complex indicates that α^2 is larger, and hence the $3d_{x^2-y^2}$ orbital is more covalent in character in this complex relative to the D_{2d} complex. From a variety of more traditional spectroscopy methods (EPR superhyperfine analysis, etc.), it is established that ψ^* in D_{4h} $CuCl_4^{2-}$ contains ~61% Cu $3d_{x^2-y^2}$ and ~39% Cl 3p character.[12] On the basis of the experimental intensity ratios for the 2820-eV transition and calibrating it for D_{4h} $CuCl_4^{2-}$ to the $\alpha^2 = 0.39$ value, the intensity of the 2820-eV feature gives a corresponding value for D_{2d} $CuCl_4^{2-}$ of $\alpha^2 \simeq 0.29$ and thus approximately 71% Cu character. While traditional spectroscopic approaches are not as accessible for D_{2d} $CuCl_4^{2-}$, Xα calculations predict a decrease of ~6% in the $3d_{x^2-y^2}$ orbital on going to the D_{2d} distorted tetrahedral structure, which is consistent with our XAS experimental findings.[13]

Ligand XAS spectroscopy thus provides a powerful new approach for probing covalent character in valence orbitals of transition-metal complexes.[14] This method, while having clear parallels with superhyperfine analysis in EPR, can in many cases be an advantageous alternative approach, in that obtaining a resolvable superhyperfine signal is often not possible, as is the case with D_{2d} $CuCl_4^{2-}$. This XAS method will be most powerful in the 2-3-keV energy region, based on the high-energy resolution, which allows it to be applied to P, S, and Cl ligands. Other ligands such as Br, which have much higher K-edge energies, can also be studied,[15] but the lower energy resolution will make interpretation less straightforward.

Acknowledgment. This research was supported by NSF CHE-8817702 and NIH RR-01209 (to K.O.H.) and NSF CHE-8613376 (to E.I.S.). Experimental data were recorded at the Stanford Synchrotron Radiation Laboratory, which is supported for operation by the Department of Energy's Office of Basic Energy Sciences, Division of Chemical Sciences, using instrumentation and resources provided by the National Institutes of Health, Division of Research Resources.

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Efficient Entry to Bicyclic Lactones via van Halban-White Cyclizations

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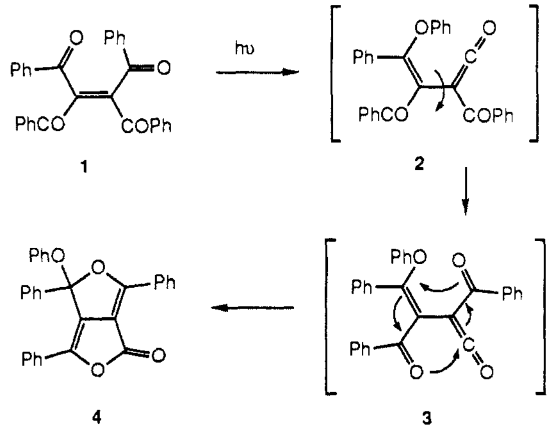
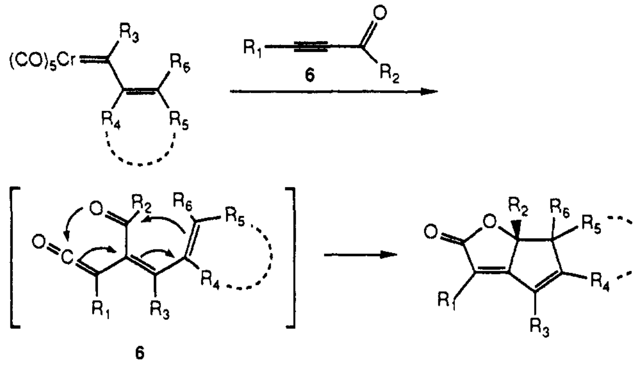
The photochemistry of tetrabenzoylethylene was first examined by van Halban 78 years ago;[1] however, the structure of the photoproduct was finally determined to be **4** by White only 11 years ago.[2] This reaction involves migration of a phenyl group from carbon to oxygen to generate the cross-conjugated ketene **2**,[3] which undergoes rotation about the center bond to generate the conformer **3** necessary for the double cyclization that gives rise to the dilactone **4**. Although no other examples of cyclizations of this type are known, it is nonetheless a prototype for a class of reactions that in their fullest scope could have value in organic synthesis for carbocyclic as well as heterocyclic systems. We report here that the reactions of ketoalkynes with group 6 alkenylcarbene complexes[4] give bicyclic lactones whose formation can be interpreted to be the result of a van Halban-White type double-cyclization of cross-conjugated ketenes of the type **6**.





