Table II. ^{1}H 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)$_3$M–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)$_2$M–ER$_2$ and the Double-Bonded Complexes Cp(CO)$_2$M=ER$_2$[1,2]

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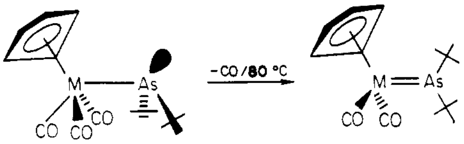
Summary: Infrared spectroscopic evidence is presented to show that photolysis of Cp(CO)$_3$M—ER$_2$ complexes (M = Mo, W; E = As, Sb; R = Me, *i*-Pr, *t*-Bu) isolated at high dilution in CH$_4$ matrices at 12 K leads to the formation of the double-bonded complexes Cp(CO)$_2$M=ER$_2$ via the 16-electron species Cp(CO)$_2$M—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)$_3$M–AsR$_2$ (M = Mo, W; R = Me, *i*-Pr, *t*-Bu; Cp = η^5-C$_5$H$_5$)[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)$_3$M-ER$_2$ (**3a–e**) (see Table I).[6]

Infrared spectra from a matrix isolation experiment[7] with Cp(CO)$_3$W–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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Table I. Infrared Band Positions (cm^{-1}) Observed in the Terminal CO Stretching Region for the Complexes **3a–e** and Their Photoproducts in CH_4 and N_2 Matrices at 12 K

complex	CH_4 matrix	N_2 matrix
$Cp(CO)_3Mo{-}AsMe_2$ (**3a**)	2001.5, 1933.2, 1913.0	2004.6, 1935.8, 1916.5
$Cp(CO)_2Mo{-}AsMe_2$ (**4a**)	1948.4, 1870.0	1950.5, 1875.4
$Cp(CO)_2Mo{=}AsMe_2$ (**5a**)	1974.7, 1888.2	1976.3, 1892.7
$Cp(CO)_2(N_2)Mo{-}AsMe_2$ (**6a**)[a]		1950.5, 1890.7
$Cp(CO)_3W{-}AsMe_2$ (**3b**)	1997.5, 1924.8, 1907.6	
$Cp(CO)_2W{-}AsMe_2$ (**4b**)	1941.8, 1860.3	
$Cp(CO)_2W{=}AsMe_2$ (**5b**)[b]	1971.8, 1887.6	
(**5b′**)[b]	1963.5, 1882.5	
$Cp(CO)_3W{-}As(i\text{-}Pr)_2$ (**3c**)	1995.9, 1918.6, 1902.8	1997.0, 1921.7, 1904.8
$Cp(CO)_2W{-}As(i\text{-}Pr)_2$ (**4c**)	1933.4, 1855.2	1934.7, 1857.4
$Cp(CO)_2W{=}As(i\text{-}Pr)_2$ (**5c**)	1963.0, 1884.0[c]	1968.6, 1887.1
$Cp(CO)_3W{-}As(t\text{-}Bu)_2$ (**3d**)	1994.5, 1919.6, 1895.0	1997.0, 1920.7, 1898.0
$Cp(CO)_2W{-}As(t\text{-}Bu)_2$ (**4d**)	1933.2, 1853.8	1935.2, 1855.8
$Cp(CO)_2W{=}As(t\text{-}Bu)_2$ (**5d**)	1962.0, 1881.6[c]	1968.4, 1884.6
$Cp(CO)_3Mo{-}SbMe_2$ (**3e**)	1997.0, 1926.0, 1904.5	2001.0, 1931.4, 1908.0
$Cp(CO)_2Mo{-}SbMe_2$ (**4e**)	1940.3, 1866.6	1942.6, 1871.0
$Cp(CO)_2Mo{=}SbMe_2$ (**5e**)	1971.6, 1886.2	1970.8, 1885.5
$Cp(CO)_2(N_2)Mo{-}SbMe_2$ (**6e**)[a]		1942.6, 1883.0

[a] ν_{NN} at 2183.6 cm^{-1}. [b] Two rotomers; see text. [c] Broad bands; only one rotamer observed.

