those of the solvent and the carbon atoms of the C21–C30 pentamethylcyclopentadienyl ring, were anisotropically refined. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144326, CCDC-144327, and CCDC-144328. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[18] The ^{1}H NMR spectrum of **2** in [D$_8$]toluene at $-70\,^\circ$C showed two types of η^5-C$_5$Me$_5$ and NH ligands (2:1 ratio), consistent with the solid-state structure.

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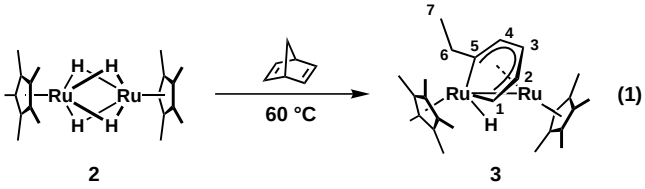
Novel Mode of C–C Bond Cleavage of Norbornadiene on a Dinuclear Ruthenium Complex**

Yasuhiro Ohki and Hiroharu Suzuki*

The activation of C–C bonds by transition metal complexes has attracted considerable attention in the field of organometallic chemistry due to its applicability to industrial processes such as petroleum refining and cracking. Most of the reported examples of C–C bond activation by transition metal complexes involve highly strained systems, pre-aromatic organic substrates such as alkylated cyclopentadienes,[1] or intramolecular ligand activation in which the C–C bond is favorably oriented towards the metal center.[2] In the last ten years, we have intensively studied substrate activation on a multimetallic site and reported a novel selective C–C bond cleavage of cyclopentadiene on a trinuclear ruthenium pentahydride complex [{(η^5-C$_5$Me$_5$)Ru}$_3$(μ-H)$_3$(μ_3-H)$_2$] (**1**).[3] As well as this triruthenium cluster, the dinuclear ruthenium tetrahydride [{(η^5-C$_5$Me$_5$)Ru}$_2$(μ-H)$_4$] (**2**) has been shown to provide an active species for multimetallic activation and to undergo cleavage of various types of bonds such as C(sp^2)–H, Si–H, and P–C(aryl) bonds under mild conditions.[4] We have now focussed our attention on the activation of C–C bonds by a dinuclear complex and have examined the reaction of **2** with a variety of 1,3- and 1,4-cyclic dienes because these dienes have geometries suitable for coordination to a dimetallic site. We report herein an unprecedented type of selective carbon–carbon bond cleavage of norbornadiene by the dinuclear ruthenium tetrahydride complex **2**.

Treatment of **2** with three equivalents of norbornadiene in toluene at 60 °C resulted in the formation of the dinuclear 2-ethylruthenacyclohexadienyl complex [{(η^5-C$_5$Me$_5$)Ru}$_2$-(μ-η^5:η^1:η^1-C$_5$H$_4$C$_2$H$_5$)(H)] (**3**) as the result of a C–C bond cleavage [Eq. (1)] (yield ca. 65% from ^{1}H NMR data). The



2 **3** (1)

new complex **3** was isolated as a red crystalline solid in 44% yield by column chromatography on neutral alumina, and identified on the basis of the ^{1}H and ^{13}C NMR, and ^{13}C-^{1}H HETCOR spectra. The ^{13}C NMR spectrum exhibited two characteristic signals for bridging alkenyl carbons, C1 and C5, at $\delta = 168.1$ ($J_{C,H} = 141.9$ Hz) and $\delta = 186.2$, respectively. The gated ^{13}C NMR spectrum showed three doublets at $\delta = 91.1$ ($J_{C,H} = 156.3$ Hz, C2), $\delta = 85.8$ ($J_{C,H} = 159.5$ Hz, C3), and $\delta = 90.2$ ($J_{C,H} = 151.0$ Hz, C4) for the carbon atoms of the ruthenacycle, and the chemical shifts were comparable to those observed in the related η^5-cyclohexadienylruthenium complexes.[5] A resonance signal due to the hydrogen atom attached to the α-carbon (C1) appeared at $\delta = 9.33$ in the ^{1}H NMR spectrum. The two hydrogen atoms on C6 are diastereotopic and their resonance signals appeared at $\delta = 2.38$ and $\delta = 3.18$.

There are two possible modes of C–C bond cleavage that account for the formation of the ruthenacycle **3**. One involves C–C bond cleavage at C1–C2 and C4–C5 of norbornadiene. The other pathway involves the C1–C2 and C4–C7 bond cleavage (Scheme 1). The latter mode of C–C bond cleavage is observed in the protonation of [(η^5-C$_5$R$_5$)Co(η^4-norbornadiene)].[6] To elucidate the reaction pathway to **3**, complex **2** was allowed to react with 7-methylnorbornadiene[7] under similar conditions to those with norbornadiene. This reaction generated the analogous ruthenacycle [{(η^5-C$_5$Me$_5$)Ru}$_2$(μ-η^5:η^1:η^1-C$_5$H$_3$CH$_3$C$_2$H$_5$)(H)] (**4**) in which a methyl group was bound to C4 [Eq. (2)]. Complex **4** was isolated as a red

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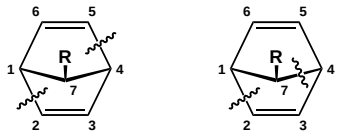
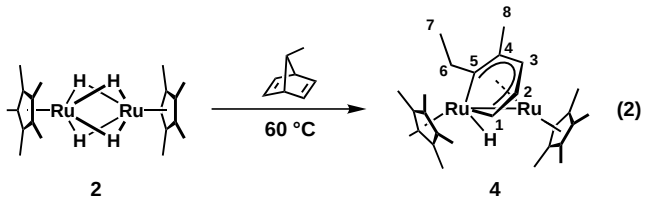
[**] We are grateful to the Kanto Chemical Co., Inc., for a generous gift of pentamethylcyclopentadiene.



