University, for the valuable information on the intermediate, and to Associate Prof. Y. Fukazawa, Hiroshima University, for MM 2 calculations. Thanks are also due to Associate Prof. K. Saigo and Dr. N. Yonezawa, University of Tokyo, for the measurement of 400-MHz ^{1}H NMR spectra. Financial support from the Ministry of Education, Science and Culture of Japan is deeply acknowledged.

Supplementary Material Available: General experimental procedure and a listing of the physical properties for compounds **4**, **5**, **10b–d**, **11**, **12**, **17**, **18**, **19**, **26**, **30**, **31**, and **33** (5 pages). Ordering information is given on any current masthead page.

1,3-Dipolar Cycloaddition Reactions of Transition-Metal Carbene Complexes and the Formal [3 + 2 + 1] Pyridinannulation of the Cycloadducts

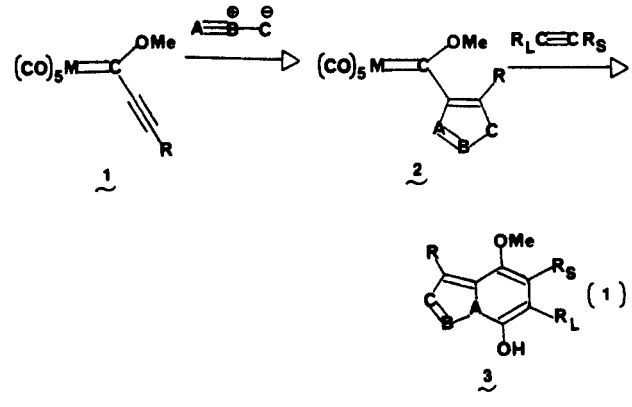
Kin Shing Chan and William D. Wulff*

Contribution from the Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received September 16, 1985*

Abstract: The first examples of 1,3-dipolar cycloadditions of α,β-unsaturated carbene complexes are described. The reaction of alkynylcarbene complexes with diazomethane gives a mixture of two products. The first arises from a [3 + 2] cycloaddition on the carbon–carbon triple bond of the alkynyl complex to give a pyrazole carbene complex and the second is most likely a secondary product which arises from attack of diazomethane on the metal–carbon double bond of the pyrazole complex. Substitution of trimethylsilyldiazomethane for diazomethane suppresses the second reaction and provides good yields of pyrazole carbene complexes for a variety of alkynylcarbene complexes. The regioselectivity of these reactions was established in two cases to be greater than 300:1, whereas in the corresponding carbon analogues (tetrolate esters) the selectivity is 35:65. The chromium or tungsten pentacarbonyl groups also has a large influence on the rates as well as on the regioselectivity and thus can be considered as reactivity auxiliaries. The regioselectivity was shown to correlate with the ^{13}C NMR chemical shifts of the α- and β-acetylene carbons of these complexes which were assigned on the basis of carbon–carbon coupling constants. Other substituted diazoalkanes such as 3-diazopropene also give selective formation of the pyrazole [3 + 2] cycloadducts. The alkynylcarbene complexes can serve as synthons for acetylenic esters in the 1,3-dipolar cycloaddition reactions with diazoalkanes since the pyrazole carbene complexes can be efficiently converted to pyrazole esters. The pyrazole carbene complexes are demonstrated to have synthetic value that transcends their ability to be converted to pyrazole esters since their reactions with alkynes produces pyrazolo[1,5-*a*]pyridines.

The [3 + 2]-cycloaddition reactions of 1,3-dipoles have been intensely investigated in the last 20 years[1] and their importance in natural product synthesis has been thoroughly established.[2] Transition-metal carbene complexes bearing an alkenyl[3] or alkynyl[4] group on the carbene carbon have recently been found to be potent dienophiles. These complexes undergo rapid and highly stereo- and regioselective [4 + 2] cycloaddition reactions with a variety of dienes and can serve as synthons for a number of dienophiles in the Diels–Alder reaction.[3] This report describes for the first time the isolation of cycloadducts from the [3 + 2] cycloadditions of α,β-unsaturated carbene complexes with 1,3-dipoles and discusses an initial examination of the synthetic potential of the annulation reactions of the cycloadducts of the type **2** with alkynes (eq 1).

The clearest cut example of a 1,3-dipolar cycloaddition to a transition-metal–carbon double bond is the [3 + 2] cycloaddition of a nitrile oxide to the metal–carbon double bond of a carbon monoxide ligand that produces a stable cycloadduct.[5] Casey was the first to report that the metal–carbon double bond of a carbene complex could be cleaved with diazoalkanes to give enol ethers of the type **6**.[3,6,7] It is possible that these enol ethers result from



the fragmentation of an initially formed [3 + 2] cycloadduct. α,β-Unsaturated carbene complexes such as the alkynyltungsten complex **9** have two possible sites for 1,3-dipolar cycloadditions: the tungsten–carbon double bond and the carbon–carbon triple bond. Thirteen years ago Fischer observed that in the presence of 4 equiv of diazomethane complex **9** is converted to the tungsten pentacarbonyl coordinated pyrazole **10** which has incorporated 2 of the 4 equiv of diazomethane.[8a] One explanation for the formation of **10** is that diazomethane reacts with the carbon–carbon triple bond to give the pyrazole carbene complex **7** which

(1) *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vols. 1, 2.
(2) *Natural Products Synthesis Through Pericyclic Reactions*; Desimoni, G., Tacconi, G., Barco, A., Pollini, G. P., Eds.; American Chemical Society: Washington, DC, 1983.
(3) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.
(4) (a) Wulff, W. D.; Yang, D. *C. J. Am. Chem. Soc.* **1984**, *106*, 7565. (b) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23.
(5) Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 370.
(6) Casey, C. P.; Bertz, S. H.; Burkhardt, T. J. *Tetrahedron Lett.* **1973**, 1431.
(7) (a) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *105*, 503. (b) Burkhardt, T. J. Ph.D. Thesis, University of Wisconsin, Madison, 1974. (c) Brunsvold, R. Ph.D. Thesis, University of Wisconsin, Madison, 1976.
(8) (a) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G. *J. Organomet. Chem.* **1973**, *57*, C9. (b) Reference 1, Vol. 1, pp 507–510. (c) Noel, M.; Vo-Quang, Y.; Vo-Quang, L. *C. R. Acad. Sci. Ser. C* **1970**, *270*, 80.

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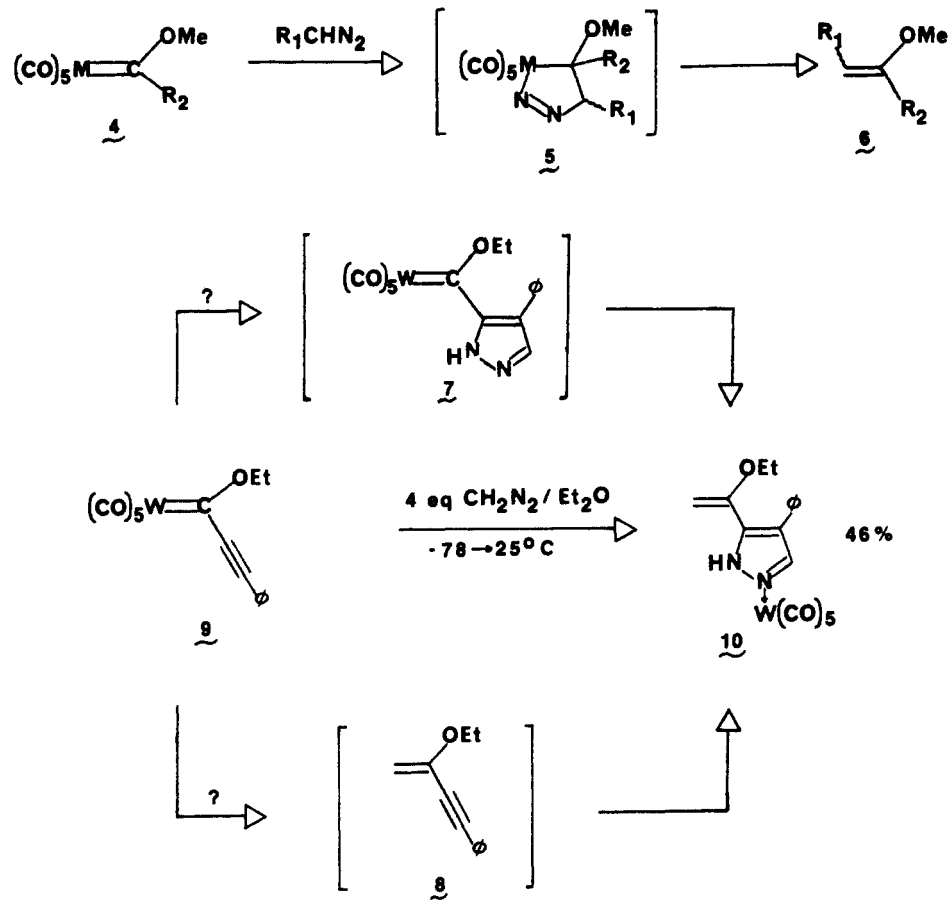
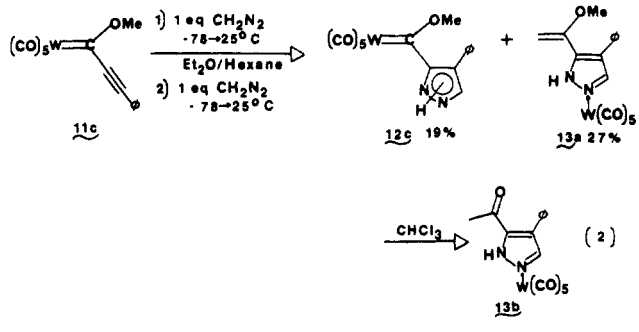
Scheme I



then reacts with the second equivalent of diazomethane to give **10**. However, it is not clear that a pyrazole carbene complex is in fact an intermediate since there is an alternative mechanism that involves the cleavage of the tungsten–carbon double bond of **9** to give the enol ether **8** which could undergo a [3 + 2] cycloaddition with diazomethane to give **10**. Conjugated enynes are reactive with diazoalkanes;[8b] 4-methoxybutenyne will react slowly with diazoalkanes at room temperature with exclusive [3 + 2] cycloaddition at the triple bond[8c] (Scheme I).