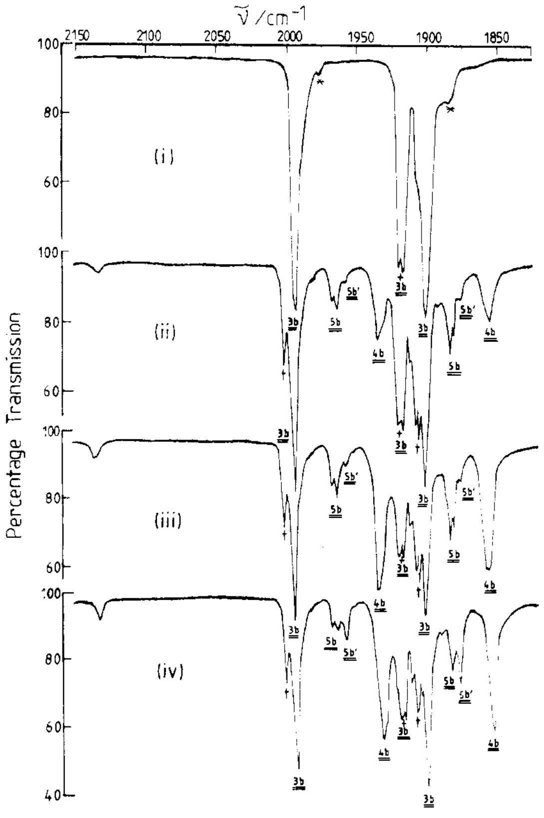
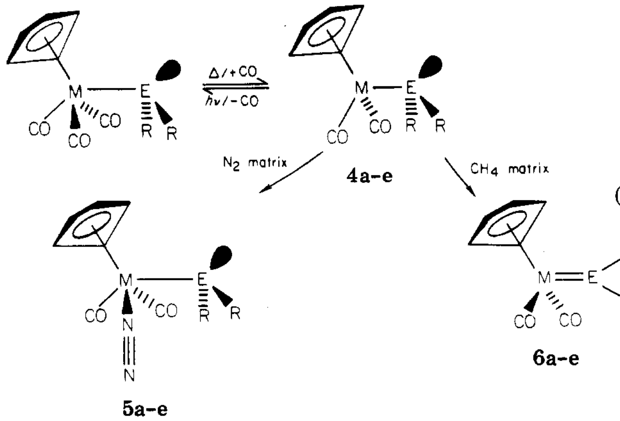


Figure 1. Infrared spectra from an experiment with **3b** isolated at high dilution in a CH_4 matrix at 12 K: (i) after deposition, (ii) after 10-min photolysis using λ > 400 nm, (iii) after a further 40-min photolysis using the same source, and (iv) after annealing to ca. 30 K for 2 min. Bands marked (+) are due to matrix splitting effects, those marked (*) are due to $Cp(^{12}CO)_2(^{13}CO)W{-}AsMe_2$ present in natural abundance, and those marked **4b–5b** are due to new photoproducts (see text). IR spectra were recorded on a Nicolet 7199 Fourier transform infrared (FTIR) spectrometer (resolution 0.5 cm^{-1}).

1924.8 (A′(2)), and 1907.6 (A″) cm^{-1} for the C_s symmetry molecule $Cp(CO)_3W{-}AsMe_2$ (**3b**) (Figure 1i). Irradiation of the matrix with visible light (λ > 410 nm) produced free CO (2138.0 cm^{-1}) and four distinct new bands at 1971.8, 1941.8, 1887.6, and 1860.3 cm^{-1} (Figure 1ii). A further period of photolysis with the same source showed all the new bands increasing at the expense of the parent bands (bands marked **3b**). Annealing the matrix to 35 K showed that the bands at 1941.8 and 1860.3 cm^{-1} (bands marked **4b**) are not related to those at 1971.8 and 1887.6 cm^{-1} (bands marked **5b**), because the pairs of bands changed their relative intensities (Figure 1iv). Not only did the pair **5b** bands decrease but new bands (bands marked **5b′**) appeared. The high dilution used, as indicated by the absence of any dimer product bands, e.g., $Cp_2W_2(CO)_6$, and the reversibility enabled the bands at 1941.8 and 1860.3 cm^{-1} to be assigned to the 16-electron species $Cp(CO)_2W{-}AsMe_2$ (**4b**). This behavior is analogous to the formation of $CpM(CO)_2R$ species on photolysis of $CpM(CO)_3R$ complexes (M = Mo, W; R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu) in matrices at 12 K.[7,8] The other pairs of bands marked **5b**, **5b′** are assigned to two different rotamers of the W–As double-bonded species $Cp(CO)_2W{=}AsMe_2$, where the $AsMe_2$ group lies in or out of the plane bisecting the CO ligands. A precedent for such rotamers is found in the asymmetric olefin hydrido complexes $CpW(CO)_2(Olefin)H$ together with facile cis/trans isomerization of such complexes on annealing the matrices to 35 K.

