using the BIVOET routine in NRCVAX. SHELXTL: G. M. Sheldrick, Bruker AXS, Madison, WI, **1995**. NRCVAX: E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee, P. S. White, *J. Appl. Crystallogr.* **1989**, *22*, 384. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151479. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Synthesis of the First (1-3:6,7-η-Cyclodecadienyl)ruthenium Complex by the Intramolecular Reaction of an Alkene and a Vinylcyclopropane**

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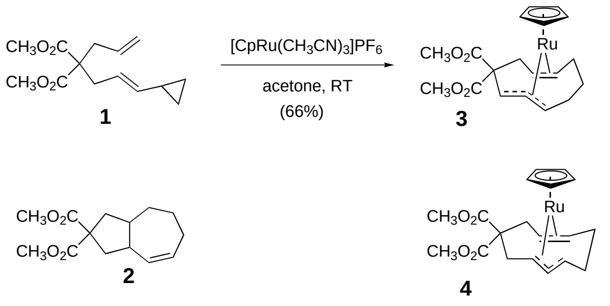
The development of cyclization methods constitutes a continuing challenge because of the ubiquitous occurrence of cyclic structures, especially among bioactive targets. Improving synthetic efficiency by expanding the cycloaddition type protocols, especially to rings that cannot be formed by Diels–Alder type methods, and facilitating formation of unusual ring sizes, notable medium and large rings, then represent two significant objectives. Transition metal catalysis plays a major role towards meeting these objectives. In developing cyclization strategies[1] centered around $[CpRu(CH_3CN)_3]PF_6$[2] as a catalyst, we have discovered an unprecedented reaction that led to the formation of a novel organometallic complex in which a medium-sized carbocycle was effectively created—a result that stands in sharp contrast to the Rh chemistry.

We have recently reported that $[CpRu(CH_3CN)_3]PF_6$[2] catalyzes the intramolecular [5+2] cycloaddition of alkynes and vinylcyclopropanes.[3] To establish the scope and limitations as well as compare the Ru catalyst to the highly successful Rh system developed by the Wender group,[4] we investigated the extension of the ruthenium-catalyzed reaction to alkenes and vinylcyclopropanes. Reaction of diene **1** with 10% $[CpRu(CH_3CN)_3]PF_6$ in acetone did not produce any of the desired [5+2] adduct **2**, but produced a small amount of an unknown ruthenium complex along with recovered diene. By carrying out the reaction of **1** with 0.5 equivalents of $[CpRu(CH_3CN)_3]PF_6$, we were able to isolate an air-stable ruthenium complex in 66% yield [Eq. (1)].[5]



(1)

Analysis of the ^1H NMR spectrum of the complex indicated that the product possessed a cyclopentadienyl moiety and a second ligand derived from **1**. Notably, the spectrum showed that the methoxycarbonyl groups were no longer equivalent and that the ligand derived from **1** had one proton less than the starting diene. Based on the ^1H and ^{13}C NMR data and the structure of the substrate **1**, we tentatively assigned the structure of the unknown complex as the (1-3:7,8-η-cyclodecadienyl)ruthenium complex **4**. However, since we could not find previous examples of η^5-cyclodecadienyl[6] complexes, it was difficult to confirm the structure. Gratifyingly, we were able to grow crystals of the complex suitable for X-ray structure analysis.[7] X-ray analysis concretely established the structure as the (1-3:6,7-η-cyclodecadienyl)ruthenium complex **3** (Figure 1).

Complex **3** has a distorted octahedral structure with the two η^2-olefin carbon atoms and the terminal carbon atoms of the η^3-allyl moiety occupying one plane. The η^2-olefin is situated *endo* and the cyclopentadienyl ligand *exo* with respect to the η^3-allyl group. Similar geometry is found in (arene)ruthenium-(1-3:5,6-η-cyclooctadienyl) complexes.[6a,e] Despite the presence of a quaternary carbon atom adjacent to C1,[8] the η^3-allyl moiety and η^2-olefin in complex **3** are essentially symmetrically bound to the ruthenium center. This symmetry is also similar to that of the neutral complex [Ru(1-3:6,7-η-cod)(η^5-pyrrole)],[6a] but differs from that of the cationic complex $[Ru(1\text{-}3{:}5,6\text{-}\eta\text{-cod})(cot)]^+$ which shows a difference of 0.25 Å in the ruthenium–allyl terminal carbon bond lengths (cod = 1,5-cyclooctadienyl; cot = cyclooctatriene).[6b] The sp^3-carbon atoms adjacent to the π-allyl group are placed *exo* to the allyl plane, with the quaternary carbon atom C(10) having a greater displacement. The deviation from planarity is only slightly less than observed in the [Ru(1-3:5,6-η-cod)] complexes. However, the olefin in complex **3** is essentially planar

