structure[10b] of **1** is shown in Figure 1. Two Rh^{II} centers are bridged by three $\eta^1:\eta^1:\mu_2$ AcO^- groups across a somewhat long Rh–Rh single-bond distance of 2.475 (2) Å.[2] A chelating bpy and a chelating AcO^- are bound to Rh1 and Rh2, respectively. The chelating AcO^- is asymmetrically ligated (Rh2–O27, 2.051 (8) Å; Rh2–O29, 2.466 (8) Å) as a consequence of the axial/equatorial location of O27 and O29; such asymmetrically chelating carboxylates are extremely rare,[11] symmetrical chelating being much more common.[12] Note that restrictions imposed by the four-membered chelate ring prevent O29 from occupying the true axial position (Rh1–Rh2–O29, 163.5 (2)°). The two Rh1–bpy linkages are also different (Rh1–N3, 2.039 (9) Å, Rh1–N14, 2.120 (10) Å) although to a lesser degree. The molecule possesses virtual C_s symmetry (mirror plane: N3, N14, Rh1, Rh2, O27, O29). It is reasonable to propose that complex **1** forms by initial binding of one bpy nitrogen (N14) to the axial position of Rh1 followed by binding of N3 to the equatorial position; the latter requires displacement of one equatorial acetate oxygen atom, which may then conveniently provide axial ligation at Rh2.

Conductivity measurements in CH_2Cl_2 show **1** to be a nonelectrolyte (Λ_M = 2S·cm²·mol⁻¹). The ^1H NMR spectrum of a freshly prepared solution in CD_2Cl_2 shows three methyl singlets at δ values of 1.67, 2.13, and 2.16 ppm in a 2:1:1 integration ratio, respectively, consistent with retention of the C_s-symmetry solid-state structure on dissolution. In the aromatic region, eight resonances (two slightly overlapping) are observed in the 7.46–9.64-ppm range, again consistent with the inequivalence of the two bpy rings under C_s symmetry. Two $\nu_{as}(COO)$ bands (1578, 1561 cm^{-1}) and two $\nu_s(COO)$ bands (1440, 1426 cm^{-1}) are observed in the IR spectrum (Nujol mull). The bands at 1578 and 1426 cm^{-1} are assigned to the bridging AcO^- groups, and those at 1561 and 1440 cm^{-1} to the chelating AcO^- group.[13] The UV/vis spectrum of a CH_2Cl_2 solution of **1** shows several features, with λ_{max}/nm (ϵ_M/L·mol⁻¹·cm⁻¹) values of 609 (350), 446 (2110), 426 (2005), 300 (19085), 276 (20760), and 244 (16710). $Rh_2(O_2CR)_4L_2$ (L = monodentate axial ligand) complexes usually display four bands near 600, 450, 250, and 220 nm,[1] but the greater number of bands for **1** is reasonable, given its lower symmetry. Cyclic voltammetric measurements on complex **1** reveal only an irreversible oxidation in CH_2Cl_2 (~0.45 V vs ferrocene).

From a purely inorganic viewpoint, the structure of **1** is novel for a Rh^{II}_2 compound in several ways, particularly its high asymmetry, the presence of only three bridges, and the occurrence of two different types of carboxylate coordination (bridging and chelating).[2] It is possible that the different coordination environments of the two metals will result in differing reactivity characteristics. From the biological viewpoint that stimulated this work, the identification of **1** firmly establishes that the $Rh_2(OAc)_4$ core can indeed readily bind to a chelating N ligand while resisting incorporation of a second chelating group (under the conditions used to date). If bpy is accepted as a reasonable model for chelation by two adjacent guanine groups, the identity of **1** suggests that the binding of $Rh_2(OAc)_4$ to DNA may be similar to that established for *cis*-$(NH_3)_2PtCl_2$ and that their antitumor activity may thus have a similar mechanism. Indeed, this possibility that $Rh_2(OAc)_4$ binds to DNA through more than just the axial sites is consistent with the observations of Howard et al.,[4d] who noted "because the inhibitory effects of rhodium(II) carboxylates are not reversible, by resuspension in fresh medium, it seems unlikely that reversible axial ligation reactions between the rhodium(II) dimer and biological ligands could account for the observed biological activity".

The identification of complex **1** now encourages us to move on to the logical second phase of this work, the attempted crystallization and structural characterization of an adduct between $Rh_2(OAc)_4$ and d(pGpG), as accomplished for *cis*-$(NH_3)_2PtCl_2$.[14]

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Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for **1** (3 pages). Ordering information is given on any current masthead page.

