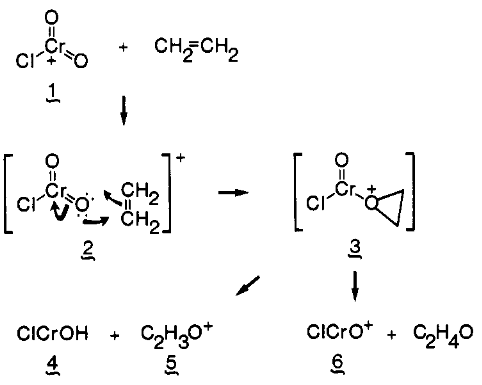
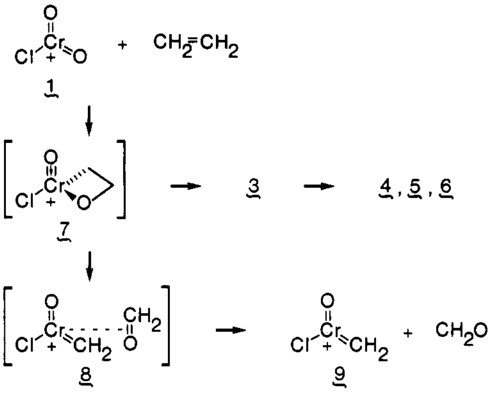
Scheme I



Scheme II



Thus, as shown in Scheme I, the $C_2H_3O^+$ (**5**) and $ClCrO^+$ (**6**) ions may derive from a "classical" direct oxygen transfer to the alkene, affording the complex **3** via an intermediate or transition state represented by structure **2**. Hydride transfer in **3** may then give the chromium hydride species **4** and the major observed ion **5**. Alternatively, dissociation of C_2H_4O from complex **3** would give the Cr(IV) oxo species **6**. Experimentally, the pathway leading from **6** and oxirane to the ion **5** is established, since oxirane reacts rapidly[7] with $ClCrO^+$ (**6**) in the flow tube to give $C_2H_3O^+$ (**5**) as the only observed ionic product. This scheme, however, does not readily explain the formation of the carbon-containing ionic product.

A topologically distinct mechanistic framework in which carbon-metal-bonded intermediates are involved is shown in Scheme II. Thus, on the basis of the elegant speculations of Sharpless and the pioneering theoretical work of Goddard and Rappê,[8] epoxide may derive from initial stereospecific insertion of the alkene into an oxo bond in a formal 2 + 2 process to give the oxametallacyclobutane **7**.[9] In structure **7**, the "spectator oxo" bond is drawn as a triple bond analogous to the CO bond in carbon monoxide, according to the Goddard-Rappê theory. A reductive elimination with retention of configuration then results in the Cr(IV) complex **3**. However, the ion **7** may fragment in an alternative manner by retro "2 + 2" to afford the complex **8**. Loss of formaldehyde would then give the chromium oxo carbene species **9**. The latter mechanism links the Cr oxo oxidation of alkenes with the mechanistically and commercially important olefin metathesis process,[10] which is known to involve d^0 oxo carbene complexes of tungsten and molybdenum exactly analogous to complex **9**, at least in some cases.[11]

While other interpretations of these data are certainly possible, we believe that the observed agreement with the theoretical predictions of Goddard and Rappê argues in favor of the mechanism shown in Scheme II. It must be pointed out that if the Goddard-Rappê calculations are basically correct, then the gas-phase chemistry of $ClCrO_2^+$ in the SIFT is an excellent model, since the CrX bonds of X_2CrO_2 species are expected to be highly ionic and the theory applies to reactions of gas-phase species at room temperature.

