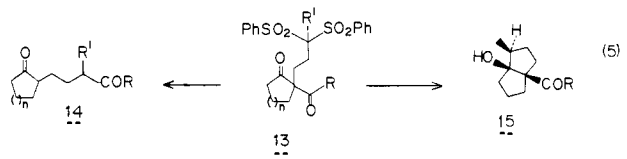
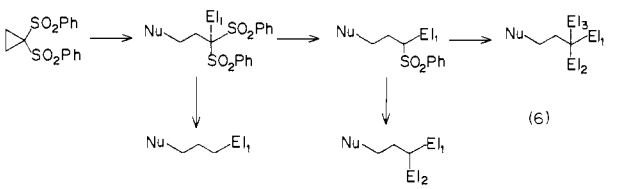
attacked the ester group preferentially to give **14**[8] (n = 2, R = OCH_3, R′ = CH_3), whose structure was proven by comparison to an authentic sample. This novel three-carbon chain extension of β-keto esters proceeds with equal facility for **13b,d,e** to give the corresponding products in 69%, 80%, and 74% yields, respectively (eq 5).[14]



(5)

In contrast to these results, the five-membered ring analogue **13a** gave the chain extended product **14** (n = 1, R = OCH_3, R′ = CH_3) in 33% yield and the product of attack at the ketone carobonyl group **15** (R = OCH_3) in 45% as a single diastereomer as shown by TLC and ^1H and ^{13}C NMR spectroscopy. On the basis of the ^{13}C shift for the methyl group[15] it is assigned the exo configuration. Sterically retarding the attack at the ester carbonyl group as in **13g** permits shifting the reaction exclusively to this latter process, i.e., to give **15** [R = $OC(CH_3)_3$] in 69% yield.

The 1,1-bis(benzenesulfonyl)cyclopropane appears to fulfill the requirements for a propylene 1,3-dipole. As summarized in eq 6, the fact that the sulfones can be sequentially removed permits



(6)

selective introduction of between one and three electrophiles. In the case of β-keto esters such versatility created a novel three-carbon insertion between the ester group and the ketone or a cyclopentane annulation. Such flexibility offers new opportunities for developing synthetic strategy toward complex targets.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. J.C. gratefully acknowledges support by the CNRS and for a NATO postdoctoral fellowship for a portion of her stay, and J.B. acknowledges an NSF postdoctoral fellowship.

Registry No. 3, 34782-46-2; **6** (RX = PhS), 84109-67-1; **6** (RX = $PhCH_2O$), 84109-68-2; **6** (RX = $(C_2H_5)_2N$), 84109-69-3; **7** (RX = PhS; R′ = CH_3), 84109-70-6; **7** (RX = PhS; R′ = $CH_2CH=CH_2$), 84109-71-7; **8** (R = R′ = CH_3), 84109-72-8; **8** (R = n-C_4H_9; R′ = CH_3), 84109-73-9; **10** (R = H), 84109-74-0; **10** (R = CH_3), 84109-75-1; **11a**, 10472-24-9; **11b**, 41302-34-5; **11c**, 5452-73-3; **11d**, 62939-87-1; **11e**, 874-23-7; **11f**, 84109-76-2; **13a**, 84109-77-3; **13b**, 84117-56-6; **13c**, 84109-78-4; **13d**, 84109-79-5; **13e**, 84109-80-8; **13f**, 84109-81-9; **13g**, 84109-82-0; **14a**, 84109-83-1; **14b**, 82257-46-3; **14d**, 84109-84-2; **14e**, 84109-85-3; **15** (R = OCH_3), 84109-86-4; **15** (R = $OC(CH_3)_3$), 84109-87-5; $PhCH_2OH$, 100-51-6; $(C_2H_5)_2NH$, 109-89-7; CH_3I, 74-88-4; $H_2C=CHCH_2Br$, 106-95-6; H_2O, 7732-18-5; $CuBr{\cdot}S(CH_3)_2$, 54678-23-8; $KCH(CO_2C_2H_5)_2$, 37892-24-3; PhSH, 108-98-5; n-C_4H_9MgBr, 693-03-8; lithium biphenylide, 34467-57-7; lithium naphthalenide, 7308-67-0; lithium phenanthrenide, 34509-57-4; acrolein, 107-02-8; 1,1-bis(benzenethio)cyclopropane, 69519-84-2.

