along with two isomers of a product tentatively identified as **18**.[22] The vinylketene complex **15c** will undergo 1,2-additions with pyrrolidine and sodium methoxide in methanol. The CO-insertion step leading to vinylketene complex formation is reversible in some systems,[9,11c,e] but there is no evidence of this for complex **15b**. Exposure of a benzene solution of **15b** to ^{13}CO (balloon) at 80 °C for 20 min led to a 14% recovery of **15b** in which no label had been incorporated into the ketene carbon (C(4)) or into the CO ligands.

The above observations establish a clear parallel between the intramolecular reactions of alkoxy and amino carbene complexes with alkynes, and the involvement of an η^4-vinylketene intermediate is strongly supported. While these results do not directly apply to the intermolecular reactions, the isolation of an η^4-vinylketene complex from the reaction of a chromium carbene complex and an alkyne will hopefully provide a tool for the more direct examination of several aspects of the mechanism of this exceedingly complex multifaceted reaction.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8821326). We thank the Organic Division of the American Chemical Society for a predoctoral fellowship sponsored by Rohm and Haas Company awarded to B.A.A. Some of the mass spectral data were obtained at the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (CHE-8211164). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599). We thank Professor L. S. Liebeskind for the communication of his results prior to publication.

Supplementary Material Available: Spectral data for compounds **7b**,**c**, **11**, **12**, **15b**,**c**, and **16–19** and X-ray crystallographic data for compound **15c** including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (10 pages); listing of F_o and F_c for compound **15c** (11 pages). Ordering information is given on any current masthead page.

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Insertion of (η^5-Indenyl)cobalt(I) into Cyclobutenones: The First Synthesis of Phenols from Isolated Vinylketene Complexes

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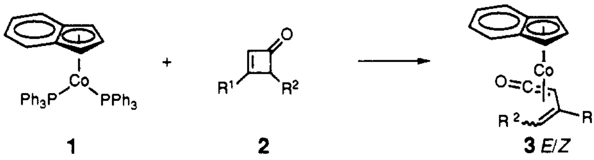
Transition-metal vinylketene complexes have been proposed as intermediates in reactions leading to a variety of organic products including phenols and naphthols, cyclohexadienones, cyclopentenones, lactams, furans, α-pyrones, and 2-furanones.[3-17]

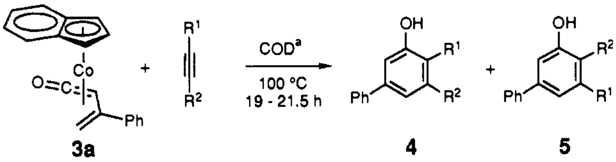
Table I. Synthesis of Vinylketene Complexes



product no.	R^1	R^2	yield, %	ratio *E*/*Z*^{a}
3a	Ph	H	32	–
3b	Ph	Me	80	19:1
3c	SiMe$_3$	Me	81	3.5:1
3d	*t*-Bu	Me	42	>98:2
3e	*t*-Bu	Ph	17	>98:2

^{a} Reactions were run in toluene for 60 min at 100 °C or reflux with a 1:1 stoichiometry.

Table II. Reaction of Vinylketene Complexes with Alkynes



entry	R^1	R^2	yield, %
1	Et	Et	**4a**, 65
2	H	Bu	**4b**, 45; **5b**, 18
3	CO$_2$Me	CO$_2$Me	**4c**, 45
4	CO$_2$Et	Me	**4d**, 42; **5d**, 50^b

^{a} Reactions employed 2 equiv of cyclooctadiene to inhibit alkyne trimerization and a 5-fold (entries 1 and 2) or 20-fold (entries 3 and 4) excess of alkyne. ^{b} NMR yield of phenol determined on a 3.9:1 mixture with alkyne trimer.[30]

Evidence for the participation of vinylketene complexes in some of these reactions comes from trapping with alcohols and from isolation of free and coordinated vinylketenes.[7,10,13,18-22] Isolated η^4-vinylketene complexes bearing 4-alkoxy substituents have been taken on to furan,[13] 2-furanone,[13] and α-pyrone[7] products, but to date none have been reported to give the important phenol or naphthol products.[23] We report here a new synthesis of η^4-vinylketene complexes of cobalt and their conversion to phenols by reaction with alkynes and to a naphthol by intramolecular cyclization.

