Acknowledgment. We are indebted to Sue Johnson, Dick Sheppard, and Dr. John Arnold for high-field NMR measurements and to Prof. T. D. Tilley for access to the results in ref 18 prior to their publication. We thank the SERC for the award of a studentship (to S.K.T.) and Prof. S. V. Ley for use of his Chemdraw 2 program, and we are ever grateful to Johnson Matthey plc, for their continued support through generous loans of platinum.

Reactions of $(CO)_5Cr{=}C(Me)N(CH_2CH_2)_2$ with Enynes: Mechanistic Insight and Synthetic Value of Changing a Carbene Donor Group from Alkoxy to Dialkylamino

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Received May 9, 1989

Summary: Reactions of the title carbene complex (**10**) with 1,6- and 1,7-enynes are described and contrasted with the results of the 1-*methoxy*ethylidene analogues. The more strongly electron-donating pyrrolidino substituent simultaneously provides considerable mechanistic insight and leads to a more generally useful synthetic tool for the preparation of bicyclic cyclopropanes.

The reaction of (1-*methoxy*ethylidene)pentacarbonyl chromium (1) with 1,6- and 1,7-enynes (2) was recently described by us.[2] The principal products (see Scheme I) included bicyclic cyclopropanes (3), bicyclic cyclobutanones (4), furans (5), and metathesized dienes (6). We proposed several mechanistic branch points: (i) the vinylogous methoxycarbene complex 7 (X = OMe) could engage the now internal alkene either before (path a) or after (path b) carbon monoxide insertion leading, respectively, to metallacyclobutane 8 or the vinylketene complex 9, (ii) the metallacyclobutane 8 could reductively eliminate to cyclopropane 3 (path c) or consummate metathesis by producing 6 (path d), and (iii) the vinylketene complex 9 could undergo net 2 + 2 cycloaddition to give the cyclobutanone 4 (path e) or rearrange to the furan 5 (path f).[3] With the hope of tailoring the reaction to only provide the useful vinylcyclopropanes 3 by avoiding path b, we have examined related reactions using (1-*pyrrolidino*ethylidene)-pentacarbonyl chromium (10) and now describe those results. This complex and the intermediates derived therefrom should exhibit greater back-bonding between chromium and carbon monoxide and, therefore, a reduced propensity for CO insertion into 7.[4] The anticipated result was the quenching of path b; such is the case.

Scheme I

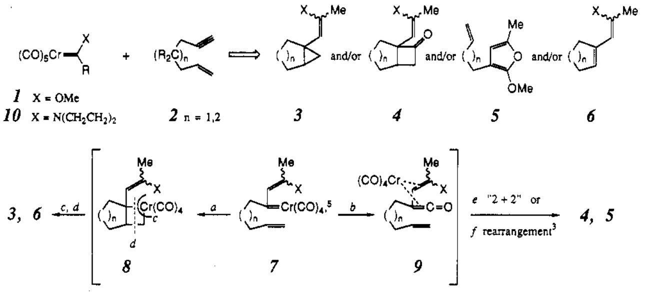
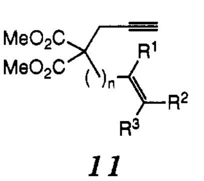
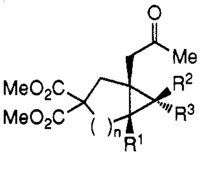


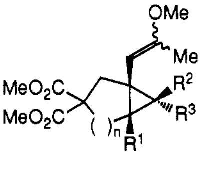
Table I



11



12



13

11-13 a-e	R^1	R^2	R^3	n	Yield[a] of *12* from 10	Yield[a] of *13* from 1 (ref 2)
a	H	H	H	1	88%[b] (76%)[b]	69%
b	Me	H	H	1	(58%)	22%[c]
c	H	H	Me	1	(62%)	2%[d]
d	H	Me	H	1	(64%)	not done
e	H	H	H	2	79% (61%)	46%[e]

a) yields are of MPLC-purified product except those in parentheses which are for material sequentially purified by MPLC and then HPLC b) ~5 mmol scale, all others ~0.5 mmol scale c) 30% cyclobutanone also formed d) 6% cyclobutanone, 30% metathesized diene, and 7% furan formed e) 20% furan formed

