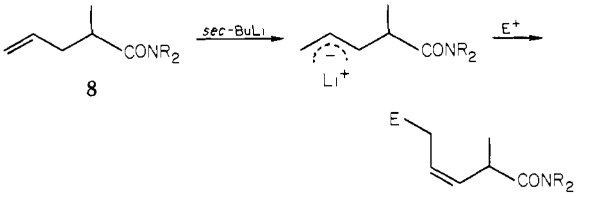
Presumably **6** is converted to **7**, which reacts via a S_E2' process as discussed by Felkin.[8]

The novel β lithiation and regiospecific addition appear to be extendable. The acyclic *N,N*-diisopropyl-2-methylpent-4-enecarboxamide (**8**) gives the δ-substituted products **9**.[6,9] The present

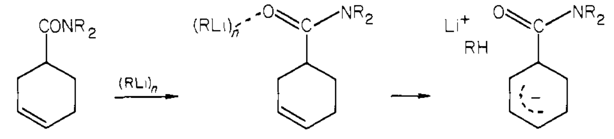


8

9, E = CH_3 (82%), $Si(CH_3)_3$ (56%), $(CH_3)_2COH$ (42%)

approach is convenient and should prove synthetically useful; reactants analogous to **1** are obtained from cycloadditions, and reactants similar to **8** are available by allyl substitution of enolates. Formally related syntheses require dianions of γ,δ-unsaturated carbonyl compounds, multistep sequences, or novel additions and carbonylations of iron carbonyl diene derivatives.[10-13]

The species expected on deprotonation of the amides **1** and **8** are the enolates. Thus, the formation of **3** is rationalized by the customary resonance and inductive effects that operate α to the carbonyl group. The novel β lithiation involving **6** is attributed to reaction via a complex, **10**, that has the organoalkyl base appropriately positioned to remove the β proton.[2-4] In the lithiations of **1** and **8** a proximity effect overcomes kinetically the more familiar and usually more powerful resonance and inductive effects of the carbonyl group.[14-16] Investigations of useful extensions of this novel lithiation as well as a search for other cases in which proximity effects provide unconventional reaction pathways are under way.



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Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for their support of this work.

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(8) The effect of magnesium salts on the regio- and stereochemistry of substitution of allyl systems has been studied, Felkin, H.; Frajerman, C. *Tetrahedron Lett.* **1970**, 1045. Hassel, T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 399. Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1 and references cited therein.

(9) The *Z* stereochemistry is assigned on the basis of a 10.9-Hz coupling of the olefinic protons and assignments of $J_{trans} = 17.5$ and $J_{cis} = 10.6$ Hz in an analogous vinyl group. Romanet, R.; Chemizart, A.; S. Duhoux, S.; and David, S. *Bull. Soc. Chim. Fr.* **1963**, 1048.

(10) For discussion of dieneone dianion derivatives and a summary of other methodologies to provide such substitution, see: Seebach, D.; Pohmakotr, M.; Schrengenberger, C.; Weidmann, B.; Mali, R. S.; Pohmakotr, S. *Helv. Chim. Acta.* **1982**, *65*, 419.

(11) For anions β to carbonyl groups, see: Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651. Goswani, R.; Corcoran, D. E. *Tetrahedron Lett.* **1982**, 1463. Goswami, R. *J. Am. Chem. Soc.* **1980**, *102*, 5973. Caine, D.; Frobert, A. S. *Tetrahedron Lett.* **1978**, 883. Delomaert, S.; Lesur, B.; Ghosez, L. *Ibid.* **1982**, 4251.

(12) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *108*, 2497.

(13) A similar β lithiation occurs on treatment of the secondary amide *N*-methylcyclohexenecarboxomide with 2 equiv of *n*-butyllithium: Kempf, D. J.; Beak, P. unpublished results.

(14) The difference in thermodynamic stabilities of the carbanionic species of **3** and **6** can be roughly estimated as $10^{9\pm2}$. This estimate is based on a ΔpK^a of 9 between a tertiary amide and propene in dimethyl sulfoxide and the fact that an alkyl group has a variable ΔpK_a effect of 1.[15,16] However, extrapolation to the competitive transition states for deprotonation in the complexes species is uncertain.

(15) The pK_a of *N,N*-dimethylacetamide is estimated at 34–35 by Bordwell and Fried (Bordwell, F. G.; Fried, M. E. *J. Org. Chem.* **1981**, *46*, 4327). The pK_a of propene is estimated as 44 on the basis of the estimation of 42 for toluene by Bordwell, Algrin, and Vanier (Bordwell, F. G.; Algrin, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817) and demonstrations that propene is about 2 pK_a units less acidic than toluene by Boerth and Streitweiser (Boerth, D. W.; Streitweiser, A. Tr. *J. Am. Chem. Soc.*, **1981**, *103*, 6443) and Jaun, Schwarz, and Breslow (Jaun, B.; Schwarz, J.; Breslow, R. *Ibid.* **1980**, *102*, 5741).

(16) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095.