Scheme 1. The two possible modes of C–C bond cleavage in norbornadiene that can account for the formation of **3**.



(2)

crystalline solid in 24% yield, and assigned as a dinuclear ruthenacycle analogous to **3** on the basis of the similarity of the ^{1}H and ^{13}C NMR chemical shifts and the coupling pattern. The observation of methyl resonance signals at $\delta_H = 1.80$ and $\delta_C = 18.7$ and the disappearance of the proton signal at $\delta =$ 4.69 (dd) for H4 proved that the methyl group was substituted at C4.

The structure of **4** was confirmed by X-ray crystallography (Figure 1) by using single crystals obtained from cold pentane.[8] The structure clearly depicts the formation of a six-membered ruthenacycle. The Ru1–C1 and Ru1–C5 distances of 1.946(6) and 1.999(5) Å, respectively, correspond to those of a Ru–C σ bond. The Ru–C distances between Ru2 and the ruthenacycle (2.176(6) – 2.227(5) Å) are within the range of those for a Ru–C π bond and are comparable to those observed in η^5-cyclohexadienylruthenium complexes.[5] The Ru–Ru distance of 2.8496(6) Å is indicative of a metal – metal single bond as anticipated from the 18-electron formalism applied to **4**.

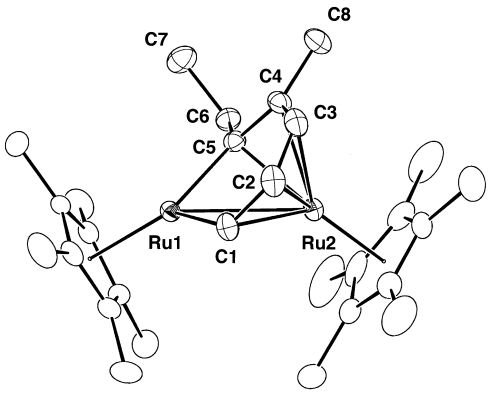


Figure 1. Molecular structure of **4** (with thermal ellipsoids at 30% probability level). Selected bond lengths [Å] and angles [°]: Ru1-Ru2 2.8496(6), Ru1-C1 1.946(6), Ru1-C5 1.999(5), Ru2-C1 2.219(5), Ru2-C2 2.179(6), Ru2-C3 2.176(6), Ru2-C4 2.222(6), Ru2-C5 2.227(5), C1-C2 1.399(8), C2-C3 1.402(9), C3-C4 1.429(8), C4-C5 1.432(7); C1-Ru1-C5 90.0(2), Ru1-C1-Ru2 86.1(2), Ru1-C1-C2 127.1(5), C1-C2-C3 123.5(5), C2-C3-C4 126.3(5), C3-C4-C5 120.9(5), C4-C5-Ru1 125.9(4), Ru1-C5-Ru2 84.6(2).

The methyl group on C4 of the ruthenacycle **4** is derived from that attached to C7 of norbornadiene, and this evidently shows that the C1–C2 and C4–C5 bonds of norbornadiene were cleaved in the reaction with the dinuclear ruthenium tetrahydride complex **2**. The C–C bond cleavage probably took place to relieve the ring strain.

The reaction proceeds most likely by way of an intermediary μ-*endo*,*endo*-η^2:η^2-norbornadiene complex, since the reactions of **2** with acyclic and cyclic 1,3-dienes afford the corresponding μ-η^2:η^2-diene complexes.[9] Furthermore, a dinuclear ruthenium complex having a μ-*endo*,*endo*-η^2:η^2-norbornadiene ligand was isolated by introducing a μ-PR_2 ligand into the diruthenium core.[10]

Thus, we have discovered an unprecedented mode of C–C bond cleavage of norbornadiene on a dimetallic site due to the cooperative action of the two adjacent ruthenium centers. To our knowledge, this is the first selective and consecutive activation of two C–C bonds of norbornadiene.