As indicated in Table I, bicyclic lactones **15**-**19** can be obtained in moderate to excellent yields from the reactions of various alkenylcarbene complexes[4a,5a,14] with acetylenic ketones, aldehydes,

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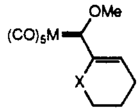
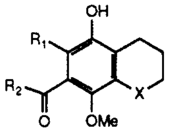
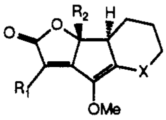
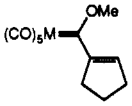
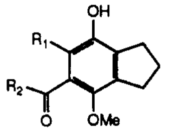
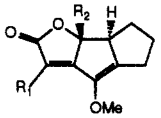
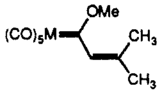
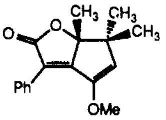
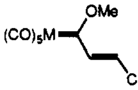
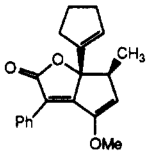
0002-7863/90/1512-1645$02.50/0

Table I. Reaction of Group 6 Carbene Complexes with Ketoacetylenes[a]

Entry	Complex	Alkyne R_1	Alkyne R_2	Phenol, % Yield	Lactone, % Yield	Total Yield (%)
						
	X = O					
1	**7a** M = Cr	Et	Me	**12a** 33	**15a** 32	65
2	M = Cr	Et	Me	**12a** 35	**15a** 31	66[b]
3	M = Cr	Ph	Me	**12b** 6	**15b** 87	93
4	M = Cr	Ph	H	**12c** 4	**15c** 62	66
5	M = Cr	Ph	OEt	**12d** 43	**15d** 27	70
6	M = Mo	Et	Me	**12a** 23	**15a** 44	67[c]
7	**7b** M = Mo	Et	Me	**12a** <10	**15a** 7	43[b-d]
	X = CH$_2$					
8	**8c** M = W	Et	Me	**13a** 36	**16a** 20	56[e]
9	**8a** M = Cr	Me$_3$Si	Me	**13b** 8	**16b** 25	33
						
10	**9a** M = Cr	Et	Me	**14a** 18	**17a** 39	57
11	M = Cr	Ph	Me	**14b** 5	**17b** 70	75
12	**9b** M = Mo	Ph	Me	**14b** 11	**17b** 59	70
						
13	**10a** M = Cr	Ph	Me		**18** 73	73[g]
						
14	**11a** M = Cr	Ph	C$_5$H$_7$		**19** 50	50[h]

[a] Unless otherwise specified, all reactions were carried out in THF at 50 °C under argon at 0.05 M in carbene complex with 1.5–2.0 equiv of alkyne. [b] Acetonitrile solvent. [c] 25 °C. [d] A 26% yield of phenol **26** also was obtained. [e] 80 °C. [f] Lactone **17a** is unstable over a period of days to isomerization to **17a**† (see supplementary material). [g] Phenol formation was not possible; no analogous cyclohexadienone was observed (ref 5). [h] No phenol was observed.

and esters. Varying amounts of the phenols **12–14** are also produced typically as minor products in this reaction. The most reasonable way to account for the distribution between the two products is to invoke competitive formation of the two isomeric syn and anti vinylcarbene complexed intermediates **21** (Scheme I) whose involvement in the reactions of carbene complexes and alkynes has received recent theoretical support[6] and been implicated in another system.[7] Carbon monoxide insertion then generates the two isomeric vinylketene intermediates **22**. The syn isomer of **22** can undergo an electrocyclic ring closure to the alkenyl substituent to form the phenol products **12–14**. Rotation about the single bond of the vinylketene moiety in **22**-anti leads to the cross-conjugated ketene **23**-anti, which closes to the observed lactones **15–19**. The isomeric lactone **24** could have been formed from **22**-syn, but the spectral data are most consistent with the structure **15**; and this assignment was confirmed by an X-ray diffraction analysis of **15b**, which also established the anti relationship of the tricyclic ring system. It cannot be determined at this point whether the metal is complexed to intermediates **22** and **23**, but the metal cannot be η^4-bound to the vinylketene moiety in **22**-anti since this would prohibit the conformational changes necessary for cyclization. The diminished amounts of phenol products for R_1 = Ph (entries 1 and 3) may be due to the disfavored formation of **21**-syn relative to **21**-anti as the result of a steric interaction between R_1 and the alkenyl substituent in the puckered form of **21**. This effect may also be present in the reaction for entry 9 and is being further pursued.