(14) Alternatively, attack at the ketone carbonyl group could be followed by spontaneous retroaldolization to give the three-carbon ring enlarged 4-carbomethoxy-2-methylcycloalkanone. Thus, chemical transformations were also employed for the structural assignment. Baeyer–Villiger oxidation of **14b** led to a lactone that did not bear a methyl group at the oxygen-bearing carbon. Enol acetate formation under thermodynamically controlled conditions for **14d** and **14e** led to an enol acetate lacking a vinyl methyl group. Both of these observations rule out the intercalation process.

(15) Trost, B. M.; Scudder, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 7601. Hudlicky, T.; Koszyk, F. J.; Dochwat. D. M.; Cantrell, G. L. *J. Org. Chem.* **1981**, *46*, 2911.

Sulfur Activation of Azides toward Addition of Organometallics. Amination of Aliphatic Carbanions

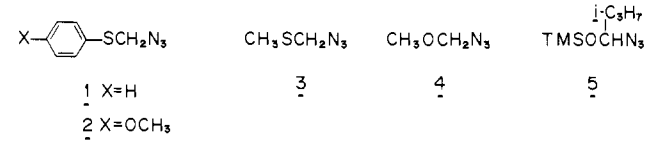
Barry M. Trost* and William H. Pearson

McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received October 13, 1982

The growing importance of carbanions as reactive intermediates stimulates the search for electrophilic partners. The successful use of azidomethyl phenyl sulfide[1] as a synthon for $^+NH_2$[1-3] depends upon an understanding of the addition of organometallics to azides and the subsequent decomposition of the triazenes. We report that sulfur substitution plays a beneficial role in both processes and put forth a possible rationale.

The question of the addition of organometallics to azides appears somewhat controversial.[3-5] We undertook a systematic comparison of various heteroatom substituted azides, **1-5**. Whereas



1[1,6] reacts smoothly with phenylmagnesium bromide at −78 to 0 °C, subjection of **5**[7] to identical conditions led only to recovered azide. Phenethylmagnesium bromide smoothly forms the corresponding triazene with **1** at −78 °C, but **3**[6] requires 0 °C. Moreover, **4**[8] leads to no reaction at −78 °C and only trace amounts of any triazene at 0 °C. A direct competition between

$$\mathbf{3} + \mathbf{4} + PhCH_2CH_2MgBr \rightarrow \underset{\mathbf{6}}{CH_3SCH_2N{=}NNHCH_2CH_2Ph} + \underset{\mathbf{7}}{CH_3OCH_2N{=}NNHCH_2CH_2Ph}$$

3 and **4** (1:1 ratio) for this Grignard reagent at −78 to 0 °C led to **6** and **7** in a 7:1 ratio as determined by the ratio of the signals at δ 4.52 and 2.00 for **6** and δ 4.79 and 3.22 for **7**. **1** was competed against **2** for a limited amount of phenyl- and phenethylmagnesium bromide in order to probe the effect of electron density in the arylthio series. In both cases, the corresponding triazenes were formed in a 1:1 ratio. These experiments clearly establish the order **1** ~ **2** > **3** > **4** ≫ **5**. This order does not correspond to either the Lewis basicity toward magnesium salts or to electron density. It clearly establishes the activating influence of sulfur compared to oxygen and of arylthio compared to alkylthio.

