**Table I.** Internal Rotation Fine Structure[a] Observed for Several Transitions of Dimethylsilaethylene (DMSE)

| trans | obsd, MHz | trans | obsd, MHz | trans | obsd, MHz |
|---|---|---|---|---|---|
| $4_{22} \rightarrow 4_{31}$ | 8002.586 | $3_{12} \rightarrow 3_{21}$ | 8226.010 | $2_{02} \rightarrow 2_{11}$ | 8413.286 |
|  | 8002.755 |  | 8227.761 |  | 8414.519 |
|  | 8003.202 |  | 8228.486 |  | 8415.662 |
|  | 8003.592 |  | 8230.388 |  | 8417.467 |
|  | 8005.688 |  |  |  |  |
| $2_{12} \rightarrow 2_{21}$ | 8827.380 | $3_{22} \rightarrow 3_{31}$ | 9043.514 | $0_{00} \rightarrow 1_{11}$ | 9129.760 |
|  | 8829.922 |  | 9047.287 |  | 9130.658 |
|  | 8833.588 |  | 9047.671 |  | 9131.892 |

[a] Many of the components exhibit additional partially resolved structure attributed to proton–proton hyperfine interactions.

high-temperature flow systems.[5] We judged DMSE to be too reactive[3] for these methods. Instead we based our experiment on the Mark II Flygare–Balle Fourier transform (FT) spectrometer,[6] modified to improve sensitivity, reliability, and ease of operation.[7] This type of spectrometer has been used to generate weakly bonded dimers and small clusters and observe their rotational spectra. In a typical operation, a carrier gas (Ar or "first run" neon, a Ne/He 70/30 mixture) at ~1 or 1.5 atm is seeded with a percent or so of cluster-forming species. The mixture is pulsed into an evacuated Fabry–Perot cavity through a supersonic nozzle (1 mm diameter). As the gas expands it cools to ~5 K. The cavity is a tuned element in the pulsed FT microwave spectrometer which detects the transitions of the polar species passing through the cavity.

A 3-cm length of 1.7 mm i.d. quartz tubing was attached to the outlet of the solenoid-activated valve (General Valve). The exit end of this extension was constricted to 0.6 mm i.d., and a heating coil was wound around 10–15 mm of that end, the inner length of bare tubing insulating the pulsed valve from the furnace. When operated at ambient temperature this device has little or no effect on S/N of the spectrometer, depending on the species observed. Carrier gas was saturated with the DMSCB precursor (Petrarch Systems, Inc.) by bubbling it through the liquid (bp 82 °C). It was then diluted with pure carrier. The furnace temperature was adjusted so that its operation reduced the intensity of a DMSCB transition at 8903 MHz to a tenth of its unheated value. With the furnace at ~1000 °C we observed the six transitions of DMSE listed in Table I. Because of the cooling in the expansion they are for the ground vibrational state.

The assignment of these transitions to DMSE is unamgibuous. They disappear when the temperature of the furnace is turned down. Their fine structure, with spacings of ~1 MHz, is that expected for the restricted internal rotation of the two equivalent methyl groups with a barrier of ~1 kcal/mol[8] in DMSE. The rotational constants are consistent with DMSE. The transitions found at 8004, 8831, and 9047 MHz were predicted by rotational constants from fitting the other (first) three transitions. The planar moment $P_c$ from the rotational constants is small and very close to that for isobutylene,[9] 3.022 and 3.072 u Å$^2$, respectively. This strongly supports a planar dimethylethylenic skeleton for the species found. $P_c$ is determined by mass out of the molecular plane[10] which should be the same in both cases (two protons in each of the methyl groups).[1,9]

The rotational constants obtained by fitting the approximate line centers of the six observed transitions are compared in Table II with those calculated for the DZ + d SCF theoretical structure (T), with an $r$(Si=C) of 1.692 Å, and for the electron diffraction structure (E). In the latter, we allowed for the high-temperature vibrational effects by reducing the $r_g$(Si=C) value of 1.83 Å to 1.815 Å and by using the theoretical values for the other distances.[2] DMSE is a near symmetric top. The $C_2$, dipole axis is the *b*-axis for T and the *a*-axis for E. The observed spectrum is fitted only as *b*-dipole transitions. Moreover, the fitted constants are systematically somewhat larger (15–50 MHz) than those for T and are much larger (130–300 MHz) than those for E. The microwave structure is incompatible with E and is actually somewhat more compact than T, the difference in A corresponding to an $r$(Si=C) smaller by 0.003 Å than predicted.