A number of aspects of these reactions are unprecedented. Both the phenols **12–14** and the lactones **15–19** are associated with the regiochemistry indicated in the alkyne complex **20** and not the regioisomeric complex **25**. All previous studies conclude that the regiochemistry of alkyne incorporation in phenol formation is controlled by steric factors; terminal acetylenes react regioselectively with most carbene complexes giving phenols with the alkyne substituent adjacent to the hydroxyl group (**26**, R_1 = H). Internal acetylenes generally give mixtures of regioisomers unless there is a large steric differential between the acetylene substituents.[4h,8f,9] Therefore, it is surprising that 3-hexyn-2-one reacts only with the regiochemistry indicated in **20**. This observation can be rationalized, though, when the polarization match between the ketoacetylene and the metal–carbene bond is recognized. This is apparently the first example in which the electronic nature of

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(11) Complex **27** can be prepared in 44% yield (one attempt) from 6-iodo-2-hexyne as follows: (i) 2 equiv of *t*-BuLi, ether, −78 °C, 1.5 h; (ii) transfer to 1 equiv of Mo(CO)$_6$, ether, −78 °C, 15 min; (iii) −78 → 25 °C, 1 h; (iv) Me$_3$O$^+$BF$_4^-$, CH$_2$Cl$_2$. Only a 12% yield was obtained with the procedure described for the corresponding chromium complex.[12]

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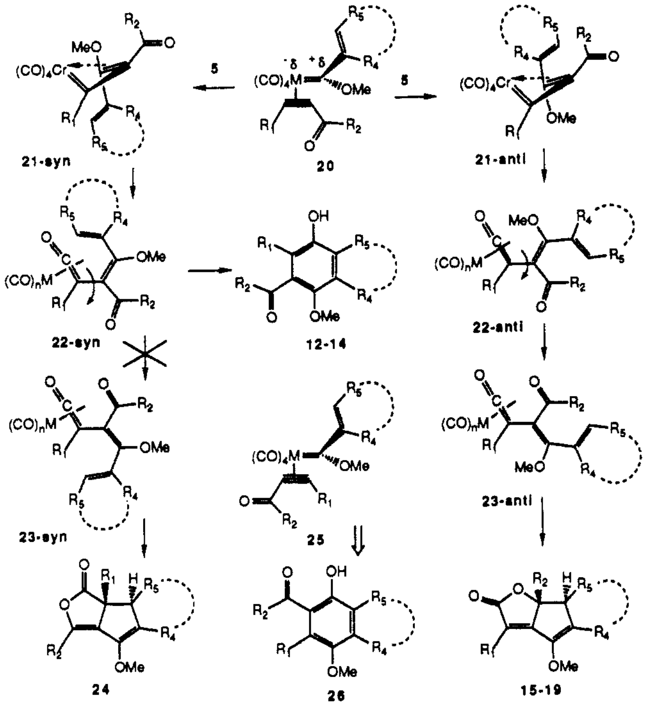
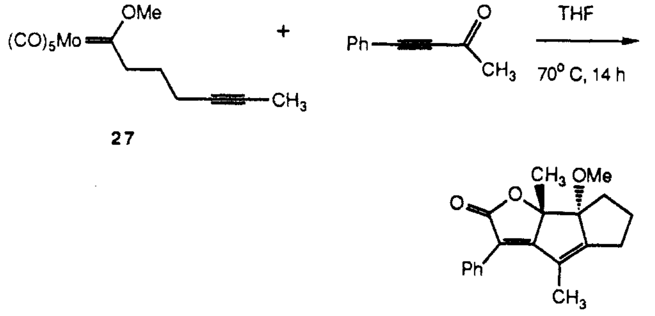
Scheme I



the acetylene substituent is controlling the regiochemistry of acetylene incorporation. Acetylenic ketones and esters have been examined previously, but in most cases they were terminal alkynes (R_1 = H) and in this situation steric factors may override electronic factors leading to phenols of the type **26** (R_1 = H). This may also explain why van Halban–White cyclization products have not been reported previously from the reactions of carbene complexes and alkynes.[8,9] Another unprecedented observation is that the regiochemistry of alkyne incorporation is affected by solvent.[10] The reaction of the molybdenum complex **7b** with 3-hexyn-2-one gives phenol **12a** and lactone **15a** in THF, whereas in acetonitrile, the phenol **26a** is the major product. The extent to which electronic factors and the nature of the solvent can control the regioselectivity in the reactions of carbene complexes with alkynes, and the extent to which the nature of the substituent R_1 can control the stereochemistry of the vinylcarbene intermediates in these reactions, are currently being investigated.



