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Synthesis of metallacyclopentenones by insertion of rhodium into cyclobutenones

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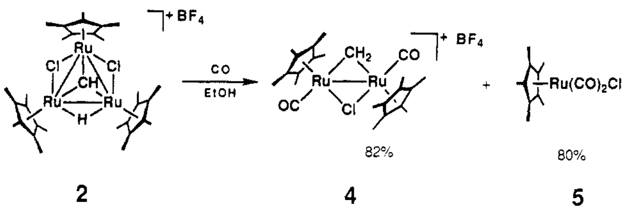
A symmetrical μ_3-methylidyne complex, $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}Cl)]_3(\mu_3\text{-}CH)](BF_4)$ (**3**), was the major product upon treatment of **2** with $CHCl_3$ at ambient temperature. The complex **3** was alternatively prepared by the reaction of **1** with $AgBF_4$ in the presence of acetaldehyde in THF (Scheme I).

The symmetrical structure of **3** was confirmed by means of ^1H and ^{13}C NMR spectroscopy.[8] In the ^1H NMR spectrum of **3**, C_5Me_5 appears at δ 1.57 as a sharp singlet and the triply bridging CH appears at δ 20.03. Methyl and ring carbons of three equivalent C_5Me_5 groups are observed at δ 11.4 (q, J_{CH} = 128.9 Hz) and 97.7 (s), respectively, and the carbon of the methylidyne ligand appears at δ 340.5 (d, J_{CH} = 165.4 Hz) in the ^{13}C NMR spectrum.

Interestingly, the cationic dinuclear μ-methylene complex $(\eta^5\text{-}C_5Me_5)Ru(CO)(\mu_2\text{-}CH_2)(\mu_2\text{-}Cl)Ru(CO)(\eta^5\text{-}C_5Me_5)$ (**4**)[9] was formed via a reductive coupling between μ_3-methylidyne and μ_2-hydride ligands when complex **2** was treated with carbon monoxide (1 atm) in ethanol (eq 3). This is the reverse process of the precedented irreversible conversion of a μ_2-methylene to a μ_3-methylidyne complex caused by liberation of carbon monoxide.[10] In this reaction, one of three "$(\eta^5\text{-}C_5Me_5)Ru$" fragments of **2** was recovered as the dicarbonyl complex $(\eta^5\text{-}C_5Me_5)Ru(CO)_2Cl$.



(3)

The structure of **4** was determined by a single-crystal X-ray diffraction study (Figure 2).[11] Two ruthenium atoms are linked by a direct metal–metal bond as well as bridging CH_2 and Cl ligands.

The key features of **4** that characterize its structural type are the ^1H and ^{13}C NMR and IR parameters associated with the μ-methylene and carbonyl ligands. In the ^{13}C NMR spectrum of **4**, the μ-methylene carbon appears at δ 166.6 (J_{CH} = 149.8 Hz) and the terminal carbonyl appears at δ 197.2. The resonance for the μ-methylene ligand is observed at δ 9.50 in the ^1H NMR spectrum. The IR spectrum reveals a strong absorption assignable to ν_{CO} at 1953 cm^{-1}.

Further mechanistic studies pertaining to the formation of **2** will be reported in due course.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates, interatomic distances and angles, and thermal parameters for **2** and **4** (12 pages); listings of calculated and observed structure factors for **2** and **4** (49 pages). Ordering information is given on any current masthead page.

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[8] **3**: IR (KBr) 2951, 2899, 1465, 1426, 1372, 1262, 1052, 1016, 890, 799, 728, 540, 505, 389 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.57 (s, 45 H, C_5Me_5), 20.03 (s, 1 H, CH); ^{13}C NMR (CD_2C_2) δ 11.4 (q, J_{CH} = 128.9 Hz), 97.7 (s, C_5Me_5), 340.5 (s, CH); mp >300 °C. Anal. Calcd for $C_{31}H_{46}Cl_3BF_4Ru_3$: C, 40.68; H, 5.07. Found: C, 40.33; H, 5.59.

[9] **4**: IR (KBr) 2909, 1953, 1450, 1380, 1362, 1277, 1152, 1092, 1051, 1019, 639, 616, 553, 517, 483, 428 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86 (s, 30 H, C_5Me_5), 9.50 (s, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 10.2 (q, J_{CH} = 129.3 Hz, C_5Me_5), 105.2 (s, C_5Me_5), 166.6 (t, J_{CH} = 149.8 Hz, CH_2), 197.2 (s, CO); mp >300 °C. Anal. Calcd for $C_{23}H_{32}ClO_2BF_4Ru_2$: C, 41.55; H, 4.85. Found: C, 41.33; H, 4.93.