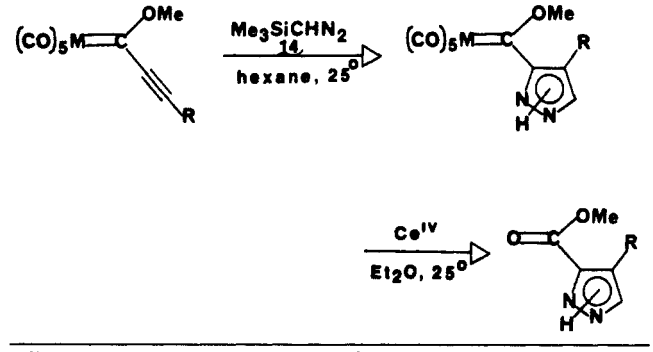
In an effort to isolate the pyrazole carbene complex that is suspected of being the precursor of the pyrazole enol ether **10**, the carbene complex **11c** was treated with 1 equiv of diazomethane at −78 °C and the temperature slowly brought to room temperature. The starting complex **11c** was not consumed; however, when treated with a subsequent equivalent of diazomethane in the same manner, the reaction had gone 84% to completion and the pyrazole complex **12c** could be isolated in 19% yield along with a 27% yield of the enol ether **13a**. The enol ether **13a** was characterized only by its ^{1}H NMR spectrum, but the corresponding methyl ketone **13b**, obtained upon hydrolysis, was fully characterized (see Experimental Section) (eq 2).



(2)

This is not a synthetically viable route to pyrazole carbene complexes, but it was anticipated on the basis of steric arguments that a substituted diazoalkane could be more chemoselective for the carbon–carbon triple bond of **11c** than for the tungsten–carbon double bond of **12c**. In fact, as can be seen from entry three in Table I, the reaction of **11c** with 1 equiv of (trimethylsilyl)diazomethane[9] (**14**) at room temperature gave a 65% yield of the pyrazole complex **12c** while less than 2% of the enol ether could be detected. All of the 1,3-dipolar cycloadditions were carried out at 0.2 M in carbene complex in hexanes with no precautions

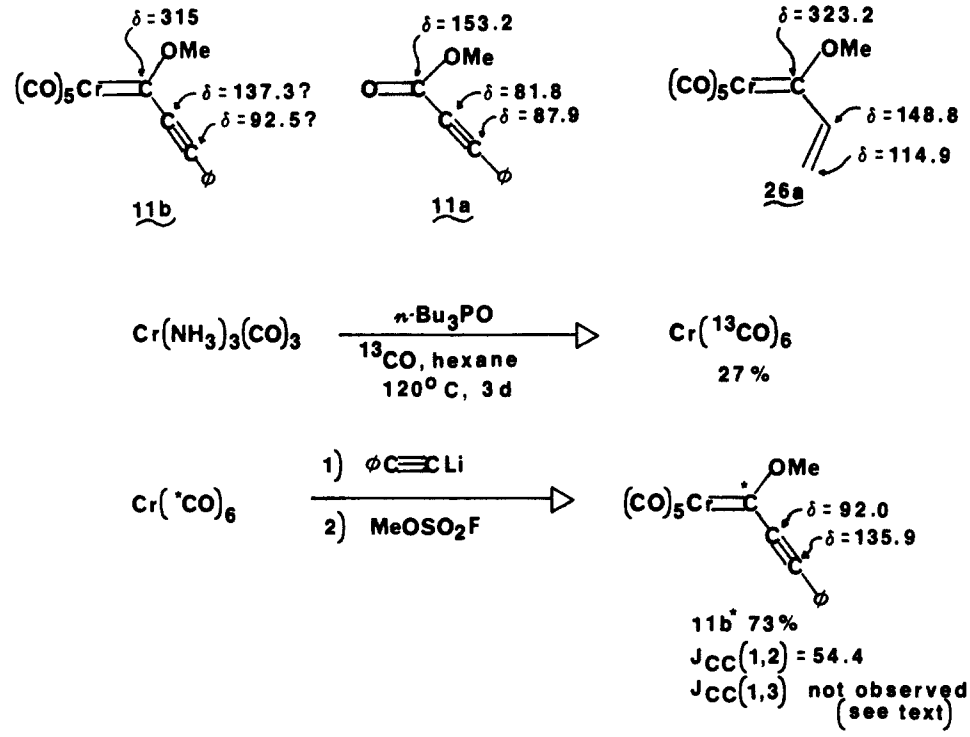
Table I. Cycloadditions with (Trimethylsilyl)diazomethane



alkyne complex	M	R	equiv of Me_3SiCHN_2	time, h	pyrazole complex	pyrazole ester
15c	W	Me	1.0	4.5	**16c**, 87%	**16a**, 78%
15b	Cr	Me	1.0	2.0	**16b**, 76%	**16a**, 97%
11c	W	Ph	1.0	2.0	**12c**, 65%	
11b	Cr	Ph	1.2	2.0	**12b**, 76%	
17	Cr	Me_3Si	1.75	7.0	**18**, 57%	
19	Cr	H_2C=C-(Me)	1.5	9.5	**20**, 60%	

(9) (Trimethylsilyl)diazomethane was purchased as a 10% hexane solution from Petrach Systems, Inc., but also can be easily prepared: (a) Barton, T. J.; Hoekman, S. K. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 297. (b) Martin, M. *Synth. Commun.* **1983**, *13*, 809.

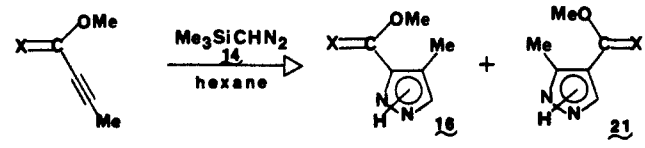
Scheme II



taken for the removal of air or oxygen. For entries 2–4 in Table I the (trimethylsilyl)diazomethane (**14**) was added as a 10% hexanes solution by a dropping funnel over 2 h, and for entries 1, 5, and 6 a syringe pump was used. Unless otherwise specified, all yields refer to purified material isolated by flash chromatography on silica gel in the presence of air. (Trimethylsilyl)diazomethane (**14**) functions as a synthon for diazomethane as the presumed intiially formed pyrazole complex loses its silyl group during the workup with saturated aqueous sodium chloride. As indicated by the many examples in Table I, the reaction of (trimethylsilyl)diazomethane with alkynylcarbene complexes offers an efficient synthetic entry to a variety of pyrazole carbene complexes that would be difficult to prepare by the standard Fischer synthesis. In each case only one regioisomeric cycloadduct was observed.

The pyrazole carbene complexes can be very efficiently oxidized to give pyrazole esters as indicated in Table I and it is for this reason that we sought to compare the reactivities and regioselectivities of the reactions of (trimethylsilyl)diazomethane and alkynylcarbene complexes with the corresponding reactions of alkynyl esters to judge the value of the former as synthons for the latter. The reaction of methyl tetrolate with (trimethylsilyl)diazomethane is slow and requires 5 days in refluxing hexanes to go to completion and produces a 65:35 mixture of isomers in which the 3-methylpyrazole **21a** predominates. The assignment of the structures for the methyl esters **16a** and **21a** were made on the basis of the published ^{1}H NMR spectral data for each.[10] The reaction of the propynyl chromium complex **15b** proceeds at the same concentration (0.2 M) at room temperature in 2 h to give exclusively the 4-methyl isomer **16b** with greater than 300:1 selectivity. The limits of the ratios of **16b/21b** and **16c/21c** were determined by ceric ammonium nitrate oxidation of the crude mixture from the reactions of **15b** and **15c** and analysis by gas chromatography (OV-1701, 25 M × 0.32 mM) and comparison with the retention times of authentic samples of **16a** and **21a**. The reaction of ethyl tetrolate with diazomethane is known and gives an 80:20 mixture of **16a** and **21a**[11] (Table II). The origin of the

Table II. Regioselectivity of Various Dipolarophiles



dipolarophile	X	temp, °C	time	16/21	yield
15a	O	69	5 days	35:65	74%
15a	O[a]	23	2 days	80:20	
15b	$Cr(CO)_5$	23	2 h	≥300:1	76%
15c	$W(CO)_5$	23	4 h	≥300:1	87%

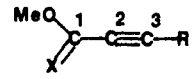
[a] Reaction with CH_2N_2.[11]

differences in the regioselectivities of alkynylcarbene complexes and alkynyl esters is not clear. It is clear that a chromium or tungsten pentacarbonyl group has a tremendous influence on the rates and regioselectivities of these cycloadditions and as such can be considered as reactivity auxiliaries. Disubstituted unsymmetrical alkynes rarely give regioselective reactions with diazoalkanes,[12] and thus alkynylcarbene complexes have considerable potential as synthons for 1,3-dipolarophiles.