Novel Chain Mechanism for the Formylmetal to Hydridometal Conversion. Free Radical, Photochemical, and Electrochemical Methods of Initiation

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Current interest in formylmetal complexes stems from their potential role as key intermediates in the industrially important catalytic reduction of carbon monoxide.[1] Unfortunately attempts to isolate formylmetal complexes have often led to the corresponding hydridometal complex, i.e.,[2]

$$HC({=}O)M \rightarrow HM + CO \qquad (1)$$

Since the microscopic reverse of eq 1 is uncommon,[3] it has not always been rigorously established whether the transformation is thermodynamically or kinetically controlled.

We wish to report a facile kinetic process for the formyl-to-hydride conversion that involves a free radical chain mechanism. The system we scrutinized was the formyldirhenate complex *cis*-$(OC)_5ReRe(CHO)(CO)_4^-Bu_4N^+$ (I), owing to its known thermal stability.[4,5] Indeed, a thoroughly degassed solution of I in either tetrahydrofuran (THF) or acetonitrile (typically 10^{-1} M) remained essentially unchanged for several days at 25 °C, provided it was not exposed even to room light. Addition of only 10 mol % of the radical initiator azobis(isobutyronitrile) (AIBN) induced the transformation of I to the corresponding hydride *cis*-$(OC)_5ReRe(H)(CO)_4^-Bu_4N^+$ (II) in 90% yield[6] within 4 h, the apparent half-life of I being only 45 min in acetonitrile (and 180 min in THF). The radical chain nature of the AIBN-induced transformation of I to II was also revealed by the marked retardation in rate observed in the presence of 1 equiv of dihydroanthracene ($\tau_{1/2} > 5$ h in acetonitrile), which is known to be an effective hydrogen atom donor.[7] A turnover number of >500 was calculated from the known rate of AIBN homolysis under these conditions.[8]

The photochemically induced transformation[4,5] of I to II also proceeds via a radical chain pathway. Thus irradiation of 10^{-1} M solutions of I in THF at 400 nm afforded II in 75% yield after 3 h ($\tau_{1/2} \sim 30$ min).[9] By use of ferrioxalate actinometry, the

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(1) (a) Olivé, G. H.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Masters, C. *Adv. Organometal. Chem.* **1979**, *17*, 61. (d) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136.

(2) Gladysz, J. A. *Adv. Organometal. Chem.* **1982**, *20*, 1.

(3) (a) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959. (b) Wayland, B. B.; Woods, B. A.; Pierce, R. *Ibid.* **1982**, *104*, 302.

(4) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544.

(5) (a) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545. (b) Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413.

(6) Disappearance of I by its ^1H NMR spectrum at 16.1 ppm and appearance of II at −7.2 ppm, using *p*-di-*tert*-butylbenzene as internal standard.[4,5]

(7) Shine, H. J.; Waters, J. A.; Hoffman, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 3613.

(8) Arnett, L. M. *J. Am. Chem. Soc.* **1952**, *74*, 2027.

(9) With Corning (3-74) cutoff or Edmund (405) interference filter.

0002-7863/83/1505-6351$01.50/0

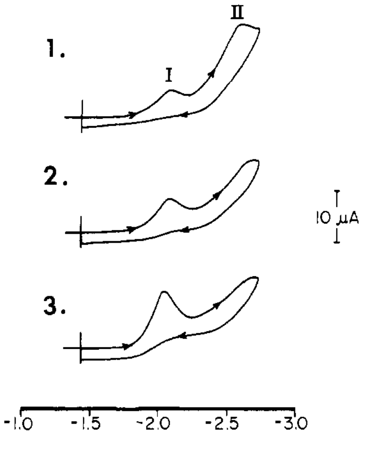

Figure 1. Cyclic voltammogram of 5.0 × 10^{-3} M $(OC)_5ReRe(CHO)(CO)_4^-$ (I) in acetonitrile containing 0.1 M TEAP at a scan rate of 200 mV s^{-1} at 25 °C. Parts 2 and 3, in the presence of 3 and 10 equiv dihydroanthracene, respectively. II is the CV wave of $(OC)_5ReRe(H)(CO)_4^-$.

quantum yield for the photoinitiated conversion to II was found to be $\Phi > 400$. Importantly, this value was markedly decreased in the presence of 1 equiv of dihydroanthracene.[10]

The long kinetic chain lengths arising from free radical and photochemical initiation indicate an efficient propagation sequence which we ascribe to the following mechanism:

Scheme I

$$\mathrm{HC({=}O)(\mathbf{re}) + \mathbf{re}\cdot \rightarrow OC(\mathbf{re})\cdot + H(\mathbf{re})} \tag{2}$$

$$\mathrm{OC(\mathbf{re})\cdot \rightarrow CO + \mathbf{re}\cdot}\ \text{etc.} \tag{3}$$

where **re** = $(OC)_5ReRe(CO)_4^-$. Precedent for both steps derives from the studies of Brown and co-workers,[11] who demonstrated the ability of carbonylrhenium radicals (i) to abstract hydrogen atoms from various donors as in eq 2 and (ii) to undergo facile exchange of carbonyl ligands as in eq 3.