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(2) Coleman, G. H.; Hermanson, J. L.; Johnson, H. L. *J. Am. Chem. Soc.* **1937**, *59*, 1896. Sheverdina, N. J.; Kocheshkov, Z. *J. Gen. Chem. USSR* **1938**, *8*, 1825. Gilman, H.; Ingham, R. K. *J. Am. Chem. Soc.* **1953**, *75*, 4843. Brown, R.; Jones, W. E. *J. Chem. Soc.* **1946**, 781. Silver, M. S.; Shafer, P. R.; Nordlander, J. E.; Ruchardt, C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 2646. Barton, D. H. R.; Bould, L.; Clive, D. L. J.; Magnus, P. D.; Hase, T. *J. Chem. Soc. C* **1971**, 2204. Vol'pin, M. E. *Pure Appl. Chem.* **1972**, *30*, 607. Alvernhe, G.; Laurent, A. *Tetrahedron Lett.* **1972**, 1007. Oguri, T.; Shioiri, T.; Yamada, S. *Chem. Pharm. Bull Jpn.* **1975**, *23*, 167, 173. Tamura, Y.; Minamikawa, J.; Ikeda, M. *Synthesis*, **1977**, 1. Boche, G.; Mayer, N.; Bernheim, M.; Wagner, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 68. Yamamoto, H.; Maruoka, K. *J. Org. Chem.* **1980**, *45*, 2739. Garst, M. E.; Lukton, D. *Synth. Commun.* **1980**, *10*, 155. Beak, P.; Kokko, B. *J. Org. Chem.* **1982**, *47*, 2822.
(3) (a) Smith, P. A. S.; Rowe, C. D.; Bruner, L. B. *J. Org. Chem.* **1969**, *34*, 3430. (b) Wiberg, N.; Joo, W.-C. *J. Organomet. Chem.* **1970**, *22*, 333. (c) Hassner, A.; Murger, P.; Belinka, B. A. *Tetrahedron Lett.* **1982**, *23*, 699.
(4) Campbell, T. W.; Day, B. F. *Chem. Rev.* **1951**, *48*, 299. Canter, F. C.; Boyer, J. H. *Ibid.* **1954**, *54*, 1. Vaughan, K.; Stevens, M. F. G. *Chem. Soc. Rev.* **1978**, *7*, 377.
(5) Dimroth, O. *Chem. Ber.* **1906**, *39*, 3905. Sieh, D. H.; Wilbur, D. J.; Michejda, C. J. *J. Am. Chem. Soc.* **1980**, *102*, 3883.
(6) Bohme, H.; Morf, D. *Chem. Ber.* **1957**, *90*, 446. Also see: Jarvis, B. B.; Nicholas, P. E.; Midiwo, J. O. *J. Am. Chem. Soc.* **1981**, *103*, 3787.
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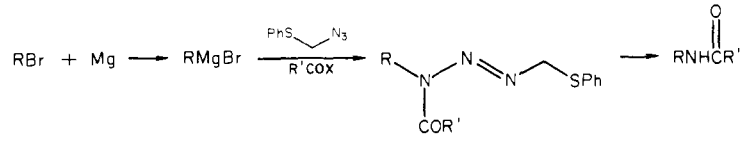
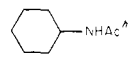
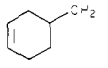
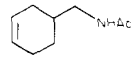
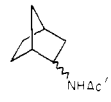
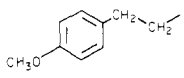
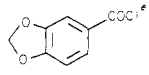
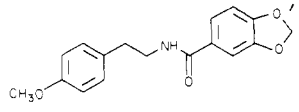
(8) Garcia-Munoz, G.; Madronero, R.; Rico, M.; Saldana, M. S. *J. Heterocycl. Chem.* **1969**, *6*, 921.

0002-7863/83/1505-1054$01.50/0

Table I. Amination of Aliphatic Carbanions

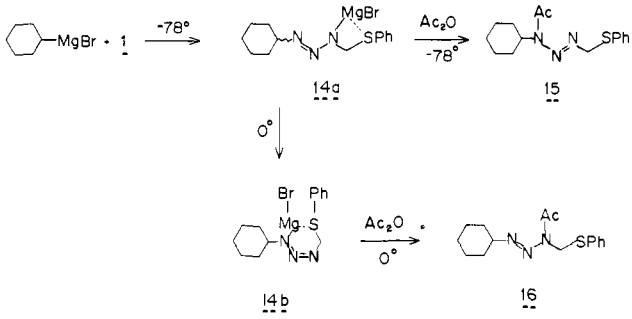


entry	R	R'COX	hydrolysis method[a]	product	yield, %
1	$PhCH_2CH_2$	Ac_2O	A	$PhCH_2CH_2NHAc$[f] (12)	86[b] (83)[c]
		Ac_2O	B		70[b] (68)[c]
		PhCOCl[e]	C	$PhCH_2CH_2NHCOPh$[g]	98[d] (50)[c]
2		Ac_2O	A B		93[b] (90)[c]
3		Ac_2O	A		64[b] (44)[c]
4		Ac_2O	A		70[b] (55)[c]
5			C		75[b] (59)[c]