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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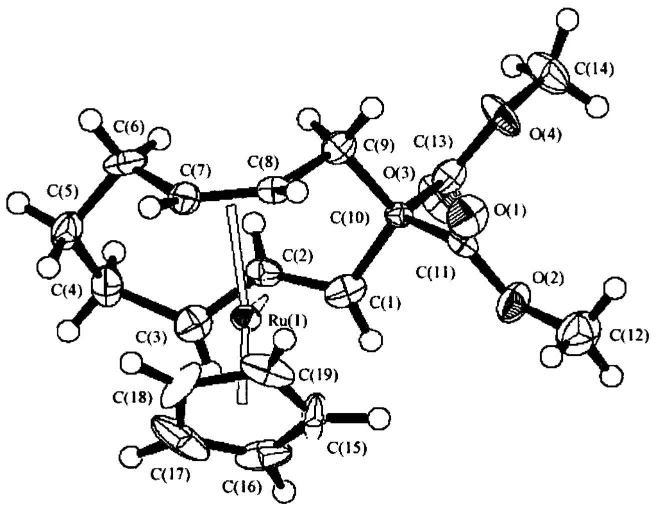
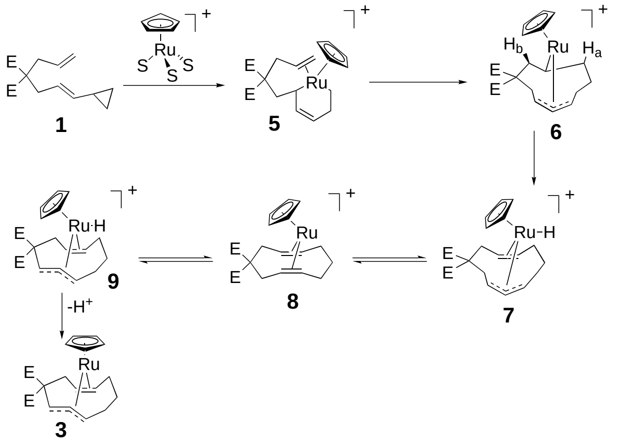


Figure 1. ORTEP drawing of complex **3**. Selected bond distances [Å], bond angles [°], and torsion angles [°] (see Supporting Information): Ru(1)-C1(1) 2.172(6), Ru(1)-C(2) 2.128(5), Ru(1)-C(3) 2.195(5), Ru(1)-C(7) 2.177(5), Ru(1)-C(8) 2.160(5), C(1)-C(2) 1.424(9), C(2)-C(3) 1.363(12), C(7)-C(8) 1.424(7); C(2)-Ru(1)-C(8) 84.2(1), Ru(1)-C(1)-H(1) 89.8, Ru(1)-C(2)-H(2) 130.8, Ru(1)-C(3)-H(3) 80.9, Ru(1)-C(1)-C(10) 111.2(4), Ru(1)-C(3)-C(4) 121.3(4), C(1)-C(2)-C(3) 128.0(6), C(6)-C(7)-C(8) 131.7(6), C(7)-C(8)-C(9) 127.7(5); C(10)-C(1)-C(2)-C(3) 23.4(6), C(1)-C(2)-C(3)-C(4) −13.0(5), C(6)-C(7)-C(8)-C(9) −5.4(9).

(torsion angle 5.4(9)°), which is different from that observed in [Ru(1-3:5,6-η-cod)(η^5-pyrrole)][6a] (torsion angle 23.9(9)°). Presumably, the planar olefin and the five sp^2-carbon atoms are better accomodated by the larger ring size of **3**.