Analogous results (Table I) were obtained by starting from other $Cp(CO)_3M{-}ER_2$ complexes in CH_4 matrices. Yields for the Mo compounds were much lower than for the W analogues. Photolysis of **3a–e** in N_2 matrices produced different results for Mo compared to W. For example, initial medium-energy UV irradiation (λ > 370 nm) of $Cp(CO)_3Mo{-}SbMe_2$ (**3e**) produced mainly $Cp(CO)_2Mo{-}SbMe_2$ (**4e**), identified by analogy with the



(2)

M = Mo, W; E = As, Sb; R = Me, *i*-Pr, *t*-Bu

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species produced in a CH_4 matrix (Table I), with a small amount of $Cp(CO)_2Mo{=}SbMe_2$ (**5e**). Reversal with long-wavelength radiation ($\lambda > 490$ nm) resulted in the appearance of three new bands at 2183.6, 1942.6, and 1883.0 cm^{-1}, while bands due to **4e** and **5e** decreased in intensity. The band at 2183.6 cm^{-1} is in the region typical for NN terminal stretching modes, e.g., $CpCo(CO)(N_2)$ (ν_{NN} at 2164.6 cm^{-1} in N_2 matrix),[9] $CpMn(CO)_2(N_2)$ (ν_{NN} at 2175 cm^{-1} in N_2 matrix[10] and at 2169 cm^{-1} in *n*-hexane solution[11]), and $Cp(CO)_2(N_2)Mo{-}CH_3$ (ν_{NN} at 2191 cm^{-1} in N_2 matrix[7]). The bands at 1942.6 and 1883.0 cm^{-1} are terminal CO stretching modes, and, therefore, the product can be identified as $Cp(CO)_2(N_2)Mo{-}SbMe_2$ (**6e**). Calculation[12] of the OC–Mo–CO bond angle ($\theta = 83°$) from relative band intensities and the energy-factored CO interaction force constant ($k_i = 46.0$ N m^{-1}) and comparison with data for *cis*-$Cp(CO)_2(N_2)Mo{-}CH_3$ ($\theta = 82°$ and $k_i = 43.3$ N m^{-1})[7] and $Cp(CO)_3Mo{-}SbMe_2$ (**3e**) ($k_{cis} = 37.3$ and $k_{trans} = 55.0$ N m^{-1}) suggest cis stereochemistry for the CO ligands in **6e**. The arsenic analogue, **3a**, also gave a dinitrogen complex (**6a**), but under these conditions the W compounds **3b–d** produced only the 16-electron and the double-bonded species.

The observation of high yields of the 16-electron species **4a–c** in matrices, even N_2 matrices, suggests strongly that the M=As complexes in eq 1 are generated via the coordinatively unsaturated species $Cp(CO)_2M{-}As(t\text{-}Bu)_2$ (M = Mo, W). Future work will seek to establish (a) whether a CO ligand cis or trans to E is ejected in complexes of the type **3a–e** and (b) whether the arsanes and stibanes $Cp(CO)_2(L)M{-}ER_2$ (L = MeNC, Me_3P, $(MeO)_3P$)[13a–c] can be converted into the double-bonded complexes $Cp(CO)(L)M{=}ER_2$.

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Registry No. **3a**, 52456-34-5; **3b**, 52456-36-7; **3c**, 88669-43-6; **3d**, 80977-53-3; **3e**, 88685-54-5; **4a**, 88669-44-7; **4b**, 88669-45-8; **4c**, 88669-46-9; **4d**, 85442-86-0; **4e**, 88685-55-6; **6a**, 88669-47-0; **6e**, 88685-56-7.

