Table II. Examples of Stabilization Energies, Q, for Intragroup Two-Ligand Gas-Phase Transition-Metal Complexes Showing Ideal (Statistical) Behavior[a]

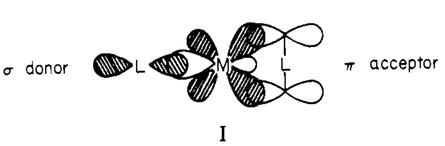
M	A[b]	B[b]	Q[c]	$D(M^+{-}2B) - D(M^+{-}2A)$
	(A) σ-Base/σ-Base Complexes, AMB^+			
Co	Me_2O	*n*-PrOH	0.01	1.66
Co	Me_2CO	MeCOEt	0.04	1.33
Co	*n*-PrCHO	*i*-PrOH	0.02	0.15
Ni	$EtCO_2Et$	Et_2CO	−0.10	2.30
Ni	MeCHO	EtOH	0.09	0.46
Ni	*t*-BuCHO	Me_2CO	−0.11	1.39
Cu	EtBr	*i*-PrCl	0.03	0.34
Cu	EtCl	CH_2O	0.04	0.53
Cu	EtCHO	*n*-BuOH	−0.05	0.49
Cu	Et_2CO	*n*-$PrCO_2Et$	0.02	0.67
Cu	MeNCO	EtBr	0.08	0.43
Cu	$MeNO_2$	MeOH	0.10	0.01
	(B) π-Base/π-Base Complexes, AMB^+			
Ni	C_6H_5Cl	C_6H_6	0.14	1.33
Ni	C_2H_2	$CH_2{=}C{=}CH_2$	0.14	0.19
	(C) N-Base/N-Base Complexes, AMB^+			
Ni	MeCN	$MeNH_2$	0.07	0.14
Ni	EtCN	Me_3N	0.12	1.20

[a] All data in kcal/mol. [b] B is always the stronger ligand and A the weaker ligand. [c] $Q = [D(AM^+{-}B) + D(BM^+{-}A) - D(AM^+{-}A) - D(BM^+{-}B)]/2$, see Scheme I. The mean and standard deviation of the distribution of Q for 85 intragroup equilibria is $\overline{Q} = 0.01 \pm 0.09$ kcal/mol.

Results for a number of ligand pairs show synergistic stabilization of the mixed species. Values of Q for these pairs are given in Table I along with the total enthalpy change for exchange of both ligands, $D(M^+{-}2B) - D(M^+{-}2A)$. The observed values of Q do not correlate with the relative ligand-binding energies, $D(M^+{-}2L)$, or the ligand-binding energy difference for the ligand pair, $D(M^+{-}2B) - D(M^+{-}2A)$. The molecules studied fall into four groups: (1) σ bases (alkyl halides, alcohols, ethers, aldehydes, ketones, esters, isocyanates, and nitro compounds), (2) S bases (alkyl mercaptans and sulfides), (3) N bases (alkyl amines and cyanides), and (4) π bases (olefins and aromatics). Complexes with both ligands from the same group show no special stability for the mixed AMB^+ species. A few examples of the results for the intragroup complexes are given in Table II. Altogether 85 intragroup ligand–pair complexes have been studied. The mean and standard deviation for the distribution of Q for these complexes is $\bar{Q} = 0.01 \pm 0.09$ kcal/mol.

The σ-base/π-base pairs show the largest stabilization, $Q \simeq$ 0.8, 1.2, and 0.9 kcal/mol for Co^+, Ni^+, and Cu^+ complexes respectively (Table I). Smaller stabilizations are seen for σ-base/S-base, σ-base/N-base, S-base/π-base, and N-base/π-base complexes (Table I).