Thus, in the reaction of $ClCrO_2^+$ with ethylene, both oxygen transfer and cleavage are indeed observed, with the primary channel for reaction being oxygen transfer and a minor channel being cleavage, as predicted by Goddard and Rappê. Further studies aimed at experimental verification of the structure of the ion **9** and at exploration of the reactivity of other d^0 transition-metal oxo species in the gas phase are under way.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grants CHE 82-03110 (C.H.D. and V.M.B.) and CHE 80-11391 (D.M.W.)) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 88610-58-6; 6, 88610-59-7; ethylene, 74-85-1; oxirane, 75-21-8.

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[7] $k = 1 \times 10^{-9}$ cm^3 $particle^{-1}$ s^{-1} (one determination).

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[9] We have proposed similar oxametallacyclobutane intermediates for the novel stereospecific oxidative cyclizations promoted by MnO_4^- and $CrO_3 \cdot 2py$. (a) Walba, D. M.; Wand, M. D.; Wilkes, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4396-4397. (b) Walba, D. M.; Stoudt, G. S. *Tetrahedron Lett.* **1982**, *23*, 727-730.

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Stereochemically Nonrigid Molybdenum Alkyne Complexes Studied by 2-D NMR Spectroscopy

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Summary: Intramolecular exchange processes in the molybdenum complexes $[Mo(CO)(HC{\equiv}CR)_2(Cp)]^+$ (R = *t*-Bu, Ph, CO_2Me, Me) were studied by using 2-D NMR exchange techniques in which kinetic parameters for the two independent alkyne rotations are derived from the intensities of the off-diagonal cross peaks. The exchange rates were largely governed by the steric bulk of the alkyne ligands. The 2-D NMR technique was very effective for thermally sensitive compounds in slow exchange.

Two-dimensional NMR spectroscopy[1] provides an elegant new technique for the study of chemical exchange which has not been previously applied to organo-

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[1] (a) Bax, A. "Two-Dimensional Nuclear Magnetic Resonance in Liquids"; D. Reidel: Boston, 1982. (b) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546-4553.

Table I. Derived Exchange Rate Constants for Ib-Id

			rate constants,[a,b] s^{-1}							
compd	T, K	concn, M	k_{t-c}	$k_{t-c'}$	$k_{t'-c}$	$k_{t'-c'}$	k_{c-t}	$k_{c-t'}$	$k_{c'-t}$	$k_{c'-t'}$
Ib	323	1.01	14.1		13.0		18.5	15.1		
	323	0.15	16.8		13.2		26.9	23.1		
Ic	300	0.47	*c*		1.09		*c*	1.62		
	313	0.23	*c*		3.38		*c*	4.24		
Id	333	1.00	5.7	3.1	4.4	1.4	7.1	6.7	5.2	1.9
	333	0.80	8.5	4.0	5.1	1.8	9.7	9.4	4.6	2.8

[a] Maximum estimated errors are ±29%. Average errors are ca. ±10%. [b] E.g., k_{t-c} is the trans to cis exchange rate. See ref 3 for assignments. [c] Not distinguishable due to overlapping peaks in the contour plot.

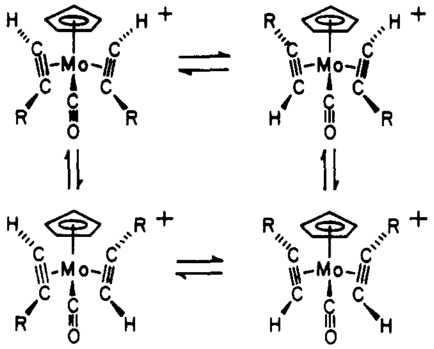

Figure 1.

transition-metal complexes. Data are presented here as contour plots of precessional frequency (f_1) vs. precessional frequency in the second dimension (f_2). In the absence of chemical exchange, peaks appear only along the diagonal of the 2-D plot. Off-diagonal peak intensity is determined by the exchange rate (k) between corresponding diagonal sites.