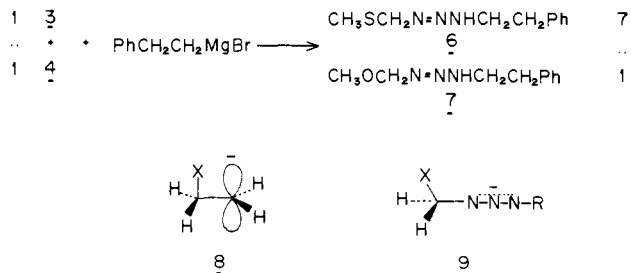
13

[a] Method A = n-$Bu_4N^+HCO_2^-$ in DMF at 45 °C. Method B = KOH in Me_2SO at 0 °C. Method C = KOH in H_2O, CH_3OH, THF at 0 °C. [b] Isolated yield of pure product based upon Grignard reagent. [c] Isolated yield of pure product based upon bromide precursor of Grignard reagent. [d] Isolated yield of pure product based upon purified triazene. [e] DMAP added to accelerate acylation step. [f] Melting point 113–114 °C.[12] [g] Melting point 114–116 °C.[12] [h] Melting point 103.5–104.5 °C.[12] [i] Melting point 123.0–124.5 °C for 54:46 endo-exo mixture.[13] [j] Melting point 153.7–154.5 °C.

Scheme I

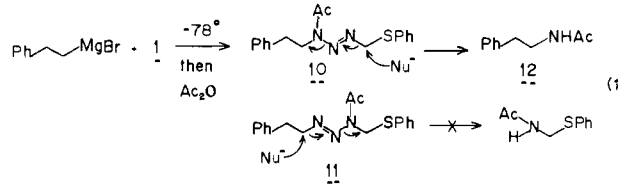


Such results are in accord with polarizability arguments. The calculations of Hoffmann et al.[9] indicate that β-substituted carbanions like **8**, are stabilized relative to ethyl anions when **X** is



more electronegative than H. Hyperconjugation of a C–S bond is more effective than that of a C–O bond due to the lower energy of the σ^* orbital of the former.[10] Application of this same argument to **9** supports the interpretation that the transition state leading to **9** (X = SR) is of lower energy than that leading to **9** (X = OR). Furthermore, this rationale nicely accommodates the higher reactivity of the arylthio compared to the alkylthio azide since the σ^* orbital of the former should be lower in energy and therefore stabilize the neighboring charge more effectively.

The structure of the initial ion was probed by quenching it at low temperature. Addition of phenethylmagnesium bromide to **1** at −78 °C and quenching with acetic anhydride at that temperature (eq 1) gave an 83% yield of a single product assigned



(1)

structure **10**.[11] The methylene singlet of **10** appears upfield (δ 5.02) compared to that for **11**[11] (δ 5.18). Chemical verification arose in the treatment of the crude product from this reaction with either KOH in Me_2SO or tetra-n-butylammonium formate in DMF to give the acetamide **12** in 70% and 86% yield respectively from the Grignard reagent. The alternative regioisomer **11** is inert under these conditions. Indeed, this approach serves as a convenient amination of aliphatic Grignard reagents as summarized in Table I.[11] Since only hydrolysis conditions are employed in the unmasking of the amide, olefins are stable (entry 3). The ability to vary the acylating agent allows direct formation of various amides. Thus, the use of piperonyl chloride in entry 5 creates the amide **13**, a potential precursor of the amaryllidaceae alkaloids.[14]

(9) Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221.

(10) Lehn, J.-M.; Wipff, G. *J. Am. Chem. Soc.* **1976**, *98*, 7498. Streitwieser, A. S., Jr.; Williams, J. E., Jr. *Ibid.* **1975**, *97*, 191. Borden, W. T.; Davidson, E. R.; Andersen, N. H.; Denniston, A. D.; Epiotis, N. D. *Ibid.* **1978**, *100*, 1604. Apeloig, Y.; Rappoport, Z. *Ibid.* **1979**, *101*, 5095.

