

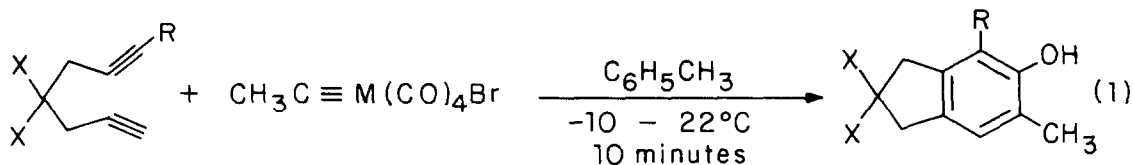
SYNTHESIS OF PHENOLS FROM METAL-CARBYNES AND DIYNES

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Summary: Metal-carbynes $RC\equiv M(CO)_4Br$ with diacetylenes give specific phenols in good yield. The reactions take only a few minutes at or below room temperature.

Metal-carbynes, unlike metal-carbenes,¹ have rarely been considered reagents for organic synthesis² although those illustrated by structure 1 have been known for a dozen years and are fairly easy to prepare.³ We reported recently that a number of tungsten metal-carbynes, by polymerizing a variety of acetylenes and cyclic alkenes, behave as though they were reactive metal-carbenes.⁴ We are reporting here that, as illustrated in equation 1, they combine stoichiometrically with a variety of diacetylenes to give specific phenols in a seemingly general process that is simple to carry out.



X = CO ₂ CH ₃ , H	<u>1</u>	42 - 60% yield (M = W)
R = H, CH ₃ , C ₆ H ₅	M = W, Cr	31 - 50% yield (M = Cr)

Concurrently, W. D. Wulff and his students discovered that metal-carbenes bring about the same transformations, but the yields are good only when the reaction mixtures are extremely dilute.⁵ In contrast, the metal-carbynes, because they are highly reactive, can be used at concentrations twenty-three times as great, and they give high yields after only ten minutes at or below room temperature. The acetylenes with which they combine are not required in large excess, and the reactions can be carried out in simple flasks. (The metal-carbenes require sealed tubes at 70 - 95 °C, and to circumvent concomitant polymerization, large, dilute, deoxygenated excesses of acetylene.)

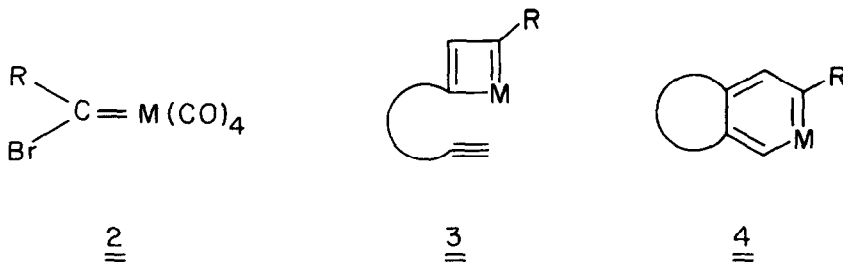
The transformation reported here incorporates carbon monoxide into the product, whereas previous reactions of metal-carbynes with acetylenes could not, because carbon monoxide was not present as a ligand or reactant.²

The procedure reported here works well with unsubstituted and monosubstituted diacetylenes, but not with disubstituted 2,7-nonadiyne. It gives phenols that are fused not only to five-membered rings, but also to those that are six- and even four-membered, these last being notable because they are strained.⁶

The transformations, summarized in the Table, were brought about by adding 1.2 equivalents of the diynes to stirred 0.1 M solutions of the carbynes in toluene under N₂ at -10 °C. Over a period of 10 minutes the mixtures were warmed to room temperature, and pentane was added to precipitate colored solids, which are probably metal salts of the phenols. The filtered solids were combined with 5 % aqueous HCl (1 part) plus tetrahydrofuran (4 parts), extracted with ether, and chromatographed quickly on silica gel.

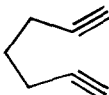
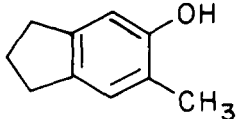
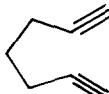
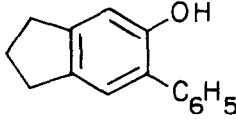
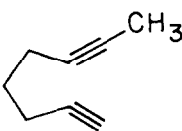
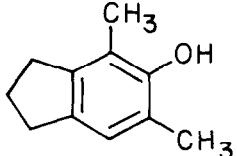
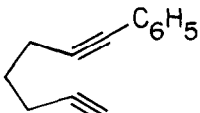
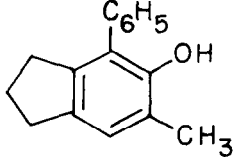
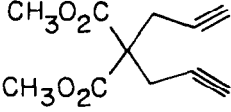
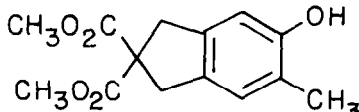
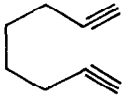
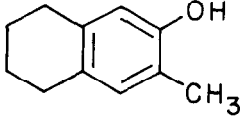
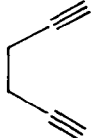
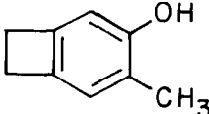
The metal-carbynes used for these syntheses did not have to be purified by laborious chromatography at low temperature.^{3a,d} After a quick preparation, they were simply washed extensively with pentane, filtered, dried, and used as needed.

