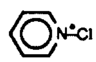
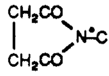
Table I. EPR Parameters for Various σ^* Radicals Related to the Pyridine–Chlorine Adduct

radical		hyperfine coupling, G[a]			ref
		$A_\parallel$	$A_\perp$	A_{iso}	
 [e]	^{14}N	66	42	50	*b*
	^{35}Cl	112	22	52	
$Ph_3P\dot{-}Cl$	^{31}P	730	555	613	*c*
	^{35}Cl	79	38	52	
	^{14}N	68	45	52.7	*d*
	^{35}Cl	115	24	54.3	

[a] G = 10^{-4} T. [b] This work. [c] Abu-Raqabah, A.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1*, in press. [d] Pace, D.; Ezell, K.; Kispert, L. D. *J. Chem. Phys.* **1979**, *71*, 3971. [e] g values of g_x = 2.026, g_y = 2.0313, g_z = 2.003.

generate pyridine radical cations in $CFCl_3$ at 77 K unambiguously,[17,18] and since these clearly have the σ-SOMO (II) rather than a π-SOMO, this should be a good system for preparing the pyridine–chlorine adduct.

(II) 

After generating pyridine cations by radiolysis at 77 K and annealing to ca. 145 K, new EPR features grew in as the $(py)^{\bullet+}$ features were lost. These clearly contain chlorine hyperfine features (Figure 2). From the data (Table I), it can be seen that the maximum hyperfine coupling components for ^{14}N and $^{35/37}Cl$ share the same direction, thus establishing that the adduct is a true three-electron-bond unit with the chlorine atom lying in the plane of the ring.

We conclude that σ^* intermediates of this type are of very wide significance and need to be considered in radical reactions whenever one of the reactants or, indeed, the solvent has a suitably localized electron pair available for bonding.

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Characterization of the First η^4-Vinylketene Metal Complex from the Reaction of a Group 6 Fischer Carbene Complex and an Alkyne[†]

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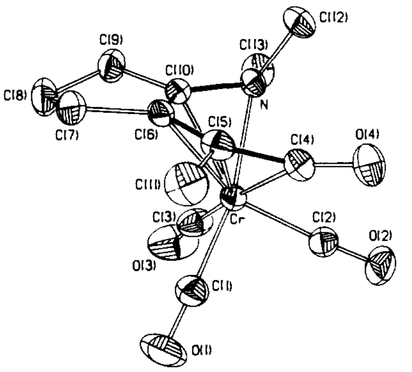
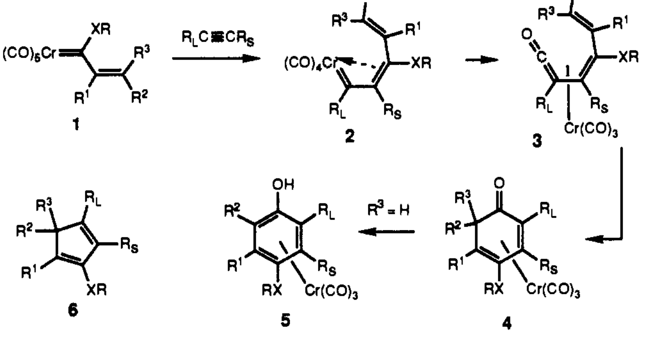


Figure 1. Molecular structure and numbering scheme for **15c** [$Cr(CO)_3(C_{10}H_{15}NO)$]. Bond lengths (angstroms) and angles (degrees): Cr–C(4), 2.024 (4); Cr–C(5), 2.219 (4); Cr–C(6), 2.200 (4); Cr–C(10), 2.130 (4); Cr–N, 2.194 (3); O(4)–C(4), 1.215 (4); C(4)–C(5), 1.430 (5); C(5)–C(6), 1.424 (6); C(6)–C(10), 1.404 (5); C(10)–N, 1.421 (4); O(4)–C(4)–C(5), 136.0 (4); C(4)–C(5)–C(6), 122.7 (3); C(5)–C(6)–C(10), 126.0 (3); C(6)–C(10)–N, 119.9 (3).