Previously cyclobutenones were found to react with ClRh(PPh$_3$)$_3$ yielding metallacyclopentenones.[24] In contrast, reaction with (η^5-C$_9$H$_7$)Co(PPh$_3$)$_2$ (**1**)[25] gave η^4-vinylketene complexes (**3**)

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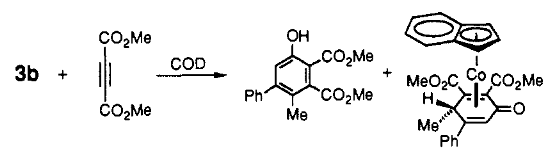
(Table I).[26,27] Compounds **3b** and **3c** were obtained as mixtures of *E* and *Z* isomers, which were identified by ^{1}H NMR shifts[28] and NOE measurements. In both cases the *E* isomer was the major kinetic product, but prolonged heating of the isolated complexes led to mixtures in which the *Z* isomer predominated.[29]

Reaction of the monosubstituted vinylketene complex **3a** with various alkynes produced phenols, unsymmetrical alkynes yielding mixtures of regioisomers (Table II).[27] Such a double C–C bond making cyclization has been suggested to account for cyclohexadienone formation from a two-alkyne reaction with a chromium carbene.[12]

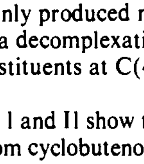
Reaction of the disubstituted vinylketene complex **3b** proceeded well only with the electron-deficient alkyne dimethyl acetylenedicarboxylate (DMAD). In addition to phenol **6**, cyclohexadienone complex **7** was obtained (eq 1).[27] The stereochemistry shown for **7** is suggested by the absence of an NOE to any indenyl hydrogens upon irradiation of the methyl doublet. Irradiation of the endo hydrogen quartet produced a small (5%) enhancement of one of the aromatic (indenyl/phenyl) multiplets.



6, 43 % **7**, 16 %

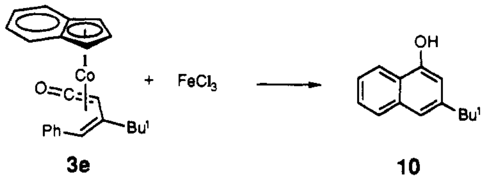
(1)

The unreactivity of **3b** with simple alkynes may be due to the methyl group sterically preventing alkyne complexation and formation of an intermediate metallacyclopentenone **8**. Consistent with this idea, CO adds readily to **3a** giving the metallacyclopentenone (η^5-C_9H_7)(CO)CoC(O)CH=C(Ph)CH$_2$ (**9**)[27] while CO will not add to **3b** even under forcing conditions. DMAD may react by an alternate mechanism which bypasses intermediate **8**.



8: L = alkyne, R = Me
9: L = CO, R = H

The (2-phenylvinyl)ketene complex **3e** represents an analogue of intermediates proposed in naphthol-forming reactions of metal carbenes. Thermolysis of **3e** led only to nonspecific decomposition, but FeCl$_3$ oxidation cleanly produced naphthol **10**[31] (eq 2). The cyclization may occur via decomplexation since free vinylketenes bearing unsaturated substituents at C(4) are known to cyclize to phenols.[32]



3e **10**

(2)

The reactions in Table I and II show that a convergent synthesis of substituted phenols from cyclobutenones and alkynes is possible via transition-metal insertion chemistry. Continuing efforts are aimed at improving the method through modification of the metal reagent.

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Supplementary Material Available: Full synthetic details and spectroscopic and analytical characterization of **1** and **3–9** (10 pages). Ordering information is given on any current masthead page.

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[26] Selected data for **3a**: Anal. C, H. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.23 (m, 3 H), 6.96 (m, 2 H), 6.87 (br d, J = 8.3 Hz, 1 H), 6.62 (br d, J = 8.5 Hz, 1 H), 6.56 (m, 1 H), 6.34 (m, 1 H), 6.16 (m, 1 H), 5.87 (m, 2 H), 3.30 (br t, J = 2.3 Hz, 1 H), 3.20 (dd, J = 2.5, 1.1 Hz, 1 H), 1.16 (dd, J = 2.0, 1.1 Hz, 1 H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 224.4 (CO), 136.0, 128.7, 127.9, 127.8, 126.0, 125.4, 121.9, 120.2, 109.8, 108.3, 104.8 (preceding three signals: two quaternary indenyl carbons and *C*C$_6$H$_5$ of vinylketene), 93.4, 74.0, 73.4, 35.3 (*C*H$_2$), 27.4 (*C*H=CO). IR (CH$_2$Cl$_2$): 1770 (s), 1749 (s), 1384, 1321, 965, 818, 668 cm^{-1}.

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Redox Properties of Porphycenes and Metalloporphycenes as Compared with Porphyrins

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The porphycenes, structural isomers of porphyrins recently synthesized at the Cologne Laboratory,[1] are attracting considerable attention.[2,3] In light of the paramount importance of redox processes in many photochemical and photobiological reactions of porphyrins, electron-transfer processes of porphycenes are of special interest. Although numerous papers have been published on the electrochemistry of porphyrins,[4] in particular on the effects

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