The observation of synergistic stabilization of the mixed ligand complex for σ-base/π-base and other intergroup pairs constitutes a direct measurement of thermodynamic trans influence in the nearly ideal case of gas-phase two-ligand metal ion complexes. Empirical trans-influence orders predict[2-4] π bases > S bases $\simeq$ N bases > σ bases, consistent with the observed order in the present work. Theories of trans influence are based on the idea that with unlike trans ligands having differing degrees of π bonding a synergistic enhancement is obtained from asymmetric distortion of the metal orbitals involved in bonding. For example, with a pure σ-donor/π-acceptor ligand pair, the empty metal σ-orbital distorts toward the σ-donor ligand and an occupied metal d-orbital distorts toward the empty ligand π-acceptor orbital (structure I).[2-4] With like ligands on both sites, a symmetric structure results, giving no enhancement. Attempts at quantitative theoretical treatment of the effect have met with only very limited success.[2-4]



I

The quantitative thermochemical data provided by the present work for relatively simple systems should facilitate development of more exact theoretical models. Future ICR studies of bond-dissociation energies for two-ligand complexes of Co^+, Cu^+, Ni^+, and other metal cations can be expected to enlarge the data set available for examination of thermodynamic trans influence in the gas phase.

Acknowledgment is made to the National Science Foundation for support of this work by Grant CHE-76-17304.

Registry No. $(EtOH)Co(EtCH{=}CH_2)^+$, 80376-26-7; $(Me_2O)Co(EtCH{=}CH_2)^+$, 80376-27-8; (*n*-PrOH)$Co(Me_2C{=}CH_2)^+$, 80376-28-9; $(Me_2C{=}CH_2)Co(EtCHO)^+$, 80376-29-0; $(MeCH{=}CH_2)Ni(Me_2O)^+$, 80376-30-3; $(Me_2C{=}CH_2)Ni(PrOH)^+$, 80376-31-4; $(Me_2O)Ni(EtCH{=}CH_2)^+$, 80376-32-5; $(CH_2{=}C{=}CH_2)Ni(MeOH)^+$, 80375-75-3; $(Me_2C{=}CH_2)Cu$(*n*-PrCHO)$^+$, 80375-76-4; $(MeCH{=}CH_2)Cu(Me_2O)^+$, 80375-77-5; $(Me_2O)Co(MeSH)^+$, 80375-78-6; $(Me_2S)Co(Me_2CO)^+$, 80375-79-7; $(Et_2O)Co$(*n*-BuSH)$^+$, 80375-80-0; (EtSH)Co(*n*-PrCHO)$^+$, 80375-81-1; $(Me_2S)Ni(Et_2CO)^+$, 80375-82-2; $(EtCOMe)Ni(Me_2S)^+$, 80375-83-3; $(Me_2CO)Cu(EtSH)^+$, 80375-84-4; (*t*-BuCHO)Cu(MeSH)$^+$, 80375-85-5; $(Et_2CO)Cu(MeNCS)^+$, 80375-86-6; (HCN)Co(*n*-PrCHO)$^+$, 80375-87-7; (*n*-PrCHO)Ni(HCN)$^+$, 80375-88-8; $(NH_3)Ni(Et_2CO)^+$, 80375-89-9; (HCN)Cu(*n*-PrCHO)$^+$, 80375-90-2; $(C_6H_6Cl)Ni(EtSH)^+$, 80375-91-3; $(EtNH_2)Ni(C_6H_5CN)^+$, 80375-92-4; $(Me_2O)Co$(*n*-PrOH)$^+$, 80375-93-5; $(Me_2CO)Co(MeCOEt)^+$, 80375-94-6; (*n*-PrCHO)Co(*i*-PrOH)$^+$, 80387-08-2; $(EtCO_2Et)Ni(Et_2CO)^+$, 80375-95-7; (MeCHO)Ni(EtOH)$^+$, 80375-96-8; (*t*-BuCHO)Ni$(Me_2CO)^+$, 80375-97-9; (EtBr)Cu(*i*-PrCl)$^+$, 80375-98-0; $(EtCl)Cu(CH_2O)^+$, 80376-02-9; (EtCHO)Cu(*n*-BuOH)$^+$, 80376-00-7; $(Et_2CO)Cu$(*n*-$PrCO_2Et)^+$, 80376-01-8; (MeNCO)Cu(EtBr)$^+$, 80375-99-1; $(MeNO_2)Cu(MeOH)^+$, 80376-03-0; $(C_6H_5Cl)Ni(C_6H_6)^+$, 80376-04-1; $(C_2H_2)Ni(CH_2{=}C{=}CH_2)^+$, 80376-05-2; $(MeCN)Ni(MeNH_2)^+$, 80376-06-3; $(EtCN)Ni(Me_3N)^+$, 80376-07-4.