Initiation of the radical chain by AIBN homolysis affords $(CH_3)_2\dot{C}CN$, which abstracts hydrogen from I to produce directly the carbonyldirhenate radical **re·** for Scheme I. Photochemical initiation derives from Re–Re bond scission[12] of I to generate two carbonylrhenium radicals, each capable of hydrogen abstraction from I.[13] Carbonylrhenium radicals can also be generated electrochemically. For example, the galvanostatic reduction of I (2.0 × 10^{-2} M) in acetonitrile containing 0.1 M TEAP consumed 0.035 F mol^{-1} (turnover number ≃ 30) to yield essentially quantitative yields of II.[6] The rapidity of the electrocatalytic process is revealed in the cyclic voltammogram in Figure 1 showing (a) the cathodic current for the irreversible wave of I at E_p −2.1 V to be only 20% of that expected for a one-electron reduction (based on ferrocene calibration) and (b) the simultaneous appearance of II by comparison of the CV wave at E_p −2.6 V with that of an authentic sample. The occurrence of a chain decomposition was also evident by the marked increase in the cathodic current for I and concomitant decrease of II by incremental additions of dihydroanthracene in Figure 1, parts 2 and 3.[14] We propose that electroinitiation proceeds via carbonylrhenium radicals formed by dissociative electron attachment[15] of I and is followed by the propagation mechanism in Scheme I. Indeed, an equivalent catalytic process can be induced chemically by reducing agents. For example, the addition of 10 mol % sodium anthracene to a 10^{-1} M THF solution of I was sufficient to effect conversion to II in 75% yield within 10 min. Thus it is not surprising that anthracene (5 mol %) promotes the electrocatalytic conversion of I to II in quantitative yield at potentials >300 mV more positive than E_p −2.1 V for I in acetonitrile (note, for anthracene E^0 −2.03 V).

We are examining the behavior of other formylmetal complexes in order to stabilize unpersistent ones and to test the generality of the radical chain mechanism.

Acknowledgment. We thank the National Science Foundation for financial support of this research.

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[10] E.g., $\tau_{1/2}$ of I increased from 30 min to >10 h in the presence of 1 equiv of dihydroanthracene.

[11] Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775 and references cited therein.

[12] Cf.: Levenson, R. A.; Gray, H. B.; Ceasar, G. P. *J. Am. Chem. Soc.* **1970**, *92*, 3653. Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; pp 89 ff. Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822. Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *Ibid.* **1982**, *104*, 1842. It is also possible that photochemical irradiation generates **re·** directly from I.

[13] See ref 11 and Byers and Brown [Byers, B. L.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527] for the homolytic reactivity of carbonylrhenium radicals.

[14] (a) Cf.: Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034. (b) Tamblyn, W. H.; Klingler, R. J.; Hwang, W. S.; Kochi, J. K. *Ibid.* **1981**, *103*, 3161. (c) However, saturation of the dihydroanthracene effect suggests the presence of a competing electrocatalytic pathway (Narayanan, B. A.; Amatore, C.; Kochi, J. K., manuscript in preparation).

[15] Cf.: Lemoine, P.; Giraudeau, A.; Gross, M. *Electrochim. Acta* **1976**, *21*, 1, for:

$$\mathrm{I} \xrightarrow{+e} [(OC)_5Re\cdot + (OC)_4ReCHO^{2-}]\ \text{or}\ [(OC)_5Re^- + (OC)_4ReCHO^{-}\cdot]$$

Preparation and Reactions of Cr^-. The Cr–H Bond Strength

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Recent studies of the chemistry of gaseous atomic metal ions have provided a valuable new source of information about metal–ligand bond strengths[1,2] as well as an opportunity to observe the reactivity of metal ions in the absence of solvation, counterions, and ligand-field perturbations.[1-3] While atomic transition-metal cations can be generated for gas-phase studies via surface ionization,[4] laser desorption,[5] and electron-impact ionization of volatile inorganic complexes such as metal carbonyls,[6] the corresponding atomic metal anions are not normally observed under these conditions,[7] and hence, their chemical reactivity has remained largely unexplored. We now wish to report that atomic transition-metal anions can be produced in good yields in a Fourier transform mass spectrometer (FTMS) utilizing collision-induced dissociation (CID) of anionic metal carbonyl complexes. We present here the results of our initial studies of the gas-phase reactivity of Cr^-, including a determination of its proton affinity and the Cr–H bond dissociation energy.

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[1] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501–6502.

[2] Jones, R. W.; Staley, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 2296–2300 and references cited therein.

[3] Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944–5950. Allison, J.; Ridge, D. P. *Ibid.* **1979**, *101*, 4998–5009. Halle, L. F.; Armentrout, P.; B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963–968.

[4] Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819–2826.

[5] Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spec. Ion Phys.* **1980**, *33*, 37–43. Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360–4367.

[6] Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332–1333.

[7] Atomic metal anions are occasionally observed in low abundance from laser desorption–ionization of metal targets. Most previous studies of atomic negative ions have utilized sputter-type ion sources, cf.: Corderman, R. R.; Engelking, P. C.; Lineberger, W. C. *Appl. Phys. Lett.* **1980**, *36*, 533–535.