Proton NMR spectra of cationic molybdenum alkyne complexes $[Mo(CO)(HC{\equiv}CR)_2(Cp)]^+X^-$ (Ia: R = *t*-Bu, $X^- = BF_4^-$; Ib: R = Ph, $X^- = BF_4^-$; Ic: R = CO_2Me, $X^- = PF_6^-$; Id: R = Me, $X^- = BF_4^-$)[2] show terminal alkyne resonances in the range 9–12 ppm.[3] Each can each exist in solution as up to two cis isomers and an enantiomeric pair of trans isomers (Figure 1).[4] Although Green originally reported that the NMR spectra of Ia and Id are temperature independent,[2a] we find that a range of chemical exchange behavior is demonstrated by Ia–d above room temperature.

Ia shows only the enantiomeric trans pair in CD_3NO_2 up to 353 K, at which temperature slow conversion to a new compound begins. The 2-D NMR spectrum (Figure 2a) thus shows no off-diagonal peaks. Ib shows one cis isomer and the trans pair. Chemical exchange between the cis and trans isomers occurs at 322 K, but *no* cross peaks appear for interchange of the two protons of the trans isomer, which would require a "double flip" of the alkynes. Despite concurrent decomposition at 313 K in CD_3NO_2, Ic displays an exchange network similar to Ib (Figure 2c). The 7-Hz separation between the protons of the cis isomer and the upfield resonance of the trans isomer represents a lower limit for obtaining kinetic parameters by 2-D NMR (at 200 MHz). Id shows all possible isomers in CD_3NO_2. Both cis isomers exchange with the trans form, but no "double-flip" (cis–cis′ or trans–trans′) cross peaks are observed (Figure 2d).

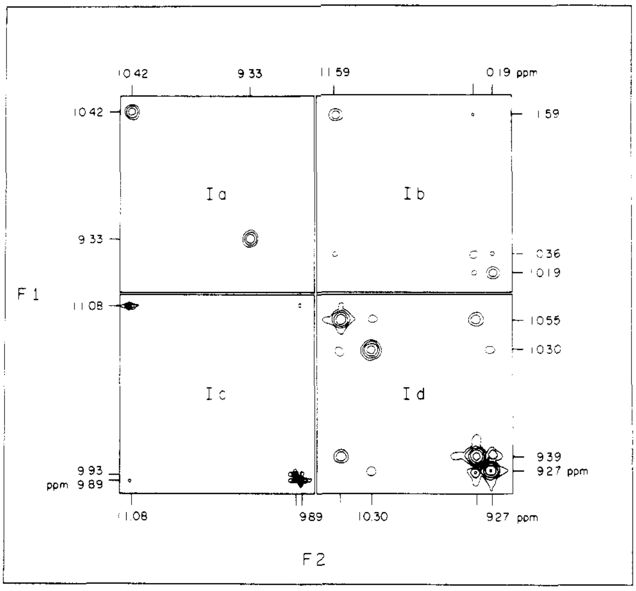

Figure 2. 200-MHz 2-D exchange spectra (contour plots) run on a Varian XL-200. A $(90°_x–t_1–90°_x–t_{mix}–90°_x–t_2)_n$ pulse sequence was used with a delay of 11 s before each acquisition and 0.05 s mix time (t_{mix}); 256 FIDs of 512 data points were accumulated at 512 t_1 values, using quadrature phase detection. The spectral width in both dimensions was 500 Hz and the acquisition time was 0.512 s. The pulse and the receiver phases were cycled in a four-step program. Gaussian weighting and zero filling precede Fourier transformation in both dimensions and symmetrized absolute-value spectra are shown. All spectra were obtained in CD_3NO_2: (a) Ia at 333 K; (b) Ib at 322 K; (c) Ic at 313 K; (d) Id at 333 K.