When the series of enynes **11a–e** was exposed to the pyrrolidinocarbene **10** in refluxing toluene[6] ([**10**] ≈ 0.7 M, ~1.3 equiv of **11**, 1 h, 120 °C external bath, sealed vessel), the ketocyclopropanes[7] **12a–e** were the only products observed upon inspection of the crude product mixture by ^{1}H NMR analysis and isolated after MPLC/HPLC on silica gel. As the data in Table I indicate, the yields of cyclopropane **12** using the aminocarbene complex **10** were essentially independent of the degree of alkene substitution

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[1] Fellow of the Alfred P. Sloan Foundation, 1985–1989.

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[4] (a) Cf. reactions of 1 (but with Me replaced by Ph and X = NR_2) with alkynes to generate indenes rather than naphthols:[5] Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (b) For a photochemically induced ketene formation from an amino-bearing carbene see: Hegedus, L. S.; de Weck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

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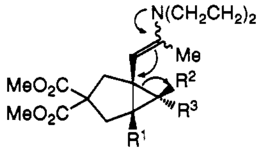
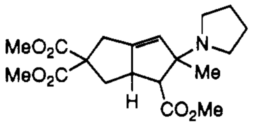
[6] THF, benzene, toluene, and DMF[4a] are all acceptable solvents for the reaction of **10** + **11a**.

[7] ^{1}H NMR analysis of the crude product mixture before chromatography or of solutions of reactions carried out in C_6D_6 gave no indication of the expected enamine intermediates **i** (cf. ref 4a). Circumstantial evidence that enamine formation is indeed occurring is found in the reaction of **10** with **11** (R^2 = CO_2Me, R^1/R^3 = H) at 120 °C which gave the bicyclo[3.3.0]octane **ii** in 53% yield and as a single diastereomer. This is best envisioned as arising via a thermodynamically controlled vinylcyclopropane rearrangement of the "push–pull" activated enaminoester intermediate **iii**. In fact, a C_6D_6 solution of ketone **12** (R^2 = CO_2Me, R^1/R^3 = H)[2] and excess pyrrolidine at 80 °C resulted after 3 h in clean conversion (^{1}H NMR) to the rearranged product **ii** [cf.[2] **1** + **11** → **13** (R^2 = CO_2Me, R^1/R^3 = H) in 64%].



	R^1	R^2	R^3
i	H or alkyl		
iii	H	CO_2Me	H



ii

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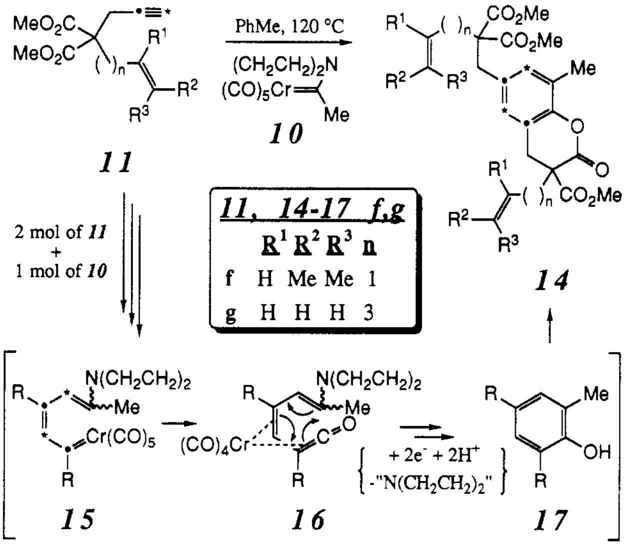
for the vinyl (**11a**), methallyl (**11b**), and (*E*)- and (*Z*)-crotyl (**11d** and **11c**) systems. This is in significant contrast to the case of the methoxy-bearing carbene **1**.[2] The fused bicyclo[4.1.0]heptane **12e**, whose formation is presumably slowed by virtue of generation of a six- rather than five-membered ring, was also formed in better yield with **10** than **1**.