(11) All compounds have been fully characterized by spectral means, and all new compounds have satisfactory combustion analysis and/or high-resolution mass spectral data.

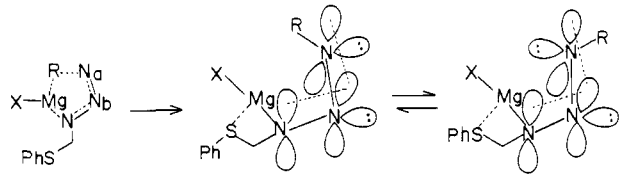
(12) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds"; Wiley: New York, 1964.

(13) Cf.: Roberts, J. D.; Lee, C. C.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 4501. Berson, J. A.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4094.

Similarly, cyclohexylmagnesium bromide gave the single acylated triazene **15**[11] (76% isolated yield) if quenched at −78 °C, but if the initial adduct is warmed to 0 °C before quenching with acetic anhydride, only the regioisomeric acyltriazene **16**[11] is isolated (65% yield). In addition to spectroscopic characterization, nucleophilically induced decomposition of crude **15** with tetra-*n*-butylammonium formate in DMF gave a 93% isolated yield (overall from Grignard reagent) of *N*-acetylcyclohexylamine (Scheme I).

The mutually exclusive formation of **15** and **16** under the above conditions suggests two different salts as their precursors. Using the reasonable assumption that the acyl group is transferred with allyl inversion (eq 1) by analogy to the reaction of allylmagnesium halides with carbonyl partners[15] suggests that the precursor of **15** is **14a** and that of **16** is **14b**. To the extent that sulfur stabilizes the magnesium salt by internal ligation, the isomerization of four-membered ring chelate **14a** to six-membered ring chelate **14b** agrees with the thermodynamic bias for the latter.

The exclusive kinetic formation of the thermodynamically less stable magnesium salt is quite striking. Since coordination of the heteroatom to the magnesium of the attacking Grignard reagent cannot account for this observation (vide supra), the explanation must reside in the mechanism of attack of a nucleophile onto an azide function. We believe, as structure **17** represents, that an



17 18 19

incoming nucleophile R and the developing lone pair at N_b are antiperiplanar. Such an attack creates the *cis*-triazene **18**, which would be expected to readily isomerize to *trans*-**19**. This phenomenon begins to emerge as a general principle for nucleophilic addition to heteroatomic unsaturation.[16,17] For example, in the addition of sodium hexamethyldisilazide to benzenediazonium chloride, the kinetic product was exclusively the *cis*-triazene, which subsequently isomerized to the trans compound.[16b] It appears that the bias for the incoming nucleophile and the developing lone pair at the heteroatom to be antiperiplanar dictates the reaction course for azides.

Sulfur also participates in the nucleophilically triggered decomposition of the acylated triazenes. Thus, treating a mixture of **10** and **11** (prepared by quenching the initial adduct at a temperature between 0 and −78 °C) with a variety of nucleophiles such as lithium thiomethoxide in HMPA, potassium superoxide in Me_2SO, tetra-*n*-butylammonium formate in DMF, or potassium hydroxide in Me_2SO led to *N*-phenethylacetamide from **10** according to eq 1 but only recovered **11**. Apparently the process represented in **11** of eq 1 is much less favorable. Attributing the ready decomposition of **10** to activation by sulfur is reinforced by the observation that 1-benzyl-3-methyltriazene and 1-aryl-3-alkyltriazenes are stable to alkali.[18,19] The ability of the lone pairs on heteroatoms to stabilize S_N2 transition states accounts for this effect.

This study revealed that the addition of Grignard reagents to azides proceeds by a stereoelectronically controlled pathway to generate the thermodynamically less stable magnesium salt of the triazene. This observation permitted the development of a successful approach for the amination of alkylmagnesium halides, thereby generalizing the utility of azidomethylphenyl sulfide as a synthon for $^+NH_2$. Further, it appears that the preference for attack on X=Y to occur by the incoming nucleophile and developing lone pair to be antiperiplanar extends to cumulative unsaturation as found in azides.

Acknowledgment. We thank the National Science Foundation and the National Institute of Health, General Medical Sciences, for their generous support of our programs.