**Table II.** Comparison of Microwave Rotational Constants for DMSE with Those Predicted for the Theoretical and Electron Diffraction Structures

| source | *A*, MHz | *B*, MHz | *C*, MHz | trans type |
|---|---|---|---|---|
| microwave[a] | 6037.1 | 5896.9 | 3093.6 | *b*-dipole |
| DZ + d SCF[1] | 6025.98 | 5845.95 | 3078.89 | *b*-dipole |
| electron diffraction[2,b] | 5845.95 | 5583.95 | 2959.70 | *a*-dipole |

[a] Rigid rotor constants from transitions in Table I. [b] See text.

There are three main structural parameters in DMSE: $r$(Si=C), $r$(Si—C), and ∠(C—Si=C). Only the A and B rotational constants are independent, so the structure is underdetermined. However, the fine structure caused by internal rotation depends on the angle between the rotor and the inertial axes. Plans are underway to fit it and/or obtain spectra of isotopically substituted species to enable a more complete structure to be determined.

**Acknowledgment.** We thank Cliff Dykstra and L. K. Montgomery for encouraging and helpful discussions. Our work was supported by NSF under Grants DMR-86-12860 and CHE-85-20519. Also, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

**Registry No. 1**, 4112-23-6.

---

(5) Gerry, M. C. L.; Lewis-Bevan, W.; Westwood, N. P. C. *J. Chem. Phys.* **1983**, *79*, 4655.

(6) Campbell, E. J.; Read, W. G.; Shea, J. A. *Chem. Phys. Lett.* **1983**, *94*, 69. See, also: Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33.

(7) Gutowsky, H. S.; Chuang, C.; Klots, T. D.; Emilsson, T.; Ruoff, R. S.; Krause, K. R. *J. Chem. Phys.* **1988**, *88*, 2919. Ruoff, R. S.; Emilsson, T.; Klots, T. D.; Chuang, C.; Gutowsky, H. S. *J. Chem. Phys.* **1988**, *89*, 138.

(8) Swalen, J. D.; Costain, C. C. *J. Chem. Phys.* **1959**, *31*, 1562.

(9) Laurie, V. W. *J. Chem. Phys.* **1961**, *34*, 1516.

(10) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley-Interscience: New York, 1984.

---

# Site Selectivity Studies on the Catalyzed Reaction of Isotopically Labeled MnRe(CO)$_{10}$ with $^t$BuNC. Implications for Metal Dimer and Cluster Reactions

Peter Johnston, Graham J. Hutchings,[†] and Neil J. Coville*

*Catalysis Programme, Chemistry Department*
*University of the Witwatersrand*
*Johannesburg, PO Wits 2050, Republic of South Africa*

*Received June 17, 1988*

In recent years a comprehensive understanding of the substitution reaction of monometallic transition-metal carbonyl complexes has emerged.[1] The same cannot be said for the substitution reactions of metal dimer and cluster carbonyl complexes in which the presence of a metal–metal bond permits a wider range of reaction mechanism and products.[2,3] This added complexity makes it possible for the site of ligand addition and loss to occur at the same or different metal atoms. For instance, the thermal reaction between MnRe(CO)$_{10}$ and L (L = PR$_3$,[4] P(OR)$_3$,[3,4] and RNC[5]) yields the Re-substituted derivative even though kinetic

---

[†] Present address: Leverhulme Centre for Innovative Catalysis, Department of IPI Chemistry, University of Liverpool, Liverpool, L69 3BX, England.

(1) For a recent comprehensive review of this area, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*: University Science Books: Mill Valley, CA, 1987; Chapter 4.

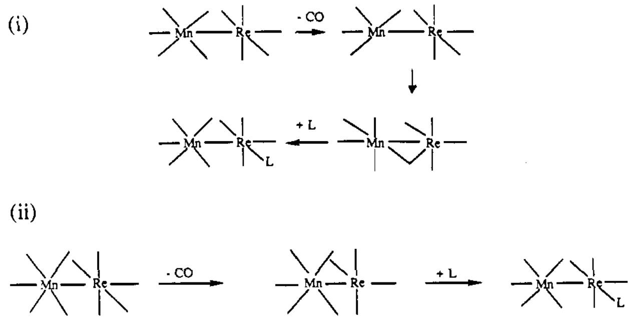
(2) Muetterties, E. L.; Burch, R. R.; Stolzenburg, A. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 89.