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(11) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

(12) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.

Reactivity of μ-Alkylidene Complexes: Bridge-to-Terminal Alkylidene Ligand Conversion in a Dimolybdenum Complex

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The synthesis and reactivity of transition-metal complexes which contain μ-alkylidene ligands have attracted considerable interest, in part because these ligands may be key surface intermediates in Fischer–Tropsch reactions for the reductive polymerization of carbon monoxide. These surface alkylidene moieties are postulated[1] to be in bridging positions because few isolable dinuclear complexes with terminal alkylidene or carbene ligands are known;[2] the vast majority contain μ-alkylidene ligands.

We reported recently the synthesis of reactive μ-alkylidene complexes by the thermal decomposition of μ-diazoalkane complexes, which are generated by the addition of diazoalkanes to a metal–metal triple bond.[3] Coordinatively saturated μ-alkylidene complexes can also be obtained from the addition of diazoalkanes to formal metal–metal double bonds.[4-6] Here, we report the first

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(1) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181–6182.

(2) Examples: Casey, C. P. *Chem. Commun.* **1970**, 1220–1221. Casey, C. P.; Cyr, C. R. *J. Organomet. Chem.* **1973**, *57*, C69–C71.

(3) (a) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789–7791. (b) This transformation can also be affected photochemically: Messerle, L.; Curtis, M. D., unpublished results.

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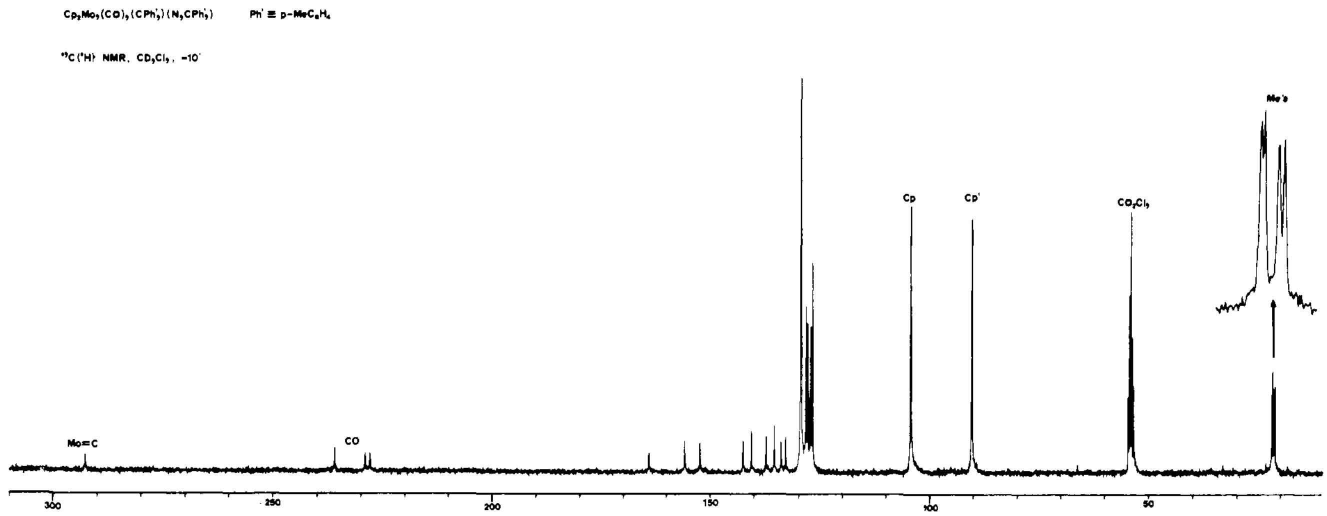

Figure 1. $^{13}C\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2 at -10 °C. Chemical shifts are referenced to CD_2Cl_2 ($\equiv\delta$ 53.8).

conversion of a μ-alkylidene ligand to a terminal alkylidene ligand, a reaction type which, by analogy to bridge ⇌ terminal carbonyl ligand exchange, may play an increasingly important role in the developing chemistry of μ-alkylidene complexes.[7]