The high regioselectivities of the 1,3-dipolar cycloadditions of alkynyl carbene complexes and the low selectivity of the corresponding propiolate esters do not correlate with the published ^{13}C NMR spectral data of these carbene complexes and their corresponding esters. The β-acetylenic carbon of the ester **11a** is more deshielded than the α-acetylenic carbon.[13] However, for the corresponding carbene complex **11b**, the α-acetylenic carbon was reported to be the most deshielded (δ 137.3 in acetone-d_6).[4b] This assignment was presumably made on the basis of the ^{13}C NMR spectrum of the vinyl complex **26a**[14] where the α- and β-carbons can be unambiguously distinguished by carbon–hydrogen couplings. The higher field absorption for the β-vinyl carbon of **26a** indicates the relative unimportance of a resonance effects, and the downfield shift of the α-carbon was attributed to an inductive effect by the chromium–carbon double bonded moiety. These data

(10) (a) **16a**: Gompper, R.; Sobottz, R. *Synthesis* **1979**, 385. (b) **21a**: Gulp, F. B.; Nabeya, A.; Moore, J. A. *J. Org. Chem.* **1973**, *38*, 2949.
(11) Entry two in Table II refers to the reaction of diazomethane with ethyl tetrolate: Aspart-Pascot, A.; Bastide, J. *C. R. Acad. Sci. Ser. C.* **1971**, *273*, 1772.
(12) Reference 1, Vol. 1, pp 502–533.
(13) Chaloner, P. A. *J. Chem. Soc., S. Perkin Trans. 2* **1980**, 1028.
(14) Wilson, J. W.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *57*, C63.

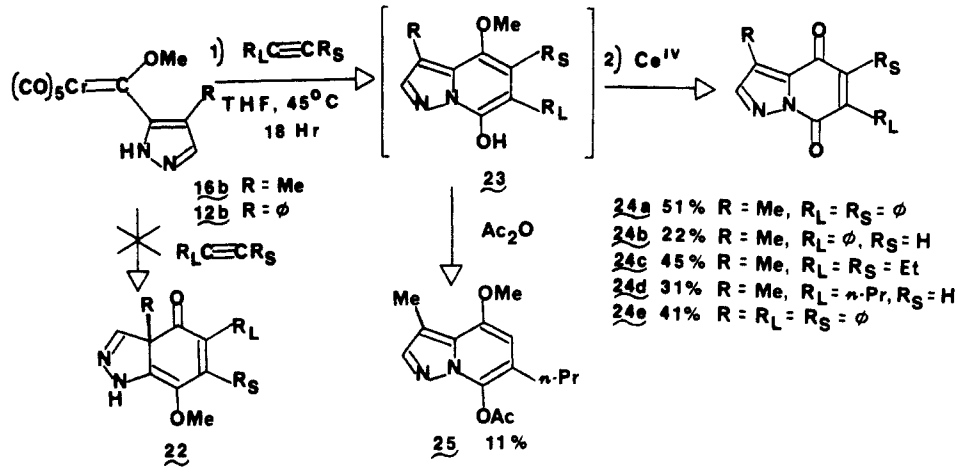
Table III. ^{13}C NMR Data for Alkynyl Carbene Complexes and Alkynyl Esters[a]



alkyne	X	R	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_3)$	$J_{CC}(1,2)$	$J_{CC}(1,3)$
11a[b]	O	Ph	153.2	81.8	87.9	127.7 Hz	19.5 Hz
15a[c]	O	CH_3	154.1	72.0	85.6	127.5	20.3
11b	$Cr(CO)_5$	Ph	315.0	92.0	135.9	54.4	*d*
15b	$Cr(CO)_5$	CH_3	319.0	85.8	136.7		
17	$Cr(CO)_5$	$SiMe_3$	326.9	87.6	105.0		
19	$Cr(CO)_5$	CH_2=C(Me)	316.0	90.3	136.4		
11c[e]	$W(CO)_5$	Ph	288.0	98.0			
15c	$W(CO)_5$	CH_3	292.0	90.7	133.7		

[a] In $CDCl_3$ unless otherwise specified. [b] Reference 13. [c] Reference 17. [d] Not observed (see text). [e] In acetone-d_6.[4b]

Scheme III



for **26a** are consistent with a preferred rotamer in which the Cr–C_{carb}–C_α plane and the C_{carb}–C_α–C_β plane are, perpendicular. The symmetry of **11b** precludes any conformation in which Π-conjugation is not possible. Therefore a resonance effect could be operative in **11b**, and thus spectral assignments for the α- and β-acetylenic carbons of **11b** may not necessarily follow from the spectral data for **26a**. Furthermore, the reported ^{13}C NMR spectral assignments for **11b** are not consistent with the direction and the high degree of regioselectivity observed in the Diels–Alder reactions of alkynyl carbene complexes[4a] (Scheme II).

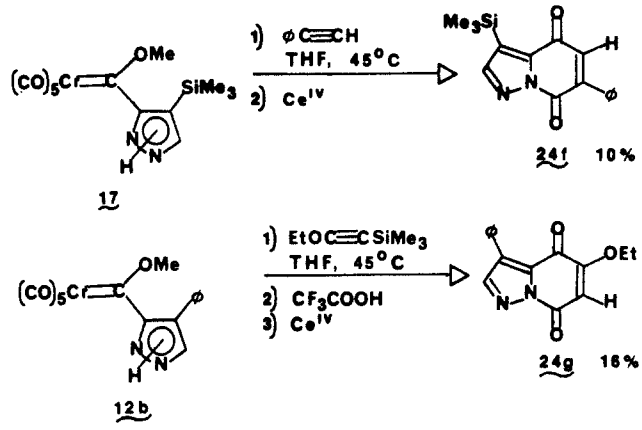
That the spectral assignments for the α- and β-acetylenic carbons of **11b** are incorrect was determined by the following labeling experiment. Chromium hexacarbonyl that was enriched 39-fold with ^{13}C was prepared by a modification of a procedure by Darensbourg.[15] The labeled chromium hexacarbonyl was then treated with lithium phenylacetylide and then methyl fluorosulfonate to produce the carbene complex **11b*** in which there was a 34-fold enhancement of ^{13}C at the carbene carbon. The ^{13}C NMR spectrum of the **11b*** revealed that the largest carbon–carbon coupling constant[16] (J = 54.4 Hz) was due to the absorption at δ 92.0 ($CDCl_3$). On the basis of the relative $J_{1,2}$ and $J_{1,3}$ for the corresponding propiolate esters **11a**[13] and **15a**[17] (Table III) the absorption at 92.0 ppm can be assigned as the α-acetylenic carbon. The coupling to the β-carbon could not be observed, and it is difficult to assign an upper limit to this coupling constant since this particular absorption for both the labeled and unlabeled alkynyl carbene complexes gives broad resonance lines of approximately 10–15 Hz. The ^{13}C NMR spectral assignments for all of the rest of the carbene complexes in Table III are based on that for **11b**. Also consistent with these assignments is the fact that in the case of the esters **11a** and **15a**, the substituent R has a much greater effect on the chemical shift of C_2 than of C_3. As evidenced by the data in Table III there is a correlation between the chemical shift difference between the α- and β-acetylenic carbons of the alkynyl carbene complexes (~40–45 ppm) and the high regioselectivity in the 1,3-dipolar cycloaddition reactions (≥300:1) when compared to the chemical shift differences for the corresponding acetylenic esters (6–13 ppm) and their regioselectivities (~1:1).

The 1,3-dipolar cycloaddition reactions of alkynyl complexes are illustrative of the way in which a part of the chemistry of carbene complexes can be anticipated from the reaction chemistry of esters.[18] However, there is a subset of the reaction chemistry of carbene complexes that cannot exist in ester chemistry due to the active involvement of the metal and its ligands. One such example is the benzannulation reaction with alkynes.[18,19] As indicated in Scheme III the synthetic potential of the pyrazole carbene complexes extends beyond their ability to be oxidatively converted to methyl esters.