Registry No. 1, 77422-70-9; **2**, 84304-06-3; **3**, 84304-07-4; **4**, 52827-27-7; **5**, 17108-22-4; **10**, 84304-09-6; **11**, 84304-10-9; **12**, 877-95-2; **13**, 84304-08-5; phenethyl bromide, 103-63-9; cyclohexyl bromide, 108-85-0; cyclohex-3-en-1-ylmethyl bromide, 34960-41-3; 2-norbornyl bromide, 29342-65-2; 2-(4-methoxyphenyl)ethyl bromide, 14425-64-0; *N*-(2-phenylethyl)benzamide, 3278-14-6; *N*-acetylcyclohexylamine, 1124-53-4; (*N*-cyclohex-3-en-1-ylmethyl)acetamide, 54385-23-8; *exo*-*N*-2-norbornylacetamide, 28607-02-5; *endo*-*N*-2-norbornylacetamide, 56895-94-4; piperonyl chloride, 25054-53-9; Ac_2O, 108-24-7; PhCOCl, 98-88-4.

Supplementary Material Available: Detailed experimental procedure for the preparation of *N*-phenethylacetamide (1 page). Ordering information is given on any current masthead.

(14) Cf.: Kotani, E.; Takeuchi, N.; Tobinaga, S. *J. Chem. Soc., Chem. Commun.* **1973**, 550. Schwartz, M. A.; Rose, B. F.; Vishnuvajjala, B. *J. Am. Chem. Soc.* **1973**, *95*, 612.

(15) Felkin, H.; Frajerman, C. *Tetrahedron Lett.* **1970**, 1045. Felkin, H.; Gault, Y.; Roussi, G. *Tetrahedron* **1970**, *26*, 3761.

(16) Cf.: (a) Hegarty, A. F.; McCarthy, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 4537 and references therein. (b) Wiberg, N.; Pracht, H. J. *Chem. Ber.* **1972**, *105*, 1392.

(17) For a discussion of the microscopically reverse situation see: Deslongschamps, P. *Tetrahedron* **1975**, *31*, 2463; *Heterocycles* **1977**, *7*, 1271. Lehn, J.-M.; Wipff, G. *J. Am. Chem. Soc.* **1980**, *102*, 1347.

(18) Dimroth, O. *Chem. Ber.* **1905**, *38*, 670. However, see: Hassner, A.; Belinka, B. A. *J. Am. Chem. Soc.* **1980**, *102*, 6185. Le Blanc, R. J.; Vaughan, K. *Can. J. Chem.* **1972**, *50*, 2544.

(19) For example, see; Grosse, H.; Hoft, E. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 335. Hayami, J.; Tanaka, N.; Kurabayashi, S.; Kotani, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3091 and references therein.

Syntheses, Chemical Properties, and X-ray Crystal Structures of Rhenium Formaldehyde and Thioformaldehyde Complexes

William E. Buhro,[1a,b] Alan T. Patton,[1a,b]
Charles E. Strouse,[1b] and J. A. Gladysz*[1a,b,2]

Departments of Chemistry, University of Utah
Salt Lake City, Utah 84112
and University of California
Los Angeles, California 90024

Fred B. McCormick*[3] and Margaret C. Etter

3M Central Research Laboratories
St. Paul, Minnesota 55101

Received October 22, 1982

The synthesis of transition-metal complexes that contain ligand types which may be transient intermediates in catalytic CO/H_2 reactions has been intensely pursued over the past few years.[4] Recently, a η^2-H_2C=O complex was postulated to be a pivotal intermediate in the partitioning of CO/H_2 between methanol and glycol over homogeneous ruthenium catalysts.[5] Hence we set out to develop a new and potentially general methodology for the synthesis of this scarce[6] class of compounds. In view of current

(1) (a) University of Utah; (b) University of California.

(2) Address correspondence concerning **1** to this author at the University of Utah. Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).

(3) Address correspondence concerning **2** to this author.

(4) This literature is extensive. Some lead reviews are as follows: (a) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (b) Articles contained in "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, D.C., 1981; *ACS Symp. Ser.* No. 152. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (e) Herrmann, W. A. *Ibid.* **1982**, *20*, 159.

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0002-7863/83/1505-1056$01.50/0