The increased electron-donating ability of the pyrrolidino compared to the methoxy substituent results in the necessity for higher temperatures to achieve comparable reaction rates (~120 °C vs ~80 °C), consistent with a slower initial dissociation of carbon monoxide to a 16-electron chromium species capable of initiating reaction with the alkyne. Moreover, the amino group expresses its donor power again at the stage of the vinylogous donor-stablized carbene complex **7** ($X = NR_2$) by slowing the rate of carbon monoxide insertion and ketene formation. However, we did eventually see products derived from carbon monoxide incorporation in reactions of **10**. The substrates **11f** and **11g** which contain additional hindrance on the alkene and a longer tether, respectively, apparently undergo cyclopropanation more slowly than any of **11a**–**e**. The only identifiable products from their reaction with **10** were the aromatic lactones **14f** and **14g** in 48% and 59% yields, respectively. These 2:1 adducts can arise via the butadienylogous aminocarbenes **15** (formed by addition of the vinylogous carbene **7** to a second molecule of enyne **2**) in which the donating capability of the pyrrolidino group to the metal center is diminished to the point where CO insertion becomes kinetically viable. The resulting ketene complexes **16** can undergo reductive cyclization to the two-alkyne phenols **17**, precursors to the lactones **14**, by a precedented redox process.[8]



11, 14-17	R^1	R^2	R^3	n
f	H	Me	Me	1
g	H	H	H	3

We believe that other applications[9] which demonstrate the advantageous behavior of amino-substituted Fischer carbene complexes will continue to surface. This work simultaneously demonstrates that amino substituents can alter the reactivity patterns of these species in synthetically profitable ways and provides new insight to the mechanism of this important class of organometallic reagents.

Acknowledgment. This investigation was supported by Grant GM-38854 awarded by the DHHS and by an award from the Alfred P. Sloan Foundation.

Supplementary Material Available: Spectral and characterization data for compounds **12a**, **12b**, **12c**, **12d**, **12e**, **14f**, **14g**, and **ii** (5 pages). Ordering information is given on any current masthead page.

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Deprotonation of Bis(dimethylphosphino)ethane Ligand of a Cationic Chromium Alkyl

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Received May 10, 1989

Summary: Reaction of cationic chromium alkyl $[Cp^*Cr(dmpe)CH_3]^+PF_6^-$ with strong base proceeded via deprotonation of a methyl group of coordinated bis(dimethylphosphino)ethane and yielded a complex containing a six-membered CrCPCCP heterocycle. The crystal structure of this compound was determined, and its isomerization and reactions with electrophiles were investigated.

As part of our study of the reactivity of paramagnetic organometallics we have recently described some cationic chromium(III) alkyl complexes of the type $[Cp^*Cr(L)_2R]^+X^-$.[1] These complexes catalyze the polymerization of ethylene and serve as homogeneous models for commercially used heterogeneous catalysts based on chromium.[2] It has been noted that olefin polymerization catalysts are closely related chemically to catalysts for the olefin metathesis reaction.[3] The latter reaction has generated some excitement as of late in the form of the ring opening metathesis polymerization (ROMP) of cyclic olefins.[4] We reasoned that deprotonation of a cationic chromium alkyl[5] might yield an alkylidene, which could initiate olefin metathesis.[6] Herein we report an unexpected result of this approach.

Addition of 1.0 equiv of the base $LiN(SiMe_3)_2$ to a THF solution of $[Cp^*Cr(dmpe)Me]^+PF_6^-$ (**1**) resulted in an im-

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