A mechanistic rationale for the formation of **3** is detailed in Scheme 1. The reaction is proposed to be initiated by conversion of the vinylcyclopropane into the ruthenacyclohexene **5**. Our previous results in the ruthenium-catalyzed [5+2] cycloaddition of alkynes and vinylcyclopropanes[3] are consistent with the initial formation of a ruthenacyclopentene rather than a ruthenacyclohexene **5**. However, the mechanism outlined in Scheme 1 suggests that, in the absence of a π-unsaturation with high coordinating ability like an alkyne, coordinatively unsaturated ruthenium(II) can rearrange a vinylcyclopropane into a ruthenacyclohexene. A similar reaction has been proposed as an alternative mechanism for the rhodium-catalyzed [5+2] cycloaddition of alkenes and vinylcyclopropanes.[4e] Ruthenacyclohexene **5** can undergo a 7-*endo*-trig carbaruthenation of the olefin to generate the 16-electron π-allylruthenium(IV) complex **6**. This coordinatively unsaturated complex is ideally suited for *syn*-β-hydrogen elimination of H_a to generate π-allylruthenium(IV) hydride **7**. Presumably, β-hydrogen elimination of H_b does not occur since the required geometry cannot be readily accessed. Reductive elimination of the hydride in **7** generates the coordinatively unsaturated 16-electron ruthenium(II) complex **8**. Insertion into the allylic C–H bond of the symmetrical diene generates η^3-allylruthenium hydride **9**. Deprotonation of **9** or hydrogen atom transfer[9] from **8** to acetone or diene **1** generates neutral [CpRu(1-3:6,7-η-cyclodecadienyl)] **3**. While other pathways, such as ones involving a series of metal-initiated cationic rearrangements, exist, the one proposed appears most reasonable at the present based upon known types of behavior.[10]



Scheme 1. Mechanistic hypothesis for the formation of complex **3**. Open coordination sites on the ruthenium centre in any of the proposed intermediates may be occupied by the solvent (acetone) or acetonitrile. E = CO_2CH_3; S = solvent.

In conclusion, we have prepared the first (1-3:6,7-η-cyclodecadienyl)metal complex from the intramolecular reaction of alkenes and vinylcyclopropanes with [CpRu(CH_3CN)$_3$]PF_6. A mechanism involving the conversion of the vinylcyclopropane into a ruthenacyclohexene and allylic C–H activation of a 1,6-cyclodecadiene is proposed.[1d] This unusual reactivity highlights the divergence in behavior between the Ru and Rh catalysts in their reactions with vinylcyclopropanes. The reaction also provides a novel entry into 10-membered rings.[11] Efforts to further understand the mechanism and to exploit the reaction for the catalytic formation of 10-membered rings are ongoing.

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[5] Preparation of **3**: To a solution of diene **1** (30 mg, 0.118 mmol) in acetone (1.0 mL) was added [CpRu(CH_3CN)$_3$]PF_6 (25 mg, 0.058 mmol). The resulting yellow solution was stirred at room temperature for 2 h and concentrated in vacuo. Flash chromatography eluting with petroleum ether/diethyl ether (6:1) gave **3** (16 mg, 66 %) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.75 (s, 5 H), 3.91 (s, 3 H), 3.73 (s, 3 H), 3.71 (m, 1 H), 3.61 (d, J = 8.4 Hz, 1 H), 3.15 (dd, J = 16.5, 8.4 Hz, 1 H), 2.89 (dd, J = 16.1, 8.6 Hz, 1 H), 2.71 (dd, J = 10.6, 8.6 Hz, 1 H), 2.55 (dd, J = 14.0, 7.3 Hz, 1 H), 1.95 (dd, J = 12.0, 5.6 Hz,

1H), 1.88 (m, 1H), 1.81 (dd, $J = 13.4$, 6.2 Hz, 1H), 1.76 (dd, $J = 14.0$, 8.6 Hz, 1H), 1.42–1.22 (m, 2H), 1.13 (q, $J = 12.3$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.5$, 171.2, 86.2, 85.2, 84.7, 74.0, 57.3, 52.5, 52.5, 51.4, 49.3, 47.1, 34.3, 24.2, 22.0.