Addition of 1 equiv of $(p\text{-}MeC_6H_4)_2CN_2$ to a benzene or ether solution of the red μ-di-*p*-tolylmethylene complex $Cp_2Mo_2(CO)_4[C(C_6H_4\text{-}p\text{-}Me)_2]$ (**1**; $Cp\equiv\eta\text{-}C_5H_5$)[3] yields carbon monoxide and amber red **2** in greater than 75% isolated yield (reaction 1).[8]

$$\underset{\mathbf{1}\ (R\,\equiv\,p\text{-}MeC_6H_4)}{Cp_2Mo_2(CO)_4(CR_2)} + R_2CN_2 \xrightarrow{-CO} \underset{\mathbf{2}}{Cp(OC)_3MoMo(CR_2)(N_2CR_2)Cp} \quad (1)$$

Formulation of **2** as a terminal di-*p*-tolylmethylene complex was supported by ^{13}C NMR spectroscopy (Figure 1), which showed the absence of the characteristic μ-alkylidene C_α signal in the region of δ 177[3] and, more importantly, the presence of a new signal at δ 292.6 in a spectral region diagnostic of terminal carbene and alkylidene ligands.[9] The signal at δ 163.8, approximately 10 ppm downfield of the usual range for phenyl ipso carbons, can be assigned tentatively to the unique diazoalkane carbon.[10] Both ^1H and ^{13}C NMR spectroscopy showed the presence of four magnetically nonequivalent aryl groups, and analytical data confirmed that the original diazoalkane nitrogens were retained. Insufficient information for determining the diazoalkane coordination mode necessitated a single-crystal X-ray diffraction study.

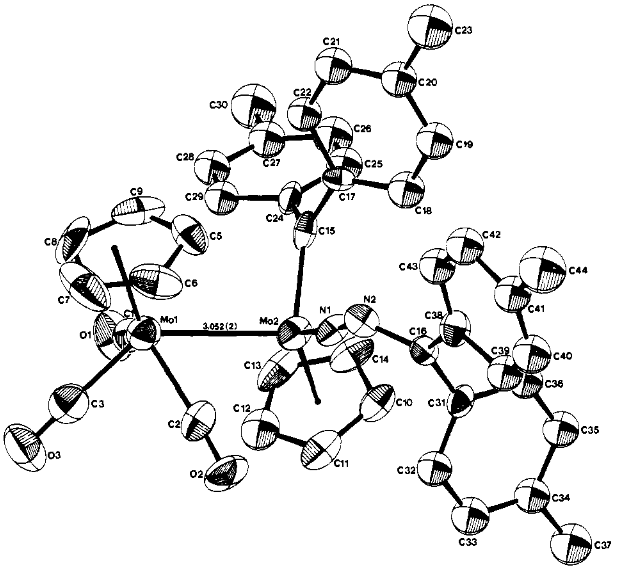

Figure 2. ORTEP view of **2** viewed approximately perpendicular to the Mo1-Mo2 bond. Bond distances are in Å.

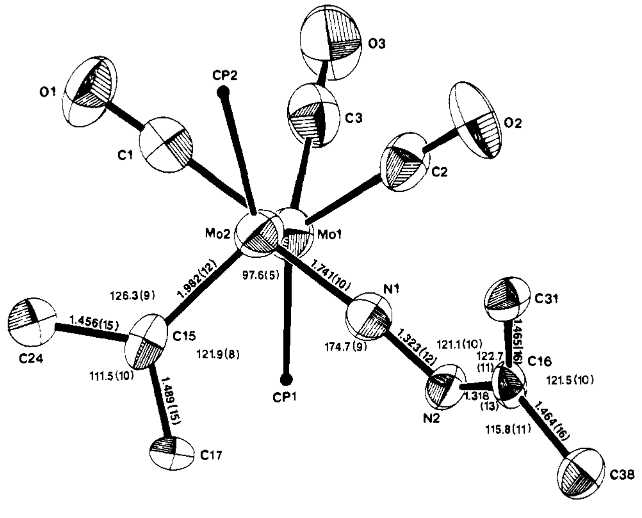

Figure 3. ORTEP view of the molecular core of **2**, as seen approximately down the Mo1-Mo2 bond. The Cp groups and all *p*-tolyl carbons except C_{ipso} are omitted for clarity. CP1 and CP2 are the centroids of the Cp rings. Bond distances are in Å and bond angles in degrees.