The reaction of the pyrazole complex **16b** with alkynes could lead to two possibilities. If the annulation occurs with cyclization on carbon, the 2,4-cyclohexadienone **22** would be produced, and this would not be an unprecedented reaction.[20] The alternative is cyclization to a nitrogen which is unprecedented in the annulation reactions of carbene complexes and alkynes and would result in a formal [3 + 2 + 1] pyridine annulation. The reaction of complexes **12b** and **16b** with a number of alkynes was found to give rise to the pyrazolo[1,5-*a*]pyridine derivatives **23** which can

(15) Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *Inorg. Chem.* **1981**, *20*, 1918.
(16) Carbon–Carbon and Carbon–Proton NMR Couplings; Marshall, J. L., Ed.; Verlag Chemie: Deerfield Beach, FL, 1983.
(17) (a) Marshall, J. L.; Miller, D. E.; Dorn, H. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 460. (b) Linde, S. A.; Jakobsen, H. J. *J. Am. Chem. Soc.* **1976**, *98*, 1041.
(18) For reviews of the chemistry of these complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Wulff, W. D.; Tang, P. C., Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5313. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Casey, C. P. *React. Intermed.* **1985**, 3. (e) Brown, E. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.
(19) For leading references, see: Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520.
(20) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132.

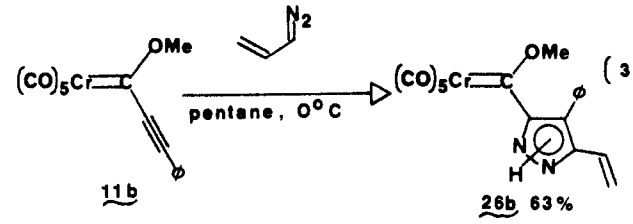
Scheme IV



be isolated as the acetate if the reaction is carried out in the presence of 1.5 equiv of acetic anhydride[21] or more efficiently obtained as the quinone **24** if an oxidative workup with excess ceric ammonium nitrate is employed.[22] Iodine and ferric chloride–DMF complex[23] are much less successful as oxidizing agents. All of the annulation reactions were carried out at 0.1 M in carbene complex in THF with 1.5 equiv of alkyne and were deoxygenated by the freeze–thaw method (−196 → 25 °C, three cycles). The best yields (~40–50%) of pyrazolopyridine quinones were obtained with disubstituted acetylenes, whereas terminal acetylenes are much less effective. Only a slight concentration dependence was observed; the yield of **24d** was 27% at 1.0 M and 10% at 0.01 M. Tungsten complexes are less effective in this pyridine annulation reaction as the reaction of **16c** with diphenylacetylene gave **24a** in 11% yield. Only one regioisomer was observed for **24b** and **24d** and the structural assignment was made on the basis of the known regiochemistry for the benzannulation reaction.[24] The trimethylsilyl complex **17** is less effective than **16b** in its reaction with phenylacetylene. The reaction of **12b** with 1-ethoxy-2-(trimethylsilyl)acetylene with a subsequent protonolysis gives the ethoxy-substituted pyrazolopyridine quinone **24b**. The regiochemistry of this reaction is based on the known regiochemistry of the annulation reaction of 1-ethoxy-2-(trimethylsilyl)acetylene with other carbene complexes.[25]

Pyrazolo[1,5-*a*]pyridines[26] are unknown with oxygen substituents in the 4- and 7-positions as are the corresponding quinones **24**. This new class of heterocyclic quinones should be of interest with regard to their biological activity given the range of activity associated with other heterocyclic quinones.[27] An imidazole quinone isomeric with the ring system in **24** has recently been reported to oxidize methoxide to formaldehyde[28] (Scheme IV).

In light of the observation that the 1,3-dipolar cycloadditions of diazomethane with the carbon–carbon triple bond of alkynyl carbene complexes suffer from competitive cleavage of the metal–carbene bond, it would be of interest to determine if selective cycloadditions could be effected with more highly substituted diazo compounds other than (trimethylsilyl)diazomethane. One preliminary result that addresses this issue is the reaction of the phenylethynyl complex **11b** with 3-diazopropene which proceeds rapidly at 0 °C to give the cycloadduct **26** in 63% yield and gives no evidence for the formation of enol ethers of the type **10** (eq 3).



In summation, alkynylcarbene complexes undergo chemoselective 1,3-dipolar cycloadditions with diazoalkanes to generate the pyrazole nucleus with vastly superior regioselectivity and with large rate enhancements as compared to the corresponding alkynyl esters. As a result, these complexes can serve as important synthons for alkynyl esters in [3 + 2] cycloadditions since the metal in the cycloadducts can be oxidatively removed to give the corresponding esters. Additionally, the alkynylcarbene complexes have synthetic value that transcends that as synthons for alkynyl esters since their cycloadducts with diazoalkanes will undergo annulation reactions with acetylenes to produce pyrazolo[1,5-*a*]pyridines. The [3 + 2] cycloadditions of other 1,3-dipoles with alkynyl and alkenyl complexes can be anticipated to be synthetically rewarding as well.

Experimental Section

Unless otherwise noted all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. ^{13}C-labeled carbon monoxide was purchased from Isotec Inc., Centerville, OH. Flash column chromatography was carried out as described by Still[29] on silica gel and this was done in air even for the various carbene complexes. Unless otherwise specified, the solvent for chromatography and the corresponding R_f values is a ternary mixture of ether, dichloromethane, and hexanes. All melting points and boiling points are uncorrected. Capillary gas chromatography was conducted on a Carlo Erba Fractovap 2900 series instrument employing a 25 m × 0.32 mm OV-1701 column with a hydrogen carrier flow rate of 0.5 m/s. Routine proton NMR spectra were recorded either on a Bruker 270 MHz or DS 1000 (Chicago built) 500-MHz spectrometer in $CDCl_3$ and, unless otherwise stated, with tetramethylsilane as an internal standard. The multiplicities of the NMR spectral absorptions are indicated by s, singlet; br s, broad singlet; d, doublet; *t*, triplet; q, quartet; m, multiplet, and dd, doublet of doublets. The ^{13}C NMR spectra were recorded on a Nicolet 200 spectrometer at 50 MHz or a Varian XL-400 at 100 MHz. Infrared spectra were recorded on a Perkin-Elmer model 283 or a Nicolet 20SXB FT-IR spectrophotometer. Low-resolution mass spectra were recorded on a Finnigan 1015 instrument. High-resolution mass spectra were carried out at the Midwest Center for Mass Spectrometry (NE) or on a VG analytical 7070E mass spectrometer. Elemental analyses were carried out by Galbraith Lab., Inc., or Micro-Tech. Lab., Inc.

Preparation of [Methoxy[(trimethylsilyl)ethynyl]methylene]pentacarbonylchromium (17). Complex **17** was prepared according to the literature procedure;[18b] however, see the cautionary note in the procedure for the preparation of **15b** below. Complex **17**: ^1H NMR (500 MHz) δ 0.31 (s, 9 H), 4.35 (s, 3 H); ^{13}C NMR (100 MHz) δ −3.49, 65.79, 87.64, 104.98, 220.77, 230.75, 326.89.

Preparation of (Methoxy-1-propynylmethylene)pentacarbonylchromium (15b). Propynyllithium was prepared by condensing 1.4 mL (24.5 mmol) of propyne in a graduated centrifuge tube sealed with a septum and cooled to −78 °C. The propyne was then transferred via cannula in a closed system to a flask containing 75 mL of anhydrous ether at −78 °C by warming the centrifuge tube above the boiling point of propyne (bp = −23 °C) and treated with 19.3 mmol of a 1.47 M solution of *n*-butyllithium (13.1 mL) in hexanes. After 30 min the clear acetylide solution was warmed to 0 °C at which point a white precipitate formed. The suspension was stirred for 30 min at 0 °C and transferred via cannula to a suspension of 5.10 g (23.2 mmol) of chromium hexacarbonyl in 170 mL of tetrahydrofuran at room temperature. Acyl metalate formation was assumed to be complete after 1 h, after which time methylation was effected after cooling the solution to 0 °C, by slow dropwise addition of 2.3 mL (29.0 mmol) of methyl fluorosulfonate. The reaction was quenched after 5 min by stirring with pH 7 buffer for 20