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(3) ^1H NMR spectra (200 MHz, CD_3NO_2 in ppm): Ia, 1.36 (s, 9 H, trans CMe_3), 1.41 (s, 9 H, trans′ CMe_3), 6.06 (s, 5 H, Cp), 9.33 (s, 1 H, trans CH), 10.42 (s, 1 H, trans′ CH); Ib, 6.37 (s, 5 H, Cp), 7.57–7.97 (m, 4 H, meta and para C_6H_5), 8.07–8.37 (d of d, 2 H, ortho C_6H_5), 10.19 (s, 1 H, trans CH), 10.36 (s, 1 H, cis CH), 11.59 (s, 1 H, trans′ CH), trans/cis = 75/25; Ic, 3.98 (s, 3 H, trans CH_3), 4.00 (s, 3 H, cis CH_3), 4.01 (s, 3 H, trans′ CH_3), 6.27 (s, 5 H, cis Cp), 6.28 (2, 5 H, trans Cp), 9.89 (s, 1 H, cis CH), 9.93 (s, 1 H, trans CH), 11.08 (s, 1 H, trans′ CH), trans/cis = 65/35; Id, 2.96 (d, 3 H, J = 1.57 Hz, trans CH_3), 3.00 (d, 3 H, J = 1.59 Hz, cis CH_3), 3.20 (d, 3 H, J = 1.61 Hz, trans′ CH_3), 3.30 (d, 3 H, J = 1.60 Hz, cis′ CH_3), 6.13 (s, 5 H, trans Cp), 6.16 (s, 5 H, cis Cp), 9.27 (q, 1 H, J = 1.62 Hz, trans CH), 9.39 (q, 1 H, J = 1.59 Hz, cis CH), 10.30 (q, 1 H, J = 1.59 Hz, cis′ CH), 10.55 (q, 1 H, trans′ CH), trans/cis/cis′ = 48/35/17.

(4) On the basis of the observed isomer ratios and on intramolecular nonbonding distances estimated from the published coordinates for $[Mo(CO)(MeC{\equiv}CMe)_2(Cp)][BF_4]$,[5] the pair of trans isomers is the least crowded, followed by the cis isomer with the hydrogen atoms directed away from the carbonyl ligand. Steric interactions between the two nonhydrogen substituents make the cis′ isomer with the two hydrogen atoms directed toward the CO ligand the least stable.

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(6) Equilibrium constants (K) can be derived from both integrated isomer ratios and rate constants ($K = k_f/k_r$). Agreement between independent K values is acceptable for dilute samples in which decomposition is slow, e.g., 0.15 M Ib at 323 K where $K_{cis-trans}$ = 3.0 from isomer ratios and 1.7 ± 0.3 from values in Table I. We attribute discrepencies to differences in T_2 for the exchanging sites and to concomitant decomposition occurring at different rates in exchanging isomers.

Table II. ^1H Coalescence Parameters of Ib-Id at 200 MHz[a]

compd	T_c, K	k_c, s^{-1}	ΔG_c, kJ/mol	ΔH_c, kJ/mol	ΔS_c, J/(K mol)	E_a, kJ/mol
Ib[b]	338	55	67.4	59.3	−23.7	62.3
Ic[c]	332	50	74.0	65.3	−26.2	68.2
Id[b]	363	44	75.6	70.1	−14.6	73.1

[a] Estimated errors are ±4 kJ/mol. [b] Calculated from line widths at cis-trans coalescence. [c] Calculated from cross peak intensities at cis-trans coalescence.

Kinetic parameters derived from the intensities of the 2-D cross peaks are presented in Table I.[6] Steric factors play a major role in determining both the isomer ratios and the rates of site exchange. Thermodynamic parameters (Table II) fall within the range ($\Delta G^{\ddagger}$ = 60–90 kJ mol^{-1}) determined for related alkyne complexes by line-shape analysis.[7-9]

The 2-D NMR experiment has several advantages over line-shape analysis,[10] spin-saturation labeling,[11] and related relaxation time measurements.[12] The technique works best when the system is in slow exchange.[2] Thermally sensitive compounds can be examined without obtaining spectra at the fast-exchange limit. The slow-exchange limit need not be reached. Small chemical shift differences between sites can be tolerated. Multisite exchanges are readily treated, and exchange networks are intuitively evident from the contour plots.