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(4) Clauss, A. D.; Dimas, P. A.; Shapley, J. R. *J. Organomet. Chem.* **1980**, *201*, C31-C34.

(5) Boag, N. M.; Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1171-1173.

(6) (a) Herrmann, W. A.; Bauer, C. *J. Organomet. Chem.* **1981**, *204*, C21-C24. (b) Herrmann, W. A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 193-196. (c) Bauer, C.; Herrmann, W. A. *J. Organomet. Chem.* **1981**, *209*, C13-C16.

(7) (a) Dyke et al. have recently reported ^1H NMR spectroscopic evidence for bridge ⇌ terminal alkylidene ligand exchange in a diruthenium μ-dimethylmethylene complex.[7b] (b) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. A. *J. Chem. Soc., Chem. Commun.* **1981**, 861-862.

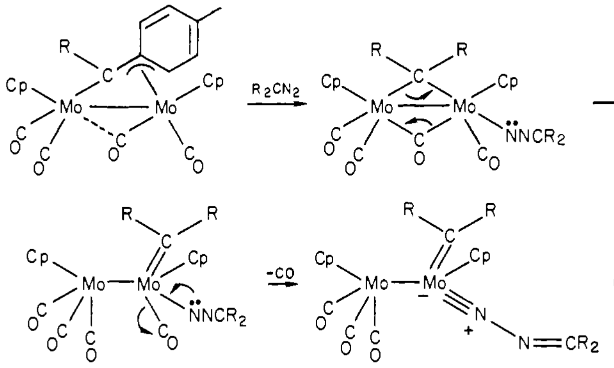
(8) Anal. Calcd for $Mo_2C_{43}H_{38}O_3N_2$: Mo, 23.32; C, 62.77; H, 4.67; N, 3.40. Found: Mo, 20.70; C, 62.94; H, 4.85; N, 3.30; ^1H NMR (δ, $CDCl_3$, 0 °C, 360 MHz) 2.324 and 2.384 (alkylidene tolyl methyls, 6), 2.361 and 2.367 (diazoalkane tolyl methyls, 6), 4.960 (Cp, 5), 5.507 (Cp′, 5), and 6.780-7.402 (tolyl aromatic protons, 16); ^{13}C NMR (δ, CD_2Cl_2, $\{^1H\}$ and gated $\{^1H\}$, -10°, 90.56 MHz) 21.0, 21.1, 21.5, 21.6 (tolyl methyls), 90.0 (Cp, $^1J_{CH}$ = 175 Hz), 104.0 (Cp′, $^1J_{CH}$ = 178 Hz), 126.6-129.3 (tolyl ortho and meta carbons), 132.7, 133.7, 135.2, 137.0, 140.4, 142.3, 152.1, and 155.6 (tolyl ipso and para carbons), 163.8 (N_2C), 227.9, 228.9, and 235.8 (CO), and 292.6 (alkylidene C_α); IR (cm^{-1}, CH_2Cl_2) 1951 s, 1860 shoulder, 1847 s (ν_{CO}).

(9) (a) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135-213. (b) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299-436. (c) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98-104. (d) Beatty et al.[9e] reported an alkylidene C_α shift of δ 384.2 in mononuclear $Mo(CO)_5(CPh_2)$. (e) Beatty, R. P.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 238-239.

(10) (a) The terminal diazoalkane complex $WBr_2(N_2CMePh)(PMe_2Ph)_3$[10b] has a diazoalkane C_α shift of δ 177.6 in CD_2Cl_2. (b) Bevan, P. C.; Chatt, J.; Hidai, M.; Leigh, G. J. *J. Organomet. Chem.* **1978**, *160*, 165-176.