(21) Yamashita, A.; Scahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, 2969.
(22) For a recent example of a formal [3 + 2 + 1] pyridine annulation that does not involve a metal, see: Kelly, T. R.; Liu, H. *J. Am. Chem. Soc.* **1985**, *107*, 4998.
(23) Tobinaga, S.; Kotani, E. *J. Am. Chem. Soc.* **1972**, *94*, 309.
(24) (a) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293. (b) Dötz, K. H.; Muhlemeier, J.; Schubert, V.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187. (c) Wulff, W. D.; Tang, P. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677.
(25) Wulff, W. D.; Chan, K. S., unpublished results.
(26) Hardy, C. R. *Adv. Heterocycl. Chem.* **1984**, *36*, 345.
(27) (a) *The Chemistry of Antitumor Antibiotics*; Remers, W. A., Ed.; Wiley-Interscience: New York, 1979. (b) Frincke, J. M.; Faulkner, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 265. (c) Omura, S.; Nakagawa, A.; Yamada, H.; Hata, T.; Furusaki, A.; Watanabe, T. *Chem. Pharm. Bull.* **1973**, *21*, 931. (d) Boyer, D. L.; Panek, J. S. *Tetrahedron Lett.* **1984**, 3175.
(28) Skibo, E. B.; Lee, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 4591.
(29) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

min. The organic phase was gently washed (to avoid emulsions) with a pH 7 buffer and with saturated brine before drying over $MgSO_4$. After removal of the volatiles, the residue was extracted with hexanes and the crude product was purified by flash chromatography on silica gel and obtained upon collection of the fast moving red band with a 1:1:20 mixture of ether, methylene chloride, and hexanes (R_f 0.37) as eluent. The solution was concentrated to 10 mL on a rotary evaporator and the remaining solvent was removed with high vacuum with cooling to below 0 °C. After all of the solvents were removed the product was maintained at/or below 0 °C until it solidified. The carbene complex **15b** was thus obtained in 65–70% yield (3.71 g, 13.5 mmol) as a dark blackish red solid: mp 43.5–44.5 °C; ^{1}H NMR δ 2.47 (s, 3 H), 4.31 (s, 3 H); ^{13}C NMR (100 MHz) δ 6.50 (q, J = 131.5 Hz), 65.87 (q, J = 149.1 Hz), 85.77 (s), 136.80 (br s), 216.14 (s), 225.23 (s), 319.81 (s); IR ($CDCl_3$) ν 2060 m, 1995 w, 1950 s; mass spectrum, m/e (% relative intensity), 274 M^+ (12), 246 (12), 218 (13), 190 (19), 162 (36), 134 (100), 91 (82), 52 (100) cm^{-1}. Anal. $C_{10}H_6O_6Cr$ (C, H).

A **cautionary note** is necessary for the procedures involving the preparation of the chromium complexes **17** and **15b**. These complexes can be handled in air and purified by chromatography in air without a noticeable loss of material. However, on a number of occasions it has been observed that when aerated solutions of these complexes are stripped of solvent and the product is left to sit as an oil, an exothermic reaction can take place after a period of time, which can provide enough heat either to decompose or ignite the product. This observation has never been made on the impure product before loading on the silica gel column but rather only upon removing the solvents from the purified product.

This exothermic reaction has never been observed for these complexes in the solid form no matter how long they are handled in air and has never been observed when the above procedure is employed, i.e., when the last amount of solvent is removed at low temperature (0 °C) such that the product quickly solidifies. If necessary the flask can be submerged in a dry ice/acetone bath to hasten the solidification. This behavior has not been observed for the chromium complexes **11b** or **19** and has not been a problem with the tungsten complexes.

Preparation of (Methoxy-1-propynylmethylene)pentacarbonyltungsten (15c). The complex **15c** was prepared according to the procedure described for **15b** and isolated in 63% yield as a red solid: mp 62–64 °C; R_f (hexanes) 0.17; ^{1}H NMR (500 MHz) δ 2.32 (s, 3 H), 4.25 (s, 3 H); ^{13}C NMR (50 MHz) δ 6.56 (q, J = 132.6 Hz), 66.15 (q, J = 147.1 Hz), 90.68 (s), 133.7 (br s), 197.29 (s, J_{W-C} = 126.82 Hz), 205.44 (s), 291.97 (s); IR ($CDCl_3$) ν 2182 s, 2069 s, 1964 s, 1231 s, 1140 s; mass spectrum, m/e (% relative intensity) 408 (59), 406 M^+ (68), 404 (54), 352 (49), 349 (32), 348 (46), 324 (59), 322 (66), 321 (45), 320 (60), 296 (90), 294 (100), 292 (84), 279 (38), 277 (35), 268 (65), 266 (70), 265 (39), 264 (60), 253 (33), 251 (46), 250 (22), 249 (32), 223 (40), 222 (27), 221 (42) cm^{-1}; calcd for $C_{10}H_6O_6W$ m/e 405.9673, measured m/e 405.9706.

Synthesis of Carbon-13 Enriched Chromium Hexacarbonyl. A suspension of $Cr(NH_3)_3(CO)_3$[30] (0.5 g, 2.67 mmol) and (n-Bu)$_3$PO (2.0 g, 9.17 mmol) in 100 mL of hexanes in a 250-mL round-bottom flask equipped with a threaded high-vacuum stopcock was deoxygenated by the freeze–thaw method (−196 → 25 °C, two cycles) and then heated at 120 °C for 3 days under an atmosphere of ^{13}C-enriched carbon monoxide. The solvent was evaporated and the ^{13}C-labeled chromium hexacarbonyl was purified by vacuum sublimation (20 mm) to give white needles (156 mg, 0.71 mmol, 27%): IR (CH_2Cl_2) ν 2004 s, 1981 s, 1936 s, 1908 s cm^{-1} [$Cr(^{12}CO)_6$, IR (CH_2Cl_2) 2016 s, 1984 s, 1955 s cm^{-1}]; mass spectrum, m/e (% relative intensity) 223 (9.47), 224 (0.06). The ^{13}C/^{12}C are calculated from the mass spectrum to be 43:57. The above procedure is a modification of the one previously reported by Darensbourg.[15]

Preparation of ^{13}C-Labeled (Methoxy-2-phenylethynylmethylene)-pentacarbonylchromium (11b*). To a solution of phenylacetylene (0.07 mL, 0.67 mmol) in THF (4 mL) at −30 °C was added 0.42 mL of a 1.55 M solution of n-butyllithium in hexane (0.67 mmol). The solution was warmed to 0 °C, stirred for 1 h, and then transferred via cannula to a suspension of $Cr(^{13}CO)_6$ (145 mg, 0.66 mmol) in THF (4 mL) at room temperature. After 1 h the solution was cooled to 0 °C and $MeOSO_2F$ (0.1 mL, 1.32 mmol) was added dropwise and the reaction was quenched 30 min later by addition of an aqueous $NaHCO_3$ solution and stirring for 10 min. The reaction mixture was extracted with ether, washed with brine, dried with $MgSO_4$, and evaporated to dryness. Purification by flash chromatography with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes as eluent gave **11b*** as red crystals in 73% yield: (165 mg, 0.49 mmol) R_f 0.35; ^{1}H NMR (500 MHz) δ 4.41 (t, 3 H, J_{C-H} = 2.6 Hz), 7.44 (m, 2 H), 7.49 (m, 1 H), 7.56 (m, 2 H); ^{13}C NMR (100 MHz) δ 65.83 (OMe), 91.98 (α-acetylenic), 91.96 (d, $J_{^{13}C-^{13}C}$ = 54.4 Hz), 120.86 (phenyl C_1), 128.93 (phenyl C_2), 131.75 (phenyl C_4), 135.87 (β-acetylenic), 132.73 (phenyl C_3), 216.17 (cis CO), 225.56 (trans CO), 315.00 (carbene); IR (neat) ν 2158 s, 2040 w, 1917 s, 1866 s, 1841 s cm^{-1}; mass spectrum, m/e (% relative intensity) 341 (2), 339 (4), 338, M^+ (^{12}C, 5), 337 (3), 336 (1), 285 (1), 284 (2), 283 (4), 282 (7), 281 (7), 280 (3), 279 (1), 256 (2), 255 (3), 254 (8), 252 (12), 252 (6), 228 (1), 227 (2), 226 (6), 225 (14), 224 (11), 223 (5), 205 (1), 200 (1), 199 (5), 198 (12), 197 (55), 196 (71), 195 (2), 194 (3), 169 (1), 168 (7), 167 (39), 166 (5), 165 (4), 164 (1), 154 (13), 153 (66), 152 (1), 151 (3), 150 (4), 149 (50), 71 (11), 69 (19), 57 (34), 56 (11), 55 (17), 52 (100). The assignment of the phenyl carbons in the ^{13}C NMR is based on that previously made on the corresponding ester.[13] The ^{13}C/^{12}C at the carbene carbon was calculated to be 38:62 by peak height measurements in the ^{13}C NMR and 33:67 from the mass spectrum.

For preparative purposes the unlabeled complex **11b** was prepared on 20-mmol scale in 97% yield and used in the reactions described below as the material was judged to be pure by TLC (R_f 0.35, hexanes) and by ^{1}H NMR: ^{1}H NMR (500 MHz) δ 4.41 (s, 3 H), 7.43 (t, 2 H, J = 7.6 Hz), 7.48 (~t, 1 H, J = 5.0 Hz), 7.57 (dd, 2 H, J = 1.7, 8.0 Hz).

Preparation of [(2-Phenylethynyl)methoxymethylene]pentacarbonyltungsten (11c). The preparation of this complex has previously been reported.[4b] Utilizing the same procedure described above for **11b***, complex **11c** was prepared and isolated as dark black crystals in 33% yield: R_f (hexanes) 0.22; ^{1}H NMR (500 MHz) δ 4.34 (s, 3 H), 7.41 (t, 2 H, J = 7.6 Hz), 7.50 (t, 1 H, J = 7.6 Hz), 7.60 (d, 2 H, J = 7.0 Hz); IR (CH_2Cl_2) 2170 w, 2070 s, 1960 s, 1940 s.