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[11] Complex **4** crystallized from CH_2Cl_2/Et_2O in the triclinic system, space group $P\bar{1}$, with a = 11.543 (3) Å, b = 14.054 (3) Å, c = 8.652 (2) Å, α = 98.89 (2)°, β = 98.98 (2)°, δ = 105.21 (2)°, V = 1309,4 (d) $Å^3$, and z = 2. Intensity data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation in the $2° < 2\theta < 60°$ range. Data processing was performed on a FACOM A-70 computer by using R-CRYSTAN structure solving program library obtained from Rigaku Corp. The positions of the metal atoms were determined by the Patterson method. All other atom positions except for those of the hydrogen atoms of C_5Me_5 rings were obtained by subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares technique. Hydrogen atoms were refined isotropically. The final R and R^w values are 0.0495 and 0.0515, respectively, for 5787 independent reflections with $F_o > 3\sigma(F_o)$.

Synthesis of Metallacyclopentenones by Insertion of Rhodium into Cyclobutenones

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Summary: Cyclobutenones react with $ClRh(PPh_3)_3$ to give 5-rhoda-2-cyclopenten-1-ones (η^2-vinylketenes). Ligand exchange gave $(\eta^5\text{-}C_5H_5)(PPh_3)\overline{RhCH_2C(CEt){=}C(Et)CO}$, which was characterized by X-ray crystallography. Benzocyclobutenones react with $ClRh(PPh_3)_3$ to give mixtures of two regioisomeric rhodaindanones.

Metallacyclic compounds derived from insertion of transition-metal reagents into cyclobutenediones have

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[2] Camille and Henry Dreyfus Foundation Teacher-Scholar, 1985–1990.

[3] Correspondence regarding the X-ray crystallography should be directed to this author.

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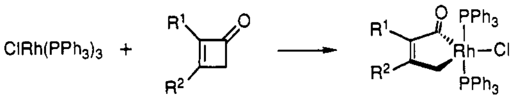
Table I. Insertions into Cyclobutenones

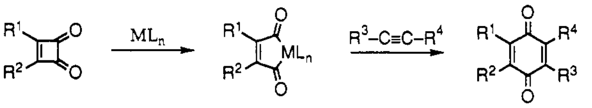


3 4

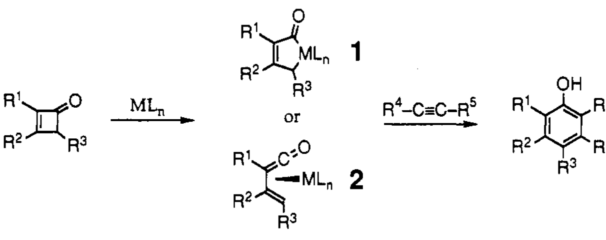
entry no.	product	R^1	R^2	conditions	yield, %[a,b]
1	**4a**	Et	Et	90 °C, 18 h	75
2	**4b**	H	Bu	90 °C, 5 h	71
3	**4c**	H	Ph	60 °C, 18 h	87
4	**4d**	H	OEt	60 °C, 5 h	92

[a] Yields represent precipitated products either as the pure compound or with traces of solvent and PPh$_3$. [b] All products gave satisfactory spectroscopic and mass spectral data, and all but **4c** furnished satisfactory elemental analyses.

proven valuable in a convergent synthesis of substituted quinones (eq 1).[4-7] To generalize the use of functionalized metallacycles for the synthesis of useful organic molecules, a similarly convergent route to substituted phenols via insertions into cyclobutenones and subsequent reaction with alkynes was sought (eq 2), a reaction that would complement the direct phenol synthesis from cyclobutenones and heteroatom-substituted alkynes of Danheiser.[8,9] Reported herein are reactions of cyclobutenones with ClRh(PPh$_3$)$_3$ that lead primarily to 5-rhoda-2-cyclopenten-1-ones (**1**), complexes with an unusual η^2 binding mode for a vinylketene ligand.[10]



(1)



(2)

Several transition-metal vinylketene complexes have been isolated from reactions of metal carbonyls with cyclopropenes,[11-19] as well as a few cases by other methods.[20-26] Similar complexes have been proposed as intermediates in various organometallic reactions that lead to organic products.[25,27-36] All but a few[24] of the isolated