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Nickel(0)-Catalyzed Synthesis of Substituted Phenols from Cyclobutenones and Alkynes

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The reaction of strained small-ring organic compounds with unsaturated moieties via transition metal induced ring cleavage has been used to advantage in convergent syntheses of a variety of substituted five- and six-membered-ring structures.[3-16] An analogous reaction of substituted cyclobutenones with alkynes via the η^2-vinylketene (**1**) or η^4-vinylketene (**2**) metallic intermediates shown in Scheme I could provide a direct route to highly substituted phenols. All of the key steps in the scheme have been observed recently as discrete stoichiometric processes. Insertion of $ClRh(PPh_3)_3$ into cyclobutenones gave metallacycles of type **1** which did not react productively with alkynes,[17] while (η^5-indenyl)$Co(PPh_3)_2$ reacted to provide η^4-vinylketene complexes of type **2**, which upon heating with alkynes yielded phenols in some cases.[18] Herein is documented the first *metal-catalyzed* coupling of cyclobutenones and alkynes directly providing substituted phenols under mild conditions in good yields.

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Scheme I

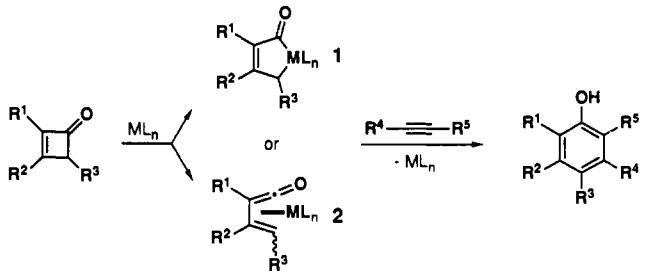
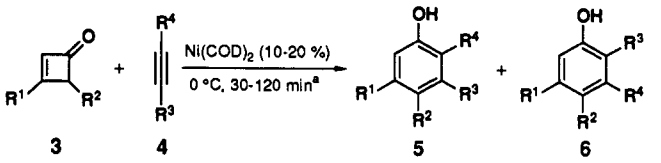


Table I. Catalytic Formation of Phenols



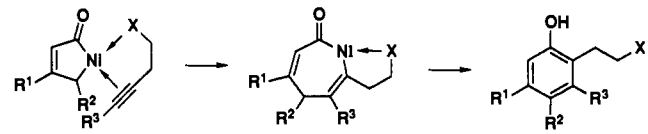
entry	products	R^1	R^2	R^3	R^4	ratio 5:6	yield,[b] %
1	**5a**	Ph	H	Et	Et		75
2	**5b,6b**	Ph	H	Me	*i*-Pr	50:50	81
3	**5c,6c**	Ph	H	Me	$SiMe_3$	45:55	58
4	**5d,6d**	Ph	H	Et	$CH_2CH{=}CH_2$	50:50[c]	60
5	**5e,6e**	Ph	H	Et	$(CH_2)_2Cl$	72:28[c]	64
6	**5f,6f**	Ph	H	Et	$(CH_2)_3Cl$	58:42[c]	57
7	**5g**	Ph	Me	Et	Et		60
8	**5h,6h**	Ph	Me	Me	$(CH_2)_2OTBDMS$[d]	75:25	63
9	**5l**	Bu	H	Et	Et		76
10	**5j,6j**	Bu	H	Me	$(CH_2)_2OTHP$[e]	65:35	47
11	**5k,6k**	Bu	H	Me	$(CH_2)_2OTBDMS$[d]	75:25	59
12	**5l,6l**	Bu	H	Me	$(CH_2)_3OTBDMS$[d]	50:50	67
13	**5m**	Bu_3Sn	H	Et	Et		43

[a] Reactions were run in diethyl ether (entries 1–8) or hexanes (entries 9–13) with a stoichiometry of 2 equiv of alkyne to 1 equiv of cyclobutenone. [b] Yields represent pure chromatographed products (ref 20). [c] Ratio was determined by ^1H NMR spectroscopy on a mixture of unseparated isomers. [d] TBDMS = *tert*-butyldimethylsilyl. [e] THP = 2-tetrahydropyranyl.

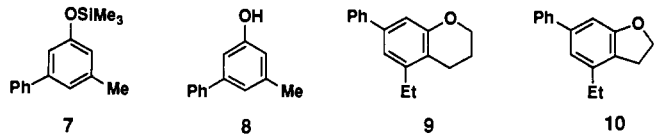
As illustrated in Table I, addition of 10–20 mol % of bis(1,5-cyclooctadiene)nickel,[19] $Ni(COD)_2$, to solutions containing 1 equiv of cyclobutenone and 2 equiv of internal alkyne led to rapid phenol formation at 0 °C.[20,21] 3-Substituted and 3,4-disubstituted cyclobutenones could be employed, while 2,3-disubstituted systems failed to react. Electronically perturbing cyclobutenone substituents (alkoxy, acyl) prevented successful reaction. However, 3-(tri-*n*-butylstannyl)cyclobutenone underwent cycloaddition giving stannylphenol **5m** (entry 13), which should be suitable for further functionalization.

