dissociation/ligand exchange of the coordinated cyclopentene and rotation about the metal−alkyl bond is necessary to produce a geometrically accessible β-hydrogen. High substitutional lability is characteristic of 17-electron complexes formed via oxidative activation.[1] Alternative, nondissociative, mechanisms are also possible, as suggested by a reviewer.

[15] (a) Chiusoli, G. P.; Cassar, L. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 124. (b) Chiusoli, G. P. *Acc. Chem. Res.* **1973**, *6*, 422. Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 186. (c) Billington, D. C. *Chem. Soc. Rev.* **1985**, 93 and references therein. (d) Camps, F.; Moretó, J. M.; Pagès, L. *Tetrahedron* **1992**, *48*, 3147. Vilaseca, F.; Pagès, L.; Villar, J. M.; Llebaria, A.; Delgado, A.; Moretó, J. M. *J. Organomet. Chem.* **1998**, *551*, 107. García-Gómez, G.; Moretó, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 878.

[16] Selected references on metal-mediated ring-methyl activation of C_5Me_5 complexes: (a) McDade, C.; Brock, C. P.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (b) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (c) Koelle, U.; Kang, B.-S.; Thewalt, U. *J. Organomet. Chem.* **1990**, *386*, 267. (d) Fan, L.; Wei, C.; Aigbirhio, F.; Turner, M. L.; Gusev, O. V.; Morozova, L. N.; Knowles, D. R. T.; Maitlis, P. M. *Organometallics* **1996**, *15*, 98. Fan, L. Turner, M. L.; Hursthouse, M. B.; Malik, K. M. A. Gusev, O. V.; Maitlis, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 385.