Preparation of [(4-Methyl-3-buten-1-ynyl)methoxymethylene]pentacarbonylchromium (19). Complex **19** was prepared according to the procedure described above for **11b***. Complex **19** was obtained as red oil in 62% yield and should be used immediately as appreciable decomposition occurred even at −20 °C. R_f (hexanes) 0.26; ^{1}H NMR (500 MHz) δ 2.06 (s, 3 H), 4.32 (s, 3 H), 5.61 (s, 2 H); ^{13}C NMR (50 MHz) δ 22.40, 65.74, 90.34, 126.10, 128.06, 136.42, 216.00, 225.55, 315.23; IR ($CDCl_3$) 2145 s, 2160 s, 1950 s, 1600 s, 1095 s, 945 s.

Reaction of Complex 11c with Diazomethane.[8a] To a 0.2 M solution of complex **11c** (658 mg, 1.44 mmol) in 7 mL of hexanes at −78 °C was added 7.2 mL of a 0.2 M solution of CH_2N_2 in ether over a period of 1 h with a syringe pump. The solution was then stirred for 1 h and then slowly warmed up to room temperature. The reaction was incomplete as indicated by TLC. The solution was cooled to ~−30 °C and a second equivalent of CH_2N_2 was added by suringe pump over a period of 1 h. Upon warming up to room temperature, the solution was diluted with ether, washed with brine, and dried over $MgSO_4$. After removal of the volatiles, the residue was flash chromatographed on silica gel with a mixture of ether/CH_2Cl_2/hexanes (1:1:6) as eluent to give three fractions. Fraction 1, Rf (1:1:6) 0.52, was a black crystalline solid that was identified as the starting complex **11c** (108.4 mg, 0.23, mmol, 16% recovery). Fraction 2, R_f (1:1:6) 0.25, was an orange solid (114 mg, 0.22 mmol, 15% yield; 19% based on unrecovered starting material) that was identified as **12c**: mp 124–126 °C dec (color changed from red to black at 121–123 °C); (CH_2Cl_2/hexanes) ^{1}H NMR (500 MHz) δ 4.4 (s, 3 H), 7.21 (d, 2 H, J = 7.3 Hz), 7.31 (t, 1 H, J = 7.4 Hz), 7.36 (t, 2 H, J = 7.6 Hz), 7.60 (s, 1 H), 10.48 (br s, 1 H); IR ($CDCl_3$) 3440 s, 2070 s, 1950 s, 1605 m, 1440 m, 1255 s, 1230 s. Anal. Calcd for $C_{16}H_{10}N_2O_6W$: C, 37.65; H, 1.96; N, 5.49. Found: C, 37.35; H, 2.00; N, 5.51. Fraction 3, R_f (1:1:6) 0.14, was a red solid (168 mg, 0.31 mmol, 22% yield; 27% based on unrecovered starting material) that was identified as **13a**; ^{1}H NMR (500 MHz) δ 3.74 (s, 3 H), 4.34 (d, 1 H, J = 3.2 Hz), 4.63 (d, 1 H, J = 3.2 Hz), 7.38 (m, 5 H), 7.64 (s, 1 H), 10.2 (br s, 1 H). The structure of **13a** was confirmed by hydrolysis in chloroform solution which after 2 days gave the ketone complex **13b**: mp 142–145 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3 H), 7.35 (m, 2 H), 7.48 (m, 3 H), 7.75 (d, 1 H, J = 2.4 Hz), 11.46 (br s, 1 H); IR (500 MHz) ν 3421 m, 3256 m, 2861 s, 2074 s, 1954 s, 1679 s, 1132 s cm^{-1}; mass spectrum, m/e (% relative intensity) 510 M^+ (3), 354 (16), 352 (19), 350 (16), 298 (19), 296 (18), 294 (16), 270 (33), 268 (35), 267 (17), 266 (28), 242 (20), 240 (23), 238 (18), 214 (21), 212 (23), 210 (21), 186 (100), 185 (29), 184 (19), 182 (16), 171 (62), 153 (11), 89 (16); calcd for $C_{16}H_{10}N_2O_6W$ m/e 510.0048, measured 510.0044.

Reaction of the Propynyl Tungsten Complex 15c with (Trimethylsilyl)diazomethane (14). To a 0.2 M solution of the complex **15c** (540 mg 1.33 mmol) in 8 mL of hexanes at room temperature was added 1 equiv of **14** as a 10% solution in hexanes over a period of 4 h with a syringe pump. The solution was washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was flash chromatographed on silica gel with a solvent mixture of CH_2Cl_2/ether/hexanes (1:1:4) and provided **16c** as an orange-red solid in 87% yield (506 mg, 1.16 mmol): mp 120–121 °C (decomposed to a black solid; R_f (1:1:4) 0.28; ^{1}H NMR (500 MHz) δ 2.15 (s, 3 H), 4.73 (s, 3 H), 7.38 (s, 1 H), 10.52 (s, 1 H); IR ($CDCl_3$) 3440 s, 3020 s, 2030 s, 1980 s, 1940 s, 1600 m, 1200 s. The structure of **16c** was confirmed by its conversion to **16a** (vide infra).

(30) Razuvaov, G. A.; Artemov, A. N.; Aladjin, A. A.; Sirotkiv, N. I. *J. Organomet. Chem.* **1976**, *111*, 137.

Reaction of the Propynyl Chromium Complex 15b with 14. This reaction was carried out as described above for **15c** except that **14** was added with a dropping funnel over a period of 2 h. Complex **16b** was isolated in 76% yield as an orange-red solid (decomposed >120 °C): R_f (1:1:4) 0.25; ^{1}H NMR (500 MHz) δ 2.15 (s, 3 H), 4.92 (s, 3 H), 7.35 (s, 1 H), 8.3–8.6 (br s, 1 H); IR ($CDCl_3$) ν 3690 s, 3440 s, 2060 s, 1930 s, 1220 s; mass spectrum by field desorption, *m/e* (% relative intensity), 316 M^+ (100). The structure of **16b** was confirmed by conversion to **16a** (vide infra).

Reaction of the Phenylethynyl Tungsten Complex 11c with 14. This reaction was carried out with the procedure described for the reaction of **15c** except that **14** was added with a dropping funnel over a period of 2 h. The cycloadduct **12c** was isolated as a red solid [R_f (1:1:4) 0.38] in 65% yield and was found to be identical with the material described above.

Reaction of the Phenylethynyl Chromium Complex 11b with 14. This reaction was carried out in a manner similar to that described for **15c** except that **14** (1.2 equiv) was added over a period of 2 h with a dropping funnel. The cycloadduct **12b** was isolated in 76% yield (R_f (1:1:4) 0.27) as a red solid and was recrystallized from CH_2Cl_2/hexanes to give red needles: mp 125–127 °C dec (a change from red to dark red was noted at 113–115 °C); ^{1}H NMR (500 MHz) δ 4.52 (s, 3 H), 7.16 (d, 2 H, J = 7.2 Hz), 7.28 (t, 1 H, J = 7.4 Hz), 7.32 (t, 2 H, J = 7.6 Hz), 7.54 (s, 1 H), 10.65 (br s, 1 H); ^{13}C NMR [100 MHz, $(CD_3)_2CO$] δ 67.09, 118.77, 127.16, 128.48, 129.47, 129.90, 134.05, 217.40, 225.22, 333.92; IR ($CDCl_3$) ν 3440 m, 2060 s, 1980 s, 1940, 1600 s cm^{-1}. Anal. Calcd for $C_{16}H_{10}O_6N_2Cr$: C, 50.79, H, 2.65, N, 7.41. Found: C, 50.53, H, 2.75, N, 7.34.

Reaction of the (Trimethylsilyl)ethynyl Chromium Complex 17 with 14. This cycloaddition was carried out with the procedure described above for the reaction of **15c** except that **14** (1.75 equiv) was added over a 1.75-h period with a syringe pump. Complex **18** was isolated in 57% yield as a red solid: mp 132–133 °C dec; R_f (1:1:4) 0.36, ^{1}H NMR (500 MHz) δ 0.20 (s, 9 H), 4.91 (s, 3 H), 7.48 (s, 1 H), 11.5 (br s, 1 H); ^{13}C NMR (50 MHz) δ −0.27, 65.79, 111.28, 135.12, 167.11, 217.24, 224.35, 332.29; IR ($CDCl_3$) ν 3430 w, 2060 s, 1980 s, 1940 s cm^{-1}; mass spectrum by field desorption, *m/e* (% relative intensity) 374 M^+ (100).