(3) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

(4) Sonnenberger, D. C.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.

(5) Robinson, D. J.; Darling, E. A.; Coville, N. J. *J. Organomet. Chem.* **1986**, *310*, 203.

**Scheme I.** Possible Dissociative Mechanisms for the Substitution of CO by L on $MnRe(CO)_{10}$ in Which CO Loss and L Addition (i) Occur on Different Metals and (ii) Occur on the Same Metal[a]



[a] An associative process occurring at Re would also lead to the required product. An associative mechanism occurring at Mn would yield the Mn-substituted derivative.

data are consistent with loss of CO from the Mn atom[4] (see Scheme I(i)).

Herein we report definitive evidence for a substitution reaction of a metal carbonyl dimer complex in which *CO loss and ligand addition occur at the same metal atom.* The reaction considered was the facile PdO-catalyzed reaction between $MnRe(CO)_{10}$ and ${}^tBuNC$, a reaction known to proceed without metal–metal bond cleavage and to yield the Re-substituted derivative $MnRe(CO)_9(CNBu^t)$.[5,6] The site of CO loss can be differentiated by reaction of the isotopically labeled dimer complex, viz.

$$Mn(CO)_5Re({}^{13}CO)_5 + {}^tBuNC \rightarrow$$

$$Mn(CO)_4({}^{13}CO)Re({}^{13}CO)_4(CNBu^t) + {}^{12}CO \text{ (Scheme I (i))}$$

$$Mn(CO)_5Re({}^{13}CO)_4(CNBu^t) + {}^{13}CO \text{ (Scheme I (ii))}$$

$Re_2({}^{13}CO)_{10}$ was synthesized from $Re_2(CO)_{10}$ and ${}^{13}CO$,[7] and the dimer was cleaved with $Br_2$ to yield $Re({}^{13}CO)_5Br$,[8] which was converted to the triflate $Re({}^{13}CO)_5(OSO_2CF_3)$.[9] Previous studies have indicated that CO scrambling between Mn and Re in $MnRe(CO)_{10}$ occurs at room temperature ($t_{1/2}$(25 °C) = 60 h).[9] Attempts were thus made to perform all further experimental operations at room temperature or lower and to keep reaction times to a minimum.[10] $Mn(CO)_5Re({}^{13}CO)_5$ (91% ${}^{13}CO$ label, Figure 1) was prepared from $Re({}^{13}CO)_5(OSO_2CF_3)$ and $Na[Mn(CO)_5]$ at 25 °C in THF (3 min)[11] and purified by HPLC (35 min).[12]

Benzene (1 mL) and ${}^tBuNC$ (1.0 equiv) were added to $Mn(CO)_5Re({}^{13}CO)_5$ (10 mg, $1.90 \times 10^{-2}$ mmol) and PdO (1 mg) in a specially constructed 5-mL airtight flask sealed under Ar. Gas and solution samples were drawn from the flask and analyzed by mass spectrometry. The reaction was quenched after 10 min and solvent removed. The crude residue was then divided into three fractions that were used as follows: (i) analyzed by mass spectrometry, (ii) reacted with excess $Br_2$ in $CCl_4$, and (iii) reacted with excess $I_2$ in $CH_3CN$. The products from reactions ii and iii were analyzed by mass spectrometry. Repeat experiments were performed.

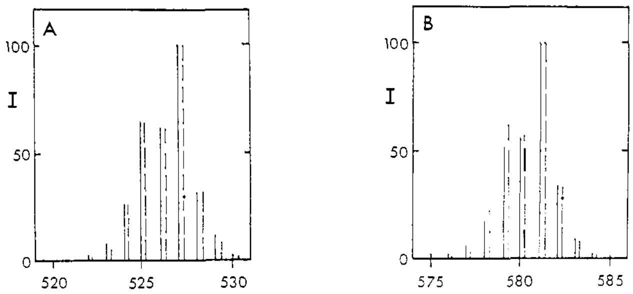


**Figure 1.** Mass spectral data. (A) Parent ion of $Mn(CO)_5Re({}^{13}CO)_5$ (full line). The simulated spectrum (broken line) assuming 90% ${}^{13}CO$ on Re is shown for comparison. (B) Parent ion of $Mn(CO)_5Re({}^{13}CO)(CNBu^t)$ (full line). The simulated spectrum assuming replacement of ${}^{13}CO$ on $Mn(CO)_5Re({}^{13}CO)_5$ by ${}^tBuNC$ (broken line) is also shown.