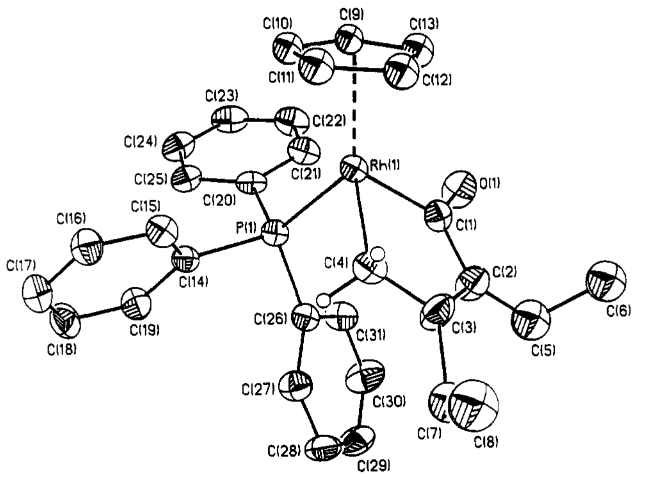
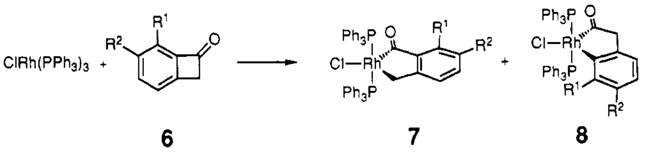


Figure 1. Molecular structure of **5**. Shown is the opposite enantiomer from the coordinates given in the supplementary material with all hydrogens except those on C(4) omitted for clarity. Ellipsoids are shown at the 35% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Rh(1)–C(1), 2.012 (5); Rh(1)–C(4), 2.089 (6); C(1)–O(1), 1.208 (6); C(1)–C(2), 1.473 (8); C(2)–C(3), 1.344 (8); C(3)–C(4), 1.475 (8); C(1)–Rh(1)–C(4), 80.6 (2); Rh(1)–C(1)–O(1), 121.5 (4); Rh(1)–C(1)–C(2), 115.7 (3); Rh(1)–C(4)–C(3) 110.7 (4); C(1)–C(2)–C(3), 113.9 (5); C(2)–C(3)–C(4), 118.7 (6); O(1)–C(1)–C(2), 122.7 (4).

Table II. Insertions into Benzocyclobutenones



6 7 8

entry no.	product	R^1, R^2	conditions	ratio 7:8	yield, %[a,b]
1	**7a, 8a**	H, H	130 °C, 16 h	1:3	71
2	**7a, 8a**	H, H	130 °C, 5 days	1:1.1	77
3	**7b, 8b**	OCH$_2$O	130 °C, 5 h	1:2	50
4	**7b, 8b**	OCH$_2$O	130 °C, 5 days	1:30	64

[a] Yields represent pure mixtures of the two isomers. [b] All compounds furnished satisfactory spectroscopic, mass spectral, and analytical data.

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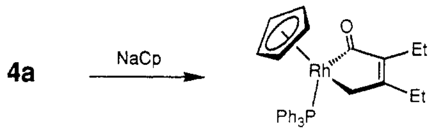
examples contain the vinylketene ligand bound to the metal center in an η^4 fashion (i.e. **2**).

In contrast, heating mixtures of $ClRh(PPh_3)_3$ with 3-substituted or 2,3-disubstituted cyclobutenones **3**[37] produced rhodacyclopentenones **4** in good yields (Table I). Only 4-substituted cyclobutenones failed to give clean products. Electronegative substituents seem to facilitate the reaction, ethoxy-substituted **4d** forming most rapidly in highest yield (entry 4), followed by phenyl-substituted **4c** (entry 3).

The metallacycles **4** are characterized by IR carbonyl absorptions around 1645 cm^{-1}, quite distinct from the range of 1785–1715 cm^{-1} reported for η^4-vinylketenes.[11-16,18,19,22,24,25,38] The ^1H NMR spectra are consistent with the symmetric metallacycle structure, having equivalent ring methylene protons (2.2–3.2 ppm) and equivalent PPh_3 ligands. In the ^{13}C NMR spectra, both the acyl carbons (210–222 ppm) and the methylene carbons (22–34 ppm) exhibit coupling to one rhodium and two equivalent phosphorus nuclei.[39]

Because of the rarity of this type of metallacycle, we sought to characterize one of the complexes by X-ray crystallography. None crystallized adequately, but ligand exchange of **4a** with NaCp gave complex **5** (eq 3), which did provide single crystals.