Reaction of the 4-Methyl-3-buten-1-ynyl Chromium Complex 19 with 14. By use of the procedure described above for the reaction of **15c**, the reaction of **19** was effected by the addition of 1.5 equiv of **14** over a 9.5-h period with a syringe pump. Complex **20** was isolated in 60% yield as a red solid: mp 82–83 °C (melting with decomposition, turned black at 72–78 °C before melting); R_f (1:1:4) 0.27; ^{1}H NMR (500 MHz) δ 1.93 (s, 3 H), 4.75 (s, 3 H), 4.83 (s, 1 H), 5.02 (s, 1 H), 7.44 (s, 1 H), 10.5 (br s, 1 H); IR ($CDCl_3$) 3440 s, 3270 w, 2856 s, 2050 s, 1940 s, 1590 w, 1430 m. Anal. Calcd for $C_{13}H_{10}N_2O_6$: C, 45.61, H, 2.92, N, 8.19. Found: 45.80, H, 3.32, N, 8.03.

Reaction of Methyl Propiolate with 14. Methyl propiolate (260 mg, 2.65 mmol) and Me_3SiCHN_2 (**14**) (3.75 mL of a 10% solution in hexanes, 2.65 mmol) were refluxed in hexanes (13 mL) for 3 days, after which time an additional equivalent of **14** was added and refluxing was continued for a total period of 5 days. The solvent was evaporated and the two major products were separated and purified by flash chromatography using ether/hexanes (3:1) as eluent. Fraction 1 (R_f 0.19) was identified as methyl 4-methylpyrazole-3-carboxylate[10a] **16a** and obtained as a white solid in 26% yield (94.7 mg, 0.68 mmol): mp (benzene) 168–170 °C (lit.[10a] 170–171 °C); ^{1}H NMR (500 MHz) δ 2.31 (s, 3 H), 3.92 (s, 1 H), 7.44 (s, 1 H), 12.0 (br s, 1 H). Further elution (R_f 0.13) gave 0.1787 g (48%, 1.28 mmol) of an isomer that was identified as methyl 3-methylpyrazole-4-carboxylate[10b] **21a**: ^{1}H NMR (500 MHz) δ 2.36 (s, 3 H), 2.83 (s, 3 H), 7.95 (s, 1 H).

Oxidation of the Chromium Pyrazole Carbene Complex 16b with Cerric Ammonium Nitrate (CAN). An ether solution (20 mL) of the pyrazole complex **16b** (22.5 mg, 71.2 μmol) was stirred with 3.8 mL of a 0.5 M aqueous solution of cerric ammonium nitrate. After 10 min the ether layer was separated and the aqueous layer extracted with an additional portion of ether and the combined ether layer dried over $MgSO_4$. The solvent was removed and the product was purified by flash chromatography with ether/hexanes (3:1) and obtained as a white solid (9.7 mg, 70 μmmol, 97%). This material was found to have an ^{1}H NMR spectrum identical with that of an authentic sample of methyl 4-methylpyrazole-3-carboxylate **16a** and also found to have the same R_f value as **16a** on TLC and to have the same retention time on GC (vide infra).

Oxidation of the Tungsten Pyrazole Carbene Complex 16c with CAN. The complex **16c** was oxidized with the procedure described above for complex **16a** to give a 78% yield of the ester **16a**.

Determination of the Regioselectivity of the 1,3-Dipolar Cycloadditions of (Trimethylsilyl)diazomethane (14) with Propynylcarbene Complexes 15c and 15b. The crude mixtures obtained from the reactions of Me_3SiCHN_2 and the propynylcarbene complexes **15c** and **15b** were oxidized with excess CAN in ether/H_2O and were then subjected to capillary GC analysis. The retention times of authentic samples of **16a** and **21a** were 3.13 and 6.47 min, respectively (25 m × 0.32 mm, OV1701, 150 °C). The GC spectra of both reaction mixtures indicated the absence of any compound with a retention time corresponding to **21a** (6.47 min). For the oxidized reaction mixture from **15b**, a small peak at 5.5 min was taken as the detection limit for the isomer **21a**, and thereby a minimum value for the regioselectivity can be set at 300:1, which by the same analysis is also applicable to the reaction of **15c**.

Pyridinannulation of 16b with 1-Pentyne To Give Quinone 24d. A THF solution (3.2 mL) of complex **16b** (102 mg, 0.32 mmol) and 1-pentyne (0.05 mL, 0.49 mmol) was deoxygenated by the freeze–thaw method (−196 → 25 °C, three cycles) in a 25-mL pear-shaped flask that has the 14/20 joint replaced by a 8-mm threaded high-vacuum stopcock. The solution was then heated under argon at 45 °C for 18 h and then diluted with ether (10 mL) and oxidized by pouring into 5 mL of 0.5 M aqueous cerric ammonium nitrate solution and stirring at room temperature for 30 min. The organic layer was washed with water and brine and dried over $MgSO_4$. After removal of solvents the residue was flash chromatographed with an eluent mixture of CH_2Cl_2/ether/hexanes (1:1:4) to provide a pale yellow solid (20.5 mg, 0.1 mmol, 31%) which was identified as the quinone **24d** and for which the following physical and spectral data were obtained: mp 129.5–130.5 °C; ^{1}H NMR (500 MHz) δ 1.03 (t, 3 H, J = 7.3 Hz), 1.67 (sextet, 2 H, J = 7.5 Hz), 2.41 (s, 1 H), 2.61 (t, 2 H, J = 7.4 Hz), 6.67 (t, 1 H, J = 1.1 Hz), 7.70 (s, 1 H); ^{13}C NMR (100 MHz) δ 176.72, 156.73, 148.89, 147.18, 135.42, 134.42, 126.95, 32.42, 21.32, 13.67, 9.45; IR ($CDCl_3$) 1720 s, 1655 s, 1585 m; mass spectrum, *m/e* (% relative intensity), 205 (6), 204 M^+ (60), 189 (16), 176 (14), 161 (18), 109 (40), 86 (65), 84 (100); calcd for $C_{11}H_{12}N_2O_2$ *m/e* 204.0899, measured 204.0894. Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.71; H, 5.88; N, 13.73. Found: C, 64.80; H, 6.09; N, 13.26.

The yield of the quinone **24d** was 27% at 1.0 M and 10% at 0.01 M in carbene complex. The yield of **24d** dropped to 11% when ferric chloride–DMF complex[23] was employed as oxidant.

Pyridinannulation of 16b with 1-Pentyne in the Presence of Acetic Anhydride To Give the Pyrazolo[1,5-*a*]pyridine 25. A THF solution (6.5 mL) of the complex **16b** (204 mg, 0.65 mmol), 1-pentyne (0.1 mL, 0.98 mmol), and acetic anhydride (0.1 mL, 0.98 mmol) was deoxygenated by the freeze–thaw method (−196 → 25 °C, three cycles). The reaction mixture was heated under argon at 45 °C for 36 h and then diluted with ether (15 mL) and stirred in air for 4 h. The resulting solution was filtered through Celite, dried over $MgSO_4$, and evaporated to dryness. The residue was loaded onto a silica gel column which was flash eluted with a mixture of CH_2Cl_2/ether/hexanes (1:1:4) to give **25** (R_f 0.29) as white needles (19.02 mg, 0.074 mmol, 11%): mp 62–65 °C; ^{1}H NMR (500 MHz) δ 0.94 (t, 3 H, J = 7.4 Hz), 1.56 (m, 2 H), 2.23 (s, 3 H), 2.30 (t, 2 H, J = 7.5 Hz), 2.68 (s, 3 H), 3.98 (s, 3 H), 6.58 (s, 1 H), 7.96 (s, 1 H); IR ($CDCl_3$) ν 2980 s, 1720 s, 1597 s, 1320 s, 1220 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 263 (8), 262 M^+ (49), 220 (7), 206 (13), 205 (100), 177 (8), 109 (31); calcd for $C_{14}H_{18}N_2O_3$ *m/e* 262.1317, measured 262.1315. The yield of **25** is not improved if the reaction is run in the presence of trimethylamine.[21]

Pyridinannulation of the Chromium Complex 16b with Diphenylacetylene To Give Quinone 24a. This reaction was carried out by utilizing the procedure described above for quinone **24d**. The quinone **24a** was isolated as a yellow crystalline solid (R_f (1:1:1) 0.33) in 51% yield: mp (MeOH) 175–177 °C; ^{1}H NMR (500 MHz) δ 2.47 (s, 3 H), 7.03 (m, 2 H), 7.22 (m, 2 H), 7.24 (m, 6 H), 7.80 (s, 1 H); ^{13}C NMR (50 MHz) δ 9.73, 114.58, 127.83, 128.75, 128.94, 130.41, 130.56, 131.49, 132.23, 142.43, 146.79, 147.30, 156.35, 176.33; IR ($CDCl_3$) ν 1721 s, 1666 m, 1585 m, 1292 m, 1192 s; mass spectrum, *m/e* (% relative intensity) 314 M^+ (100), 285 (23), 259 (15), 178 (29), 161 (30), 151 (55), 133 (20), 113 (35); calcd for $C_{20}H_{14}N_2O_2$ *m/e* 314.1055, measured 314.1048. Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.43; H, 4.46; N, 8.92. Found: C, 76.02; H, 4.61; N, 8.74.

Pyridinannulation of the Tungsten Complex 16c with Diphenylacetylene To Give Quinone 24a. Substitution of the tungsten complex **16c** for the chromium complex **16b** in the reaction above resulted in a drop in the isolated yield of **24a** to 11%.