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[7] Crystals of **3** suitable for X-ray anaylsis were grown by slow diffusion of hexanes into a solution of **3** in methylene chloride at 0 °C. Crystal Data (also see Supporting Information): $C_{19}H_{24}O_4Ru$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 24.3072(5)$, $b = 8.0591(3)$, $c = 8.8023(1)$ Å, $V = 1724.32(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.608$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\mu(Mo_{K\alpha}) = 9.29$ cm^{-1}, $T = -114$ °C. Siemens SMART CCD diffractometer, 7710 measured reflections, 2858 unique reflections, 2005 used ($4.64° < 2\theta < 49.38°$), $R_1 = 0.032$ (1850 reflexions, $I > 4\sigma(I)$), $wR_2 = 0.051$ (all data), GOF = 0.86. Minimum and maximum peaks in the final difference map −0.34 and −0.58 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158653. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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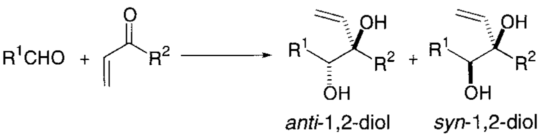
Stereoselective Cross Pinacol-Type Coupling between *α,β*-Unsaturated Ketones and Aldehydes Mediated by Chromium(II) and R_3SiCl**

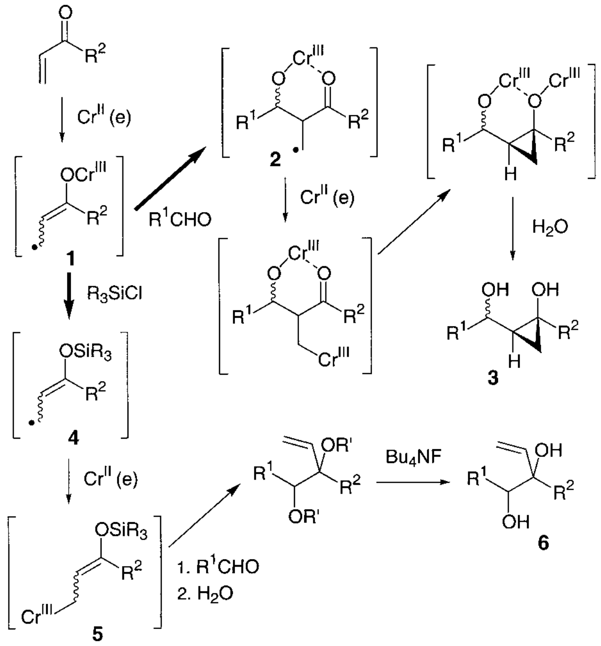
Kazuhiko Takai,* Ryotaro Morita, and Chika Toratsu

The Pinacol-type coupling of aliphatic carbonyl compounds to form 1,2-diols is an attractive and promising tool for organic synthesis.[1, 2] In contrast to the case of aromatic carbonyl compounds, reagents for the coupling of aliphatic aldehydes are limited, and intermolecular cross coupling of two carbonyl compounds in a selective manner is especially difficult. We report herein the cross pinacol-type coupling reaction between an *α,β*-unsaturated ketone and an aldehyde mediated by chromium(II) and R_3SiCl [Eq. (1)].



(1)

Aldehydes are usually unreactive to chromium(II) because of its moderate reducing ability. However, reactions promoted by a one-electron transfer from chromium(II) proceed with some carbonyl compounds, such as *α,β*-unsaturated aldehydes and ketones.[3, 4] In the first step of these reactions, a radical enolate **1** is formed (Scheme 1). When the reaction is conducted in the presence of an aldehyde under anhydrous conditions, an intermolecular aldol reaction, which leads to **2**, is followed by a cyclopropanation reaction to give the *cis*-hydroxyalkyl-substituted cyclopropanol **3**.[4] In contrast, we have found that the reaction course changes dramatically with the addition of Me_3SiCl, producing cross-pinacol coupling products 1,2-diols **6**, after desilylation with Bu_4NF. For example, a mixture of 5-phenyl-1-penten-3-one (**7**, 2.0 equiv) and nonanal (1.0 equiv) in *N,N*-dimethylformamide (DMF) was added at 25 °C to a mixture of $CrCl_2$ (8.0 equiv) in DMF in the presence of Me_3SiCl (6.0 equiv), and the resulting mixture was stirred at 25 °C for 1 h. After workup with water followed by desilylation with Bu_4NF, 1-vinyl-substituted 1,2-diols **8** were obtained in almost quantitative yield (*anti*/*syn* = 40:60).



Scheme 1. Mechanism of the coupling reactions; R = Me or Et, R′ = SiR_3 or H.

The key factor that leads to the cross pinacol-type coupling reaction is the fast trapping of an enolate with Me_3SiCl leading to a trimethylsiloxy compound.[5] Therefore, when the

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