The reaction of the 4-hexynylcarbene complex **27**[11] with 4-phenyl-3-butyn-2-one illustrates the feasibility of a triple annulation for the preparation of tricyclic lactones via an in situ generated alkenylcarbene complex.[13] These observations associated with the reaction of alkenylcarbene complexes with ketoacetylenes suggest that further investigations are warranted with regard to the scope of the van Halban–White cyclizations of cross-conjugated ketenes in various configurations.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (PHS-GM 33589). 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).

Registry No. 7a, 90150-06-4; **7b**, 124945-26-2; **8a**, 88426-08-8; **8c**, 111772-19-1; **9a**, 67746-50-3; **9b**, 124945-27-3; **10a**, 60920-65-2; **11a**, 109362-35-8; **12a**, 124945-09-1; **12b**, 124945-08-0; **12c**, 124945-18-2; **12d**, 124945-19-3; **13a**, 124945-10-4; **13b**, 124945-20-6; **14a**, 124945-11-5; **14b**, 124945-17-1; **15a**, 124945-12-6; **15b**, 124945-21-7; **15c**, 124991-96-4; **15d**, 124945-23-9; **16a**, 124945-13-7; **16b**, 124991-97-5; **17a**, 124945-14-8; **17b**, 124945-24-0; **18**, 124945-15-9; **19**, 124945-16-0; **27**, 124945-28-4; **28**, 124945-22-8; $H_3CC{\equiv}C(CH_2)_3I$, 28077-74-9; $Mo(CO)_6$, 13939-06-5; $CH_3COC{\equiv}CCH_2CH_3$, 1679-36-3; $PhC{\equiv}CCOCH_3$, 1817-57-8; $PhC{\equiv}CCHO$, 2579-22-8; $PhC{\equiv}CCO_2Et$, 2216-94-6; $TMSC{\equiv}CCOCH_3$, 5930-98-3; 1-cyclopentenyl-3-phenyl-2-propyn-1-one, 124945-25-1.

Supplementary Material Available: Spectral data for all new compounds (**12a–d**, **13a**,**b**, **14a**,**b**, **15a–d**, **16a**,**b**, **17a**,**b**, **18**, **19**, **26**, and **28**) and X-ray crystallographic data for compound **15b** including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (11 pages); a listing of F_o and F_c for compound **15** (5 pages). Ordering information is given on any current masthead page.

Solid-State ^{13}C Nuclear Magnetic Resonance Studies of Lithium Fluorenide Complexes

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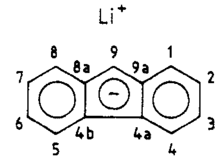
Exceptional interest in the structures of organolithium compounds has mainly been focused on the solution structure as probed by various experimental spectroscopic techniques. The solid-state structures have so far been determined by X-ray crystallography, mostly in the presence of a strong complexing agent.[1] Reports using solid-state cross-polarization/magic angle spinning (CP/MAS) NMR techniques[2] are scarce and limited to a few alkyllithium systems.[3]

In this communication we report for the first time a ^{13}C CP/MAS NMR study of a delocalized carbanion system, lithium fluorenide (**1**),[4] as a function of the complexation agent. Conflicting X-ray and solution structures of this system,[5,6] as suggested earlier, in relation to various calculations[5,7] made **1** an attractive candidate for the present study.



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(4) Complexed **1** was prepared in benzene, using *n*-butyllithium, according to a modified procedure to that given in ref 5, in the case of **1**–bisquinuclidine. In the other preparations, hexane was used as solvent. Two equivalents of the ligands were added, except for the bidentate TMEDA ligand, where 1 equiv was added. The crystals were filtered and dried for 15 min under high vacuum, before being packed into the rotor. All handling of the material was conducted under an argon atmosphere. Solid-state ^{13}C CP/MAS spectra were obtained by using a Bruker MSL 100 NMR spectrometer. Samples were rotated at 3 kHz, the repetition time was 2.5 s, and the contact time was 1 ms. Specially designed zirconium dioxide/Kel-F rotors were used throughout the study.

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