Scheme I



Premier among the many reactions of Fischer carbene complexes that have found utility in organic synthesis are the benzannulation reactions with alkynes.[2-5] This annulation produces either the cyclohexadienones **4**[5] or 4-alkoxyphenols **5**[3,4] and has provided unique strategies for the synthesis of a number of natural products (Scheme I). This reaction has long been proposed[6] to involve an η^4-vinylketene complex of the type **3** as the penultimate intermediate.[7,8] Although a number of η^4-vinylketene complexes are known for various metals, there are no examples for chromium and no examples for d^6 complexes of the group 6 metals.[9-12] We

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[†] Dedicated to Professor Leon Stock on the occasion of his 60th birthday.

(1) American Chemical Society Organic Division Rohm and Haas Fellow 1989–1990. William Rainey Harper Fellow 1990–1991.

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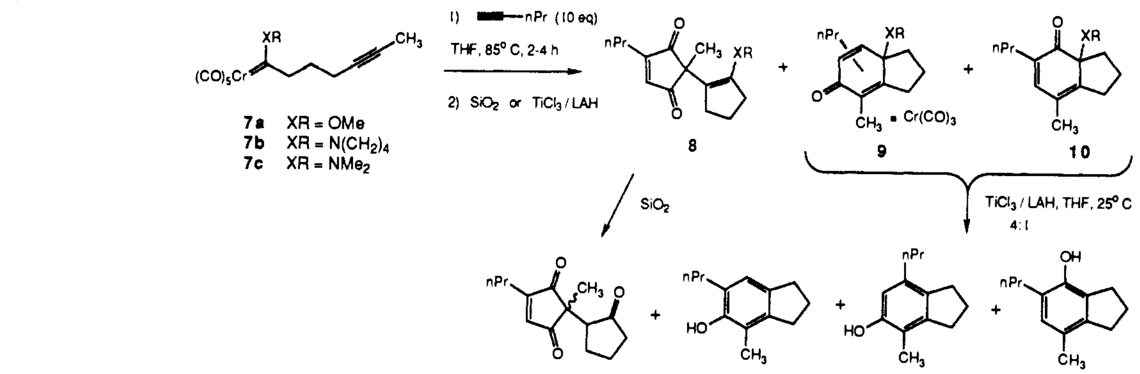
Scheme II

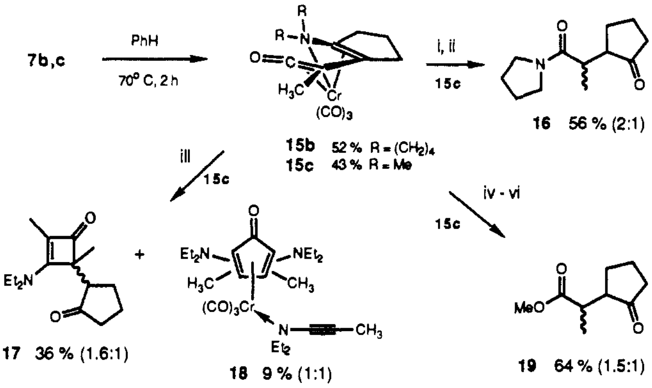


Complex	Solvent	XR	11	12	13	14
7a	THF	OMe	23 % (as **8a**)	≤1 %	≤0.3 %	7 %
7b	THF	$N(CH_2)_4$	16 % (1.1:1.0)	7 %	16 %	2 %
15b	THF	$N(CH_2)_4$	19 % (1.1:1.0)	11 %	26 %	≤1 %

report the isolation and characterization of the first examples of η^4-vinylketene complexes obtained from an intramolecular reaction of a group 6 Fischer carbene complex and an alkyne and the reactions of these vinylketene complexes with acetylenes to give cyclopentenediones and indanols.[13-15]