Key results of the molecular structure determination[11] (Figure 2) are (1) a Mo1—Mo2 single bond distance[12] of 3.052 (2) Å, (2) the presence of terminal alkylidene and N-terminal diazoalkane ligands on the same molybdenum, (3) a Mo2═C15 double bond length[13] of 1.98 (1) Å for the terminal alkylidene, (4) a Mo2—N1 bond length of 1.74 (1) Å, a N1—N2 bond length of 1.32 (1) Å, a Mo2—N1—N2 bond angle of 174.7 (9)°, and a N2—C16 bond length of 1.32 (1) Å consistent with a Mo2≡N1—N2═C16 grouping,[14] and (5) a shift of one carbonyl from Mo2 to Mo1 to give a Mo(CO)_3 group. Both molybdenums acquire 18-electron configurations, Mo1 by its array of ligands and Mo2 by the donation of the lone pair on N1 in a dative fashion to give a $\text{Mo2}^{-}\overset{\leftarrow}{\equiv}\text{N1}^{+}$ polarized triple bond. Figure 3 shows a molecular core view approximately down the molybdenum–molybdenum bond; the angle between the alkylidene and diazoalkane ligands is 97.6 (5)°, and the three angles around the trigonal alkylidene carbon C15 total 360° within experimental error.

A plausible mechanism for this bridge → terminal alkylidene conversion is shown in reaction 2. N-Terminal coordination of the diazoalkane to one molybdenum leads to an intermediate in which the semi-bridging carbonyl has assumed a bridging position; rearrangement yields an intermediate with terminal alkylidene and carbonyl ligands. The available terminal nitrogen lone pair is then donated to give carbon monoxide and the observed product.



(2)

It has been shown that the inherent coordination unsaturation of the Mo≡Mo triple bond in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ affords a starting point for the synthesis of a variety of dinuclear complexes.[15,16] The residual unsaturation in μ-alkylidene complexes of the type $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{CR}_2)$[3] makes them especially attractive models[17] of surface-adsorbed alkylidenes since surface metal atoms are also coordinatively unsaturated.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (CHE-7907748), and the AMAX Foundation for support of this research.

Registry No. **1**, 80398-83-0; **2**, 76114-00-6.

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[11] Compound **2** crystallizes from a room temperature ether solution in the triclinic space group $P\bar{1}$ (No. 2) with lattice constants a = 12.247 (5) Å, b = 14.462 (7) Å, c = 11.486 (5) Å, α = 113.22 (3)°, β = 95.60 (3)°, γ = 90.32 (3)°, Z = 2, V = 1858 (1) cm^3, ρ_{calcd} = 1.47 g cm^{-3}, and ρ_{obsd} = 1.45 g cm^{-3} (flotation). The structure was refined to anisotropic convergence on 26 nonhydrogen atoms (isotropic on all others), after removal of calculated hydrogen atom structure factors from the data (2396 reflections with $I > 3\sigma(I)$). The final R value was 5.3 and the weighted R value was 5.4.

[12] (a) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086–1090. (b) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034–5039.

[13] (a) The Mo═C double bond distance in **2**, 1.98 (1) Å, is appreciably longer than the Mo≡C triple bond distance of 1.83 (2) Å found in $\text{(OC)}_5\text{ReMo(CPh)(CO)}_4$[13b] but it is somewhat shorter than the Mo═C double bond distance of 2.06 (1) Å in $\text{CpMo(CO)}_2\text{(GePh}_3\text{)[C(OEt)Ph]}$.[13c] (b) Huttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1977**, *15*, 133–142. (c) Chan, L. Y. Y.; Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1067–1071.

[14] (a) Formal molybdenum–nitrogen triple bond distances in organoimido complexes show little variation, being approximately 1.73 Å. See: Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175. (b) The diazoalkane intraligand distances in **2** compare favorably with values observed in several mononuclear tungsten–diazoalkane complexes,[14c,d] which exhibit N—N bond distances of 1.31–1.34 Å and N═C bond distances of 1.28–1.30 Å. (c) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740–5748. (d) Ben-Shoshan, R.; Chatt, J.; Leigh, G. J.; Hussain, W. *J. Chem. Soc., Dalton Trans.* **1980**, 771–775 and references therein.

[15] Curtis, M. D.; Messerle, L.; Fotinos, N. F.; Gerlach, R. F. *Adv. Chem. Ser.* **1981**, *No. 155*, 221–257.