Unlike the thermal reaction of cyclobutenones with alkynes reported by Danheiser,[22,23] activated alkynes are not required and in fact are oligomerized by the Ni(0) catalyst rather than giving phenols. The thermal reaction, which proceeds via initial [2 + 2] cycloaddition of the alkyne with a transient vinylketene intermediate, also differs in the ultimate arrangement of cyclobutenone substituents in the phenol products.[24]

Scheme II



While terminal alkynes produced green solutions without catalytic activity, 1-(trimethylsilyl)propyne underwent cycloaddition, though with little regioselectivity (entry 3). The regioisomers were identified by the instability of **5c** toward Brook rearrangement to **7** and subsequent desilylation to **8**,[25] both of which furnished ^1H NMR spectra consistent with 1,3,5-substitution.[20] Electronically perturbing proximal alkyne substituents gave low yields, but a variety of distal functional groups was tolerated including olefin, chloro, and protected alcohol groups (entries 4–6, 8, and 10–12).



7 **8** **9** **10**

There appears to be little regioselectivity based on the size of alkyne substituents (entry 2). However, alkynes bearing heteroatom-substituted chains did show a modest selectivity which was greater with two-carbon tethers than three-carbon tethers (entries 5, 6, 8, and 10–12). In all cases the major product bears the heterosubstituted chain ortho to the hydroxyl group. These observations are consistent with a mechanism in which the alkyne inserts preferentially into the metal–C_4 bond of the vinylketene complex followed by reductive elimination. Chelation of nickel by a heteroatom-substituted alkyne[26] would cause the initial carbon–carbon bond to form at the alkyne terminus away from the chelating chain (Scheme II).

The major isomers of the oxygen-substituted products, **5h**, **5j**, and **5k**, were identified by the presence of intramolecular hydrogen bonding inferred from the hydroxyl signals in the IR and ^1H NMR spectra (~3300 cm^{-1}; 7–8 ppm), as compared with the non-hydrogen-bonded **6h**, **6j**, and **6k** (3590 cm^{-1}; 4.5–5.0 ppm). The chloro-substituted phenols **5e**/**6e** and **5f**/**6f** were identified by treatment of each mixture with excess sodium hydride in tetrahydrofuran, which led to recovery of **6e** and **6f** and isolation of dihydrobenzopyran **9** and dihydrobenzofuran **10**.[20]

The results above show that the convergent synthesis of substituted phenols is possible by nickel(0)-catalyzed ring opening and cycloaddition of cyclobutenones with alkynes. Future efforts will explore application of this method to intramolecular reactions.

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Supplementary Material Available: Full spectroscopic and analytical characterization of **5–11** (8 pages). Ordering information is given on any current masthead page.

(19) $Ni(COD)_2$ was conveniently prepared by the method of Krysan and Mackenzie: Krysan, D. J.; Mackenzie, P. B. *J. Org. Chem.* **1990**, *55*, 4229. After crystallization from toluene, the catalyst was stored under an inert atmosphere and weighed in air immediately prior to use. We thank Dr. Damian Krysan for communicating the preparation prior to publication.

(20) All new compounds were spectroscopically characterized and furnished satisfactory elemental analyses (C, H, ±0.4%) or high-resolution mass spectra. Details are provided in the supplementary material.

(21) In a representative experiment, 3-phenylcyclobutenone (288 mg, 2.00 mmol) and 3-hexyne (454 μL, 4.00 mmol) were dissolved in diethyl ether (40 mL) under argon at 0 °C. Crystalline $Ni(COD)_2$ (55 mg, 0.20 mmol, 10%) was added, giving a red-brown solution. After 45 min at 0 °C, TLC analysis revealed residual cyclobutenone. A second portion of $Ni(COD)_2$ (28 mg, 0.10 mmol, 5%) was added. Within 30 min, the cyclobutenone was consumed. The reaction mixture was exposed to air, filtered through SiO_2, concentrated, and chromatographed on SiO_2, giving **5a** (341 mg, 75%).

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(24) The thermal reaction of cyclobutenones with activated alkynes yields phenols in which the cyclobutenone C_4 substituent (R^2 in **3**) resides ortho to the hydroxyl group. The nickel-catalyzed reaction produces regioisomeric phenols. The locations of the hydrogen and methyl (R^2) substituents in phenol **5g** were determined by ^1H NOE measurement on the O-trimethylsilyl derivative **11**, made from **5g** and excess bis(trimethylsilyl)acetamide. Presaturation of the $SiMe_3$ singlet (0.26 ppm) produced at 15% enhancement of the ortho-hydrogen singlet (6.54 ppm).

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