The intramolecular reactions of alkoxycarbene complexes with alkynes in the presence of a second alkyne are known to give cyclopentenedione and indanol products.[7c,16,17] At the outset it was not clear whether the amino complexes **7b** and **7c** would give this same set of CO-insertion products since, on the one hand, it has been observed that the reactions of aryl amino carbene complexes with alkynes give non-CO-incorporated products of the type **6** (as indene derivatives)[7e,18] and, on the other, that several other reactions of amino complexes with alkynes do give CO-inserted products.[7e,14a,19] However, as shown in Scheme II, the reaction of the pyrrolidino complex **7b** with 1-pentyne led only to CO-inserted products, as does the corresponding reaction of the methoxy complex **7a**.[7c] The analysis was simplified by reduction of the crude reaction mixture with McMurray's reagent to produce a mixture of the isomeric indanols **12**–**14**. Both complexes give cyclopentenedione **8**; however, the distribution of the indanol products favors **14** from the alkoxy complex **7a** and favors **12** and **13** from the amino complex **7b**. We previously reported[7c] that alkoxy complex **7a** gives indanol **13** in benzene at lower concentrations, and studies directed to identifying the factors affecting product distribution will be published separately.

Scheme III[a]



[a] (i) Pyrrolidine (4 equiv), THF 25 °C, 30 min; (ii) HCl (aqueous); (iii) $Et_2NC{\equiv}CCH_3$, benzene, 25 °C, 18 h; (iv) MeONa/MeOH. THF. 25 °C; (v) HCl (aqueous); (vi) acetone, $FeCl_3$(DMF).

The intramolecular reactions of the alkoxy complex **7a** with alkynes were proposed to involve an η^4-vinylketene complex,[7c] and surprisingly, if the amino complex **7b** is heated in the absence of an alkyne, the η^4-vinylketene complex **15b** (Scheme III) can be isolated in 52% yield. This complex is remarkably stable, and although it is quite polar, it can be easily purified in the presence of air by elution on silica gel with a 1:1 mixture of ethyl acetate and hexane (R_f = 0.4). The ^{13}C NMR and IR spectral data of **15b,c**[20] are similar to those of known vinylketene complexes[9-12] with the carbonyl stretch of the coordinated ketene at 1726 cm^{-1} and the four coordinated carbons at δ = 23.7, 106.7, 111.2, and 253.4 ppm. The X-ray structure of **15c** revealed that the sixth coordination site on chromium is occupied by nitrogen as indicated in Figure 1.[20] The O–C–C bond angle of the coordinated ketene is 136° and is typical of vinylketene complexes that have been structurally characterized.[9-12] The short metal–carbon bond to the ketene carbon (2.024 Å) is also typical; however, it is unusual that the metal–carbon bond distance to C(10) is not the longest of the metal–carbon bonds to the four vinylketene carbons, and this may be due in this case to coordination of nitrogen at C(10).

In support of the intermediacy of vinylketene complexes in the reactions in Scheme II is the observation that the isolated vinylketene complex **15b** will react with 1-pentyne to give nearly the same distribution of products as the amino carbene complex **7b** (Scheme II). The indanols **12** and **13** can only be the result of a formal [4 + 2] cycloaddition[7c] of the vinylketene complex with 1-pentyne, which is to be contrasted with the reaction with diethylpropynylamine, which gives the [2 + 2] cycloadduct **17**[21]

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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.

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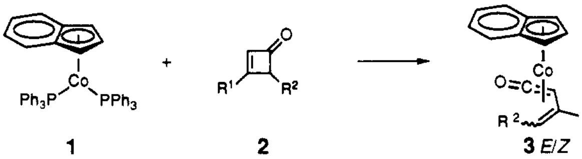
Transition-metal vinylketene complexes have been proposed as intermediates in reactions leading to a variety of organic products including phenols and naphthols, cyclohexadienones, cyclopentenones, lactams, furans, α-pyrones, and 2-furanones.[3-17]

Table I. Synthesis of Vinylketene Complexes

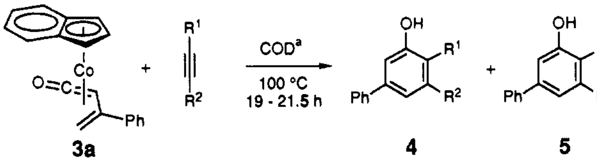


1 2 3 *E/Z*

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



3a 4 5

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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(1) National Institutes of Health Postdoctoral Fellow, 1989–1991.

(2) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1985–1990.

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