(3)

5

The spectroscopic data for **5** indicate the same type of metallacycle structure as in **4**, the main difference being the lack of a symmetry plane in **5**.[40] An ORTEP plot of **5** is shown in Figure 1.[41] The structure contains the expected planar 5-rhoda-2-cyclopenten-1-one (planar to within 0.0509 Å) with C(2) and C(3) not bonded to rhodium.

Benzocyclobutenones (**6**)[42] reacted with $ClRh(PPh_3)_3$ to give mixtures of two regioisomeric insertion products, **7** and **8** (Table II). The carbonyls of the 2-rhodaindanones **7** absorb at 1650–1660 cm^{-1} in the infrared region, similar to the case for **4**, while those of the 1-rhodaisoindanones **8** absorb at higher energy around 1695 cm^{-1}. The metallacycle CH_2 protons of **7** give rise to multiplets (~3.5 ppm) in the ^1H NMR spectrum, as do those of **4**, from coupling to rhodium and phosphorus. The corresponding CH_2 protons of **7** (~2.0 ppm) exhibit no coupling.

Reaction times with the parent benzocyclobutenone had little effect on the ratio of **7a** to **8a** (entries 1 and 2). However, with 5,6-(methylenedioxy)benzocyclobutenone, a long reaction time led to almost complete conversion to **8b** (entries 3 and 4). A similar phenomenon was previously observed in the insertion of $ClRh(PPh_3)_3$ into benzocyclobutenedione.[43]

A general synthesis of an uncommon class of metallacycles has been achieved. Preliminary studies have found these rhodium complexes not to react readily with alkynes. However, continuing studies on inserting other metal reagents into cyclobutenones suggest that the synthesis of phenols via metal-complexed vinylketenes can be achieved. These results will be reported in due course.

Acknowledgment. This investigation was supported by Grant No. CA40157, an award by the National Cancer Institute, DHHS. We acknowledge the use of a VG 70-S mass spectrometer purchased through funding from the National Institutes of Health (Grant No. S10-RR-02478) and 300- and 360-MHz NMR spectrometers purchased through funding from the National Science Foundation (Grant Nos. NSF CHE-85-16614 and NSF CHE-8206103, respectively).

Note Added in Proof. An iron-derived metallacycle related to compound **7** is known: Cotton, F. A.; Troup, J. M.; Billups, W. E.; Lin, L. P.; Smith, C. V. *J. Organomet. Chem.* **1975**, *102*, 345.

Supplementary Material Available: Full synthetic, spectroscopic, and analytical data for **4b–d**, **7a,b**, and **8a,b**, details of the data collection and structure solution for **5**, and listings of atomic coordinates and thermal parameters, bond distance and angle data, and least-squares planes (18 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(37) 2,3-Diethyl-2-cyclobuten-1-one (**3a**) was prepared according to the procedure of Dreiding: Ammann, A. A.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1987**, *70*, 321. 3-Phenyl-2-cyclobuten-1-one (**3c**) was prepared according to the procedure of Hassner: Hassner, A.; Dillon, J. L., Jr. *J. Org. Chem.* **1982**, *48*, 3382. 3-*n*-Butyl-2-cyclobuten-1-one (**3b**) was prepared according to the procedure of Danheiser: Danheiser, R. L.; Savariar, S.; Cha, D. D. *Org. Synth.* **1989**, *68*, 32. 3-Ethoxy-2-cyclobuten-1-one (**3d**) was prepared by the addition of ketene to ethoxyacetylene as described by Wasserman and co-workers: Wasserman, H. H.; Dehmlow, E. V. *Tetrahedron Lett.* **1962**, *23*, 1031. Wasserman, H. H.; Piper, J. V.; Dehmlow, E. V. *J. Org. Chem.* **1973**, *38*, 1451.