Pyridinannulation of 16b with Phenylacetylene To Give Quinone 24b. This reaction was carried out utilizing the procedure described above for quinone **24d**. The quinone **24b** was isolated as a yellow solid (R_f (1:1:4) 0.12) in 22% yield: mp 170–173 °C; ^{1}H NMR (500 MHz) δ 2.45 (s, 3 H), 6.96 (s, 1 H), 7.48 (m, 3 H), 7.6 (d, 2 H, J = 7.5 Hz), 7.77 (s, 1 H); IR ($CDCl_3$) ν 1720 s, 1660 s, 1590 s, 1432 s, 1235 s; mass spectrum, *m/e* (% relative intensity) 238 M^+ (100), 212 (58) 62 (48), 151 (162), 133 (28), 113 (45), 104 (86), 102 (40), 101 (23), 77 (44); calcd for $C_{14}H_{10}N_2O_2$ *m/e* 238.0742, measured 238.0743.

Pyridinannulation of 16b with 3-Hexyne To Give Quinone 24c. The procedure described above for quinone **24d** was employed and quinone **24c** was isolated as a yellow solid (R_f (1:1:4) 0.26) in 45% yield: mp 97–99 °C; ^{1}H NMR (500 MHz) δ 1.14 (t, 3 H, J = 7.5 Hz), 1.22 (t, 3 H, J = 7.5 Hz), 2.41 (s, 3 H), 2.60 (q, 2 H, J = 7.5 Hz), 2.71 (q, 2 H, J = 7.5 Hz), 7.67 (s, 1 H); ^{13}C NMR (100 MHz) δ 9.58, 13.67, 13.85, 19.51, 21.53, 126.90, 133.98, 144.48, 146.78, 149.07, 156.54, 176.80; IR ($CDCl_3$) ν 1710 s, 1670 s, 1612 m, 1584 s, 1229 s, 1195 s; mass spectrum, m/e (% relative intensity) 218 M^+ (100), 203 (36), 181 (39), 175 (39), 161 (13), 113 (15), 109 (14); calcd for $C_{12}H_{14}N_2O_2$ m/e 218.1055, measured 218.1056.

Pyridinannulation of 11b with Diphenylacetylene To Give Quinone 24e. This reaction was carried out by utilizing the same procedure described above for quinone **24d**. The quinone **24e** was isolated as a yellow solid (R_f (1:1:4) 0.11) in 41% yield: mp 202–204 °C; ^{1}H NMR (500 MHz) δ 7.07 (m, 2 H), 7.16–7.28 (m, 8 H), 7.44 (m, 3 H), 7.87 (m, 2 H), 8.17 (s, 1 H); IR ($CDCl_3$) ν 3064 m, 1728 s, 1669 s, 1574 s, 1329 s, 1183 s; mass spectrum, m/e (% relative intensity) 376 M^+ (80), 347 (21), 292 (86), 236 (25), 213 (40), 212 (37), 201 (38), 178 (28), 133 (41), 113 (76), 105 (35), 77 (20); calcd for $C_{25}H_{16}N_2O_3$ m/e 376.1212, measured 376.1198.

Pyridinannulation of the Trimethylsilyl-Substituted Pyrazole Complex 17 with Phenylacetylene To Give Quinone 24f. This reaction was carried out by utilizing the same procedure as described above for quinone **24d**. The quinone **24f** was isolated as a yellow solid (R_f (1:1:4) 0.32) in 10% yield: mp 160–164 °C; ^{1}H NMR (500 MHz) δ 0.37 (s, 9 H), 6.99 (s, 1 H), 7.49 (m, 3 H), 7.62 (d, 2 H, J = 7.6 Hz), 7.84 (s, 1 H); IR ($CDCl_3$) 2980 m, 1728 s, 1660 s, 1600 m, 1420 s, 1354 s; mass spectrum, m/e (% relative intensity) 296 M^+ (3), 281 (40), 179 (6), 105 (6); calcd for $C_{16}H_{16}N_2O_2Si$ m/e 296.0981, measured 296.0991.

Reaction of Complex 12b with Ethoxy(trimethylsilyl)acetylene To Give Quinone 24g. A solution of the complex **12b** (360 mg, 0.95 mmol) and 1-ethoxy-2-(trimethylsilyl)acetylene (203 mg, 1.43 mmol) in THF (9.5 mL) was deoxygenated by the freeze–thaw method (~196 → 25 °C, two cycles) and heated under argon at 45 °C for 48 h. Trifluoroacetic acid (0.22 mL, 1.9 mmol) was then added under argon and after 30 min the reaction mixture was poured into a mixture of 10 mL of a 0.5 M solution of cerric ammonium nitrate and 20 mL of ether and stirred for 30 min. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and evaporated to dryness. The product was purified by flash chromatography on silica gel with a 1:1:1 mixture of ether/methylene chloride/hexanes as eluent to give **24g** as a yellow solid (41.5 mg, 0.15 mmol, 15%), R_f (Et_2O) 0.25, which was recrystallized from MeOH to give yellow needles; mp 189–190 °C; ^{1}H NMR (500 MHz) δ 1.53 (t, 3 h, J = 7.0 Hz), 4.11 (q, 2 H, J = 7.0 Hz), 6.03 (s, 1 H), 7.43 (m, 3 H), 7.80 (dd, 2 H, J = 2.4, 7.5 Hz), 8.02 (s, 1 H); IR ($CDCl_3$) ν 1722 s, 1692 s, 1617 m, 1586 m, 1317 s, 1231 s, 1147 s, 1034 s; mass spectrum, m/e (% relative intensity) 268 M^+ (59), 254 (9), 228 (12), 224 (23), 212 (91), 202 (16), 171 (51), 161 (10), 151 (12), 120 (100), 114 (12), 89 (13); calcd for $C_{15}H_{12}N_2O_3$, m/e 268.0848, measured 268.0844.

Reaction of [Methoxy(2-phenylethynyl)methylene]pentacarbonylchromium 11b with 3-Diazopropene. The preparation was accomplished according to a literature procedure[31] from ethyl nitrosocarbamate. To a suspension of sodium methoxide (1.4 g, 26 mmol) in MeOH (10 mL) and pentane (40 mL), which was shielded from direct light and maintained at 0 °C, was slowly added ethyl nitrosocarbamate via a dropping funnel. After 2 h, an orange suspension formed. The mixture was twice washed with 5% NaOH and dried over anhydrous KOH. The solution was decanted and stored temporarily in the dark at 0 °C.

To a solution of the complex **11b** (266 mg, 0.79 mmol) in pentane (4 mL) at 0 °C was added the freshly prepared 3-diazopropene in pentane (~6 mL, ~0.79 mmol). Five minutes later, 1 more equiv (~6 mL) of 3-diazopropene was added and after $1^1/_2$ h, a red precipitate formed and the starting material **11b** had been consumed as indicated by TLC. The reaction was diluted with ether, washed with aqueous NH_4Cl and brine, and dried over $MgSO_4$. After removal of the volatiles, the residue was flash chromatographed on silica gel by using a mixture of CH_2Cl_2/ether/hexanes (1:1:6) to give a red solid (203 mg, 0.5 mmol, 63%, R_f 0.51), which was then recrystallized from CH_2Cl_2/hexanes and identified as the pyrazole carbene complex **26a**: mp >300 °C dec (>100 °C the color slowly changed from red to black); ^{1}H NMR (500 MHz) δ 4.45 (s, 3 H), 5.34 (d, 1 H, J = 11.5 Hz), 5.56 (d, 1 H, J = 18.0 Hz), 6.38 (dd, J = 11.5, 18.0 Hz), 7.10 (d, 2 H, J = 7.1 Hz), 7.30 (d, 1 H, J = 11.5, 18.0 Hz), 7.35 (t, 2 H, J = 7.5 Hz), 10.56 (br s, 1 H); ^{13}C NMR (100 MHz) δ 65.93 (q, J = 149.7 Hz), 115.66 (s, Ar C_1), 116.34 (dd, J = 151.9, 161.6 Hz, $=CH_2$), 122.63 (d, J = 161.1 Hz, =CH), 127.09 (dt, J = 7.0, 161.0 Hz, Ar C_4), 128.03 (ddd, J = 5.8, 7.9, 159.2 Hz, Ar C_3), 129.94 (dt, J = 7.0, 157.6 Hz, Ar C_3), 132.81 (t, J = 5.3 Hz, Py C_4), 138.80 (d, J = 6.3 Hz, PyC_5) 160.70 (d, J = 5.2 Hz, PyC_3), 217.17 (s, cis CO), 224.62 (s, trans CO), 333.76 (carbene); IR ($CDCl_3$) ν 3436 s, 2060 s, 2001 s, 1962 s, 1232 s, 1041 s. Anal. Calcd for $C_{18}H_{12}N_2O_6Cr$: C, 53.47; H, 2.97; N, 6.93. Found: C, 53.44; H, 3.01; N, 6.88.

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(31) Salomon, R. G.; Salomon, M. F.; Heyne, T. R. *J. Org. Chem.* **1975**, *40*, 756.