[16] Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096–2101 and references therein.

[17] (a) A molybdenum-containing Fischer–Tropsch catalyst with good selectivity for C_2–C_4 aliphatic hydrocarbons and superior sulfur tolerance was recently reported.[17b,c] (b) Murchison, C. B.; Murdick, D. A. (to Dow Chemical Company) U.S. Patent 4 151 190, 1979; *Chem. Abstr.* **1979**, *91*, 41855e. (c) Murchison, C. B.; Murdick, D. A. *Hydrocarbon Process.* **1981**, *60*, 159–164.

A Formal [1,3]-Sigmatropic Rearrangement of an Anionic Oxy-Cope System. A Consecutive Mechanism[1]

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The thermal [1,3]-sigmatropic rearrangement of the oxy- and related Cope systems[2] such as anti A or syn A to C is regarded as one of the most useful two-carbon homologation reactions. The mechanism for this simple ring expansion reaction, however, is still ambiguous not only experimentally[3] but also theoretically.[4] One possible mechanism is the direct one[5] where the C_4 carbon of anti A or syn A directly migrates to the C_1 position to achieve a formal [1,3]-sigmatropic rearrangement of A to C. Alternatively, the indirect mechanism[6] involves successive [1,3]- and [3,3]-sigmatropic rearrangements where, in the case of anti A, the C_3 carbon initially migrates to the C_6 position either with inversion or with retention of configuration to regenerate isomeric Cope systems anti B and syn B, the former of which epimerizes to syn B through syn A by successive [1,3]-sigmatropic rearrangements, and then the ordinary Cope rearrangement of syn B gives C, achieving the indirect and consecutive mechanism (Figure 1). However, difficulties in isolation and detection of regenerated Cope systems such as anti B, syn A, and syn B which often equal anti A in thermal reactivity make the reaction pathway ambiguous and hence it is difficult to discriminate between the two mechanisms.

During our extended studies on the rearrangement[7] of anionic oxy-Cope systems, we succeeded in isolation of intermediates

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[1] Organic Thermal Reaction, 52. No. 51: K. Sato, Y. Yamashita, and T. Mukai, *Tetrahedron Lett.*, 5303 (1981).

[2] The oxy- and related Cope system includes the oxy- (R = H), the methoxy- (R = CH_3), the siloxy- (R = $\text{Si(CH}_3\text{)}_3$), and anionic oxy- (R = Na, K, and Li) Cope systems. The discussion is restricted only for the rearrangement of A to C, in which the new bonding occurs between the C_1 and C_4 positions.

[3] See, for the oxy-Cope system, (a) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5017, 5019 (1964); for the methoxy-Cope system, (b) J. A. Berson and E. J. Walsh, Jr., *ibid.*, **90**, 4732 (1968); (c) J. A. Berson, T. Miyashi, and G. Jones, II., *ibid.*, **96**, 3468 (1974); for the siloxy-Cope system, (d) R. W. Thies, *ibid.*, **94**, 7074 (1972); (e) R. W. Thies and J. E. Billigmeier, *ibid.*, **96**, 200 (1974); for the anionic oxy-Cope system, (f) R. W. Thies and E. P. Seitz, *J. Chem. Soc., Chem. Commun.*, 846 (1976); (g) R. W. Theis and E. P. Seitz, *J. Org. Chem.*, **43**, 1050 (1978); see also ref 7.

[4] S. Inagaki, T. Minato, H. Fujimoto, and K. Fukui, *Chem. Lett.*, 89 (1976).

[5] The direct mechanism includes (i) a concerted direct C_4 carbon migration to the C_1 position of A via processes such as [1,3]-sigmatropic, with retention of configuration,[3c] and multicyclic interaction[4] pathways and (ii) a nonconcerted migration via processes such as diradical[3a] and ionic[3f] pathways.

[6] The indirect mechanism was tentatively proposed for anionic oxy-Cope systems.[7] See also ref 3d, e, g.

[7] T. Miyashi, A. Hazato, and T. Mukai, *J. Am. Chem. Soc.*, **100**, 1008 (1978).

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