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Synthesis and Crystal and Molecular Structure of Trimethylammonium *anti*-7,7′:8,8′-Bis(dithio)bis(7,8-dicarbaundecaborate(10))

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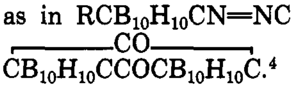
Summary: In refluxing ethanol, ammonium 7,8-dimercapto-7,8-dicarbaundecaborate(10) is formed from ammonium 1,2-disulfido-1,2-dicarbadodecaborane. Oxidation of 7,8-dimercapto-7,8-dicarbaundecaborate(10) with I_3^- in water yields 7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)). The structure of this salt, as determined by single-crystal X-ray diffraction methods ($P2_1/a$; $a = 13.318$ (4) Å, $b = 15.432$ (5) Å, $c = 7.084$ (2) Å, $\beta = 100.45$ (2)°, $D_{calcd} = 1.186$ g cm^{-3}, $Z = 2$), consists of two 7,8-dicarbaundecaborate(10) units bonded by two –S–S– bridges in such a way that the two cages are placed in an anti fashion. The ^{11}B NMR spectrum of the salt in $Me_2CO\text{-}d_6$ is in accord with the structure established by X-ray diffraction and indicates the isomeric purity of the salt.

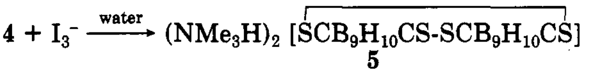
It is well-known that removal of the most positive boron atoms, B(3) or B(6), in the *o*-/*m*-dicarbadodecaborane cage (*o*-/*m*-$HCB_{10}H_{10}CH$) may be achieved with strong bases such as methoxide ion yielding $[HCB_{H10}CH]^-$.[1,2] Many *o*/*m*-dicarbadodecaborane derivatives are known to contain more than one cluster unit arranged either linearly as in $RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR$[3] or cyclically as in  $\overbrace{CB_{10}H_{10}CCOCB_{10}H_{10}C}^{CO}$.[4] Although many such compounds are known, the geometry (syn or anti) of partially degraded bis(*o*-/*m*-dicarbadodecarborane) clusters, where there is restricted rotation of the cages, has not been established. We recently found that salts of 1,2-dimercapto-*o*-dicarbadodecaborane unexpectedly undergo partial degradation without the involvement of a base when they are reacted with CH_2Cl_2 or $BrCH_2CH_2Br$ to produce dimers with 7,8-dicarbaundecaborate(10) cages symmetrically placed.[5] No indication of the geometry was then obtained. In this report we present the unexpected syntheses of 7,8-dimercapto-7,8-dicarbaundecaborate(10) and 7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)) anions and the molecular structure of the latter which shows an anti geometry.

The syntheses of the title compounds was via the route[6,7] shown in eq 1–4. Compounds **3** and **5** are stable in air.

$$\underset{\mathbf{1}}{o\text{-}HSCB_{10}H_{10}CSH} \xrightarrow{NH_3\ \text{liquid}} \underset{\mathbf{2}}{(NH_4)_2[o\text{-}SCB_{10}H_{10}CS]} \qquad (1)$$

$$\mathbf{2} \xrightarrow[\text{48-h reflux}]{EtOH} \underset{\mathbf{3}}{(NH_4)[7,8\text{-}HSCB_9H_{10}CSH]} \qquad (2)$$

$$\mathbf{3} + NMe_3HCl \xrightarrow{\text{water}} \underset{\mathbf{4}}{(NMe_3H)[7,8\text{-}HSCB_9H_{10}SH]} \qquad (3)$$



$$\mathbf{4} + I_3^- \xrightarrow{\text{water}} \underset{\mathbf{5}}{(NMe_3H)_2\ [SCB_9H_{10}CS\text{-}SCB_9H_{10}CS]} \qquad (4)$$

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[‡] Deceased May 11, 1981.

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(2) This boron removal, also known as partial degradation, is also effective for most *o*-/*m*-dicarbadodecaborane derivatives. See, for example: Totani, T.; Aono, K.; Yamamoto, K.; Tawara, K. *J. Med. Chem.* **1981**, *24*, 1492–1499 or ref 3.

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(6) Compound 1 was synthesized according to: Smith, H. D.; Oberland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013.

(7) Details will be the subject of a full paper.