The disadvantages of the 2-D NMR method are relatively few and easily remedied. Although dipolar relaxation can contribute intensity to the cross peaks, this effect is readily detected by examination of phased spectra (cross peaks due to relaxation are out of phase with diagonal peaks) and is suppressed by proper selection of mixing time and temperature.[13,14] Relaxation times (T_1) of the exchanging sites must be long enough that $k \geq 1/T_1$. For Ia–d acetylenic protons, the T_1 values are ca. 20, 10.2, 0.50, and 5.2 s, respectively.

In summary, we have demonstrated that 2-D NMR spectroscopy is an effective new method for examining chemical exchange in organometallic compounds and is of particular value under slow exchange conditions and for thermally sensitive compounds.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation, Occidental Research Corporation, and the University of Kentucky Graduate School for financial support.

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Photolysis of Transition-Metal-Substituted Arsanes and Stibanes $Cp(CO)_3M{-}ER_2$ (M = Mo, W; E = As, Sb; R = Me, *i*-Pr, *t*-Bu) at 12 K: Evidence for the 16-Electron Species $Cp(CO)_2M{-}ER_2$ and the Double-Bonded Complexes $Cp(CO)_2M{=}ER_2$[1,2]

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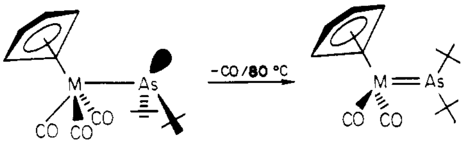
Summary: Infrared spectroscopic evidence is presented to show that photolysis of $Cp(CO)_3M{-}ER_2$ complexes (M = Mo, W; E = As, Sb; R = Me, *i*-Pr, *t*-Bu) isolated at high dilution in CH_4 matrices at 12 K leads to the formation of the double-bonded complexes $Cp(CO)_2M{=}ER_2$ via the 16-electron species $Cp(CO)_2M{-}ER_2$, which react with N_2 to give $Cp(CO)_2(N_2)M{-}ER_2$ complexes (M = Mo, E = As, Sb; R = Me) in N_2 matrices.

Thermal and photochemical reactions of transition-metal-substituted arsanes $Cp(CO)_3M{-}AsR_2$ (M = Mo, W; R = Me, *i*-Pr, *t*-Bu; Cp = η^5-C_5H_5)[3a-c] result in the preferential ejection of a carbon monoxide ligand. Among the products obtained, the most interesting ones are the complexes **2a, b** with a metal–arsenic double bond.[4] However M=As-bonded complexes could only be isolated starting from the metal arsanes **1a,b** having bulky *tert*-butyl groups (eq 1).



(1)

1a,b **2a,b**

a, M = Mo; b, M = W

In order to establish whether M=As complexes could also exist with less bulky alkyl substituents and whether their formation involves 16-electron intermediates, matrix isolation studies[5] have been carried out with the complexes $Cp(CO)_3M{-}ER_2$ (**3a–e**) (see Table I).[6]

Infrared spectra from a matrix isolation experiment[7] with $Cp(CO)_3W{-}AsMe_2$ (**3b**) isolated at high dilution in a CH_4 matrix (ca. 1:2000–1:5000) are shown in Figure 1. Before photolysis there are three strong absorption bands in the terminal CO stretching region at 1997.5 (A′(1)),

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(1) Part 40 of the series "Transition Metal Substituted Phosphanes, Arsanes, and Stibanes" and part 3 of the series "Main Group Element Transition-Metal Multiple Bonds". Parts 39 and 2: Angerer, W.; Luksza, M.; Malisch, W. *J. Organomet. Chem.* **1983**, *253*, C36.

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