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(39) Synthesis of **4a**: To a solution of 2,3-diethyl-2-cyclobuten-1-one (104 mg, 0.84 mmol) in chlorobenzene (15 mL) was added $ClRh(PPh_3)_3$ (660 mg, 0.713 mmol). The slurry was purged with argon and then stirred at 90 °C for 18 h. The solvent was removed under vacuum, the residue redissolved in benzene, and the resulting solution filtered through a coarse frit. Addition of hexane precipitated the product, which was isolated by filtration, washed with hexane, and dried under vacuum, giving a yellow powder (423 mg, 75%). Recrystallization by diffusion of hexane into benzene gave analytically pure yellow crystals of **4a**: mp 192–197 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 7.62 (m, 12 H), 7.38–7.29 (m, 18 H), 2.88 (m, 2 H), 1.46 (q, $J = 7.6$ Hz, 2 H), 1.28 (q, $J = 7.7$ Hz, 2 H), 0.51 (t, $J = 7.6$ Hz, 3 H), 0.24 (t, $J = 7.7$ Hz, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 222.4 (dt, $J = 27, 7$ Hz), 176.4, 142.6 (dt, $J = 6, 3$ Hz), 134.8 ("t", $J = 6$ Hz), 130.8 (t, $J = 22$ Hz), 130.0, 127.9 ("t", $J = 5$ Hz), 34.1 (dt, $J = 34, 6$ Hz), 24.9, 19.9, 12.7, 11.4; IR (CH_2Cl_2) 1648, 1622, 1483, 1435, 1097, 819 cm^{-1}; FAB-MS (NBA) *m/e* 751 ($M^+ - Cl$). Anal. Calcd for $C_{44}H_{42}ClOP_2Rh$: C, 67.14; H, 5.38: Cl, 4.50. Found: C, 66.95: H, 5.31; Cl, 4.55.

(40) Spectroscopic and analytical data for **5**: mp 163–164 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 7.66–7.43 (m, 15 H), 5.14 (dd, $J = 1.3, 0.6$ Hz, 5 H), 3.97 (br dd, $J = 15.3, 3.6$ Hz, 1 H), 2.04 (m, 1 H), 1.91 (br dd, $J = 15.3, 9.7$ Hz, 1 H), 1.82 (m, 1 H), 1.62 (m, 2 H), 0.79 (t, $J = 7.6$ Hz, 3 H), 0.57 (t, $J = 7.5$ Hz, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 238.8 (dd, $J = 30, 13$ Hz), 175.1, 150.1 (dd, $J = 6, 1$ Hz), 134.1 (d, $J = 47$ Hz), 134.0 (d, $J = 11$ Hz), 129.7 (d, $J = 2$ Hz), 127.6 (d, $J = 10$ Hz), 92.2 ("t", $J = 3$ Hz), 26.3, 18.9, 18.1 (dd, $J = 31, 11$ Hz), 13.6, 12.5; IR (CH_2Cl_2) 1636 (w), 1606 (s), 1481, 1434, 1167, 1094, 991, 820, 791 cm^{-1}; MS *m/e* (relative intensity) 554 (4.5, M^+), 430 (100). Anal. Calcd for $C_{31}H_{32}OPRh$: C, 67.14; H, 5.83. Found: C, 66.92; H, 5.82.

(41) X-ray crystallographic data for **5**: $C_{31}H_{32}OPRh$, yellow parallelepipeds from cooling an ether solution of **5**. The crystals belong to the monoclinic space group $P2_1/c$; cell dimensions are $a = 21.045$ (8) Å, $b = 8.208$ (3) Å, $c = 16.666$ (6) Å, $\beta = 113.22$ (3)°, $V = 2646$ (2) Å^3, $Z = 4$, and d(calcd) = 1.39 g cm^{-3}. Data were collected at 21 °C with Mo Kα radiation ($\lambda = 0.71073$ Å) by using the ω–2θ scan technique. A total of 3873 reflections were collected with 2972 being observed. The structure was solved by direct methods and refined by using full-matrix least squares to the final residuals $R = 0.0410$ and $R_W = 0.0580$.

(42) Benzocyclobutenone (**6a**) was prepared according to the procedure of Dürr: Dürr, H.; Nickels, H.; Pacala, L. A.; Jones, M., Jr. *J. Org. Chem.* **1980**, *45*, 973. 5,6-(Methylenedioxy)benzocyclobutenone (**6b**) was prepared according to a recently developed procedure: Liebeskind, L. S.; Lescosky, L. J.; McSwain, C. M. *J. Org. Chem.* **1989**, *54*, 1435.

(43) Liebeskind, L. S.; Baysdon, S. L.; South, M. S.; Blount, J. F. *J. Organomet. Chem.* **1980**, *202*, C73.