Experimental Section

3: Norbornadiene (157 μL, 1.45 mmol) was added to a solution of [{(η^5-C_5Me_5)Ru}$_2$(μ-H)$_4$] (230.6 mg, 0.484 mmol) in toluene. The reaction mixture was warmed at 60 °C and allowed to stir for 36 h. After removal of the volatile compounds under reduced pressure, the product was purified by column chromatography on neutral alumina with pentane – tetrahydrofuran (200:1) as the eluent. The product was obtained as a bright pink eluate. Removal of the solvent under reduced pressure afforded **3** (120.7 mg) as a red solid (44% yield). ^{1}H NMR (400 MHz, [D$_6$]benzene, RT, TMS): $\delta = 9.33$ (ddd, $J = 6.8$, 2.0, 1.2 Hz, 1H; H1), 5.03 (ddd, $J = 6.8$, 5.6, 1.2 Hz, 1H; H2), 4.69 (dd, $J = 6.0$, 1.2 Hz, 1H; H4), 4.18 (ddd, $J = 6.0$, 5.6, 1.2 Hz, 1H; H3), 3.18 (dq, $J = 12.0$, 7.2 Hz, 1H; H6-a), 2.38 (dq, $J =$ 12.0, 7.6 Hz, 1H; H6-b), 1.98 (s, 15H; C_5Me_5), 1.56 (s, 15H; C_5Me_5), 1.51 (dd, $J = 7.6$, 7.2 Hz, 3H; H7), −20.76 (d, $J = 2.0$ Hz, 1H; Ru-H); ^{13}C NMR (100 MHz, [D$_6$]benzene, RT, TMS): $\delta = 186.2$ (s; C5), 168.1 (d, J(C,H) = 141.9 Hz; C1), 97.4 (s; C_5Me_5), 91.1 (d, J(C,H) = 156.3 Hz; C2), 90.2 (d, J(C,H) = 151.0 Hz; C4), 89.0 (s; C_5Me_5), 85.8 (d, J(C,H) = 159.5 Hz; C3), 43.6 (t, J(C,H) = 125.1 Hz; C6), 18.1 (q, J(C,H) = 125.5 Hz; C7), 11.9 (q, J(C,H) = 125.9 Hz; C_5Me_5), 11.0 (q, J(C,H) = 126.4 Hz; C_5Me_5).

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[8] X-ray structural determination of **4**: Crystals of **4** were grown at $-20\,^{\circ}C$ from a solution of the compound in pentane. Data were collected at $-50\,^{\circ}C$ on an AFC-7R diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation. The compound crystallizes in space group $P2_1/a$, with $a = 15.264(1)$, $b = 14.446(2)$, $c = 11.618(2)$ Å, $\beta = 96.391(10)^{\circ}$, $V = 2546.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.515\ g\,cm^{-1}$. A total of 6079 unique reflections were recorded in the range $6^{\circ} \le 2\theta \le 55^{\circ}$, of which 3387 were used ($F > 3\sigma(F)$) for solution and refinement. In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data. The structure was solved by the Patterson method (DIRDIF92 PATTY), and all non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on *F*. The final structure of **4** was refined to $R = 0.034$, $R_w = 0.032$, and GOF = 1.31 for 286 parameters. 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-142799. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[10] Y. Ohki, H. Suzuki, unpublished results.

Asymmetric, Catalytic Phenyl Transfer to Aldehydes: Enantioselective Synthesis of Diarylmethanols**

Carsten Bolm,* Nina Hermanns, Jens P. Hildebrand, and Kilian Muñiz

Chiral diarylmethanols are important intermediates for the synthesis of biologically and pharmaceutically active substances.[1] Two major approaches exist for their enantioselective synthesis: the asymmetric reduction of unsymmetrical diaryl ketones and the enantioselective aryl transfer to benzaldehydes. The most prominent examples of the former are based on Corey's CBS reduction methodology[2] and Noyori's enantioselective ketone hydrogenation catalyzed by 2,2′-bis(diphenylphosphanyl)-1,1′binaphthyl (BINAP)/diamine ruthenium complexes.[3] Both reactions work well but also require certain substrate attributes such as electronically very different aryls or *ortho*-substitution of one of the aryl groups. Successful examples of the second strategy have only recently been described.[4] In organozinc chemistry,[5] enantioselective phenyl transfers to aldehydes were first reported by Soai and co-workers who employed a zinc reagent prepared in situ from $ZnCl_2$ and phenylmagnesium bromide and stoichiometric amounts of *N*,*N*-dibutylnorephedrine as chiral ligand (up to 82 % *ee*).[5b, 6] Interestingly, salt-free diphenylzinc behaved differently and gave unsatisfactory results. The first successful application of isolated diphenylzinc in this reaction was described by Fu and co-workers in 1997 who demonstrated that a chiral azaferrocene catalyzed its addition to 4-chlorobenzaldehyde affording the corresponding diarylmethanol with 57 % *ee*.[7] Soon after, Pu and co-workers[8] and Bolm and Muñiz[9] independently developed other catalysts for the asymmetric phenylation of aldehydes based on 2,2′-dihydroxy-1,1′-biphenyl (BINOL) derivatives and planar-chiral ferrocenyl oxazoline **3**,[10] respectively. Here we report on an improvement of the existing methodology which allows the catalytic synthesis of a wide range of arylphenylmethanols **2** from benzaldehydes **1** with very high enantioselectivities.

A major difficulty in the development of an efficient asymmetric phenyl transfer from diphenylzinc to aldehydes **1** is the rapid competitive uncatalyzed pathway, which diminishes the enantioselectivity. To compensate this effect some

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