It is not clear what accounts for the reactivity of the metal-carbynes. It might reflect the facility with which they become coordinatively unsaturated, either (as previously speculated) by isomerizing to metal-carbenes 2⁴ and following the course of pentacarbonyl-(1-methoxyethylidene)tungsten,⁵ or perhaps by losing a cis-ligand⁷ and following a path via 3 or 4.^{2b,8} We hope experiments in progress will distinguish these alternatives.



Acknowledgement. We are grateful for the support of the U.S. Navy, Office of Naval Research.

Table. Yields in Reactions of Diynes with $\text{CH}_3\text{C}\equiv\text{M}(\text{CO})_4\text{Br}$ ($\text{M} = \text{W}$ or Cr) or with $\text{C}_6\text{H}_5\text{C}\equiv\text{W}(\text{CO})_4\text{Br}$ ^a

Diyne	Product	Yield %	M
		54	W
		50	Cr
		18 ^b	W
		52	W
		46	Cr
		42	W
		31	Cr
		60	W
		52	Cr
		38	W
		33	Cr
		16	W
		12	Cr

^aThe methyl-carbynes were used for all experiments except the third in the table, for which the phenyl-carbyne was used. The reactions were run (with one exception, see note b) as described in the text. The ¹H NMR and IR spectra of the 3-methyl-5,6,7,8-tetrahydro-2-naphthol and 2,3-dihydro-6-methyl-1H-inden-5-ol are identical to those published.⁵ The ¹H NMR spectra of the other products, all previously unknown, showed the resonances and intensities required. There were no extra resonances. The high resolution mass spectra displayed the required parent peaks, and the IR spectra plausibly correct absorptions. ^bReaction effected at room temperature.

References and Notes

- (1) (a) K. H. Dötz, Angew. Chem. Int. Ed. Engl., 23, 587 (1984). (b) K. H. Dötz, Pure Appl. Chem., 11, 1689 (1983). (c) W. D. Wulff and D. C. Yang, J. Am. Chem. Soc., 106, 7565 (1984) and references therein. (d) K. A. Brown-Wensley, S. L. Buchwald, L. Cannizzo, S. Ho, D. Meinhardt, J. R. Stille, D. Straus, and R. H. Grubbs, Pure Appl. Chem., 55, 1733 (1983). (e) T. J. Katz, Adv. Organomet. Chem., 16, 283 (1977).
- (2) Schrock showed that metal-carbynes metathesize acetylenes and yield a variety of organometallic structures: (a) R. R. Schrock, J. H. Freudenberger, M. L. Listeman, and L. G. McCullough, J. Mol. Catal., 28, 1 (1985) and references therein. (b) R. R. Schrock, S. F. Pedersen, M. R. Churchill, and J. W. Ziller, Organometallics, 3, 1574 (1984) and references therein.
- (3) (a) E. O. Fischer and G. Kreis, Chem. Ber., 109, 1673 (1976). (b) E. O. Fischer and U. Schubert, J. Organometal. Chem., 100, 59 (1975). (c) U. Schubert in "The Chemistry of the Metal-Carbon Bond", F. R. Hartley and S. Patai, Eds., John Wiley and Sons, New York, 1982, Vol. 1, Chapter 5. (d) E. O. Fischer, U. Schubert, and H. Fischer, Inorg. Syn., 19, 172 (1979).
- (4) T. J. Katz, T. H. Ho, N.-Y. Shih, Y.-C. Ying, and V. I. W. Stuart, J. Am. Chem. Soc., 106, 2659 (1984).
- (5) W. D. Wulff, R. W. Kaesler, G. A. Peterson, and P.-C. Tang, J. Am. Chem. Soc., 107, 1060 (1985).
- (6) Vollhardt previously demonstrated that cyclopentadienyl(dicarbonylcobalt) condenses appropriate acetylenes to benzocyclobutenes: (a) R. L. Hillard III and K. P. C. Vollhardt, J. Am. Chem. Soc., 99, 4058 (1977). (b) K. P. C. Vollhardt, Angew. Chem. Int. Ed. Engl., 23, 539 (1984).
- (7) H. Fischer and F. Seitz, J. Organomet. Chem., 268, 247 (1984).
- (8) J. H. Freudenberger, R. R. Schrock, M. R. Churchill, A. L. Rheingold, and J. W. Ziller, Organometallics, 3, 1563 (1984) and references therein.

(Received in USA 27 February 1985)