Comparison of the mass spectrum of the parent ion of $Re({}^{13}CO)_4(CNBu^t)Br$ from reaction ii with the spectrum of the product obtained from the direct reaction between $Re({}^{13}CO)_5Br$ and ${}^tBuNC$ indicates <5% scrambling of CO has occurred in the reaction.[13] Similar results were observed for the $Mn(CO)_5I$ parent ion obtained on analysis of the product from reaction iii. Analysis of the CO gas produced in the reaction clearly indicated >80% ${}^{13}CO$ in the gas phase of the reaction flask. Analysis of the $MnRe(CO)_9(CNBu^t)$ parent ion obtained by mass spectral analysis of the solution extract gives a complex pattern (Figure 1) centered at $m/z = 581$, consistent with loss of ${}^{13}CO$ and not ${}^{12}CO$. The simulated spectra[14] are also in agreement with >90% loss of ${}^{13}CO$. Further, the independent synthesis of $Mn(CO)_5Re({}^{13}CO)_4(CNBu^t)$ from $Na[Mn(CO)_5]$ and $Re({}^{13}CO)_4(CNBu^t)(OSO_2CF_3)$ gave a product with a mass spectrum identical with that obtained from the direct reaction between the labeled dimer and ${}^tBuNC$.

These results are consistent with CO loss and ${}^tBuNC$ addition occurring at the Re atom, a process that could occur via either an associative or dissociative (see Scheme I(ii)) pathway. The effect of the catalyst on the reaction *rate* is dramatic, but at this stage the manner in which the catalyst interacts with this and other related reactants to induce the increased reactivity is still a matter of conjecture.[15]

These results are to be contrasted with kinetic data from the thermal uncatalyzed reaction[4] that *suggest* CO loss occurs at the Mn atom[16] and photolytic studies[17] performed on labeled $MnRe(CO)_{10}$ in which CO displacement was *shown* to occur at the Mn atom (Scheme I(i)). Although the products from the catalyzed and uncatalyzed studies are identical, the mechanistic routes to their formation are not. This suggests that catalytic routes to substituted dimer and cluster complexes could give rise to products different from the classical routes (thermal, photolytic) and we are presently attempting to ascertain whether this possibility can be exploited.

**Acknowledgment.** We thank the FRD and the University for financial support. We also thank Dr. D. J. Robinson, Dr. L. Fourie, and Mr. I. Hazelby (mass spectral data collection) as well as Dr. M. D. Booth and Mr. K. Lampert (HPLC facility).

---

(6) The reaction between $MnRe(CO)_{10}$ and ${}^tBuNC$ yields only $Mn(CO)_5Re(CO)_4(CNBu^t)$. The synthesis of the alternative isomer $Mn(CO)_4(CNBu^t)Re(CO)_5$ and attempted isomerization studies (none occurs, 95 °C) have been reported.[5]

(7) $Re_2(CO)_{10}$ (1.1 mmol) in hexane (85 mL) under ${}^{13}CO$ (310 mL, enriched to 97% ${}^{13}C$, 6% ${}^{17}O$, and 1% ${}^{18}O$) was irradiated for 19.5 h (Hanovia lamp, 450 W). CO exchange was monitored by IR spectroscopy, and the ${}^{13}CO$ was replaced when exchange equilibrium was reached (after 1 and 4 h). Mass spectrometric analysis of the final material indicates a ${}^{13}CO$ content of 91%.

(8) Yield 89%; IR ($CH_2Cl_2$) [$\nu$(CO)] 1988, 1940 cm$^{-1}$.

(9) Schmidt, S. P.; Basolo, F.; Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1894.

(10) Trial runs were initially performed on unlabeled material to optimize reaction times and conditions.

(11) A total of 0.25 mmol of reactants in 7 mL of THF was used. Product was extracted with 3 × 5 mL of hexane.

(12) Du Pont 870 preparative HPLC: column, Zorbax Sil, 21.2 mm × 250 mm; mobile phase, hexane; flow rate, 12 mL/min at 26 bar; UV detector at 230 nm. Retention times: $Mn_2(CO)_{10}$, 8.1 min; $MnRe(CO)_{10}$, 8.8 min; $Re_2(CO)_{10}$, 9.2 min. Injection sample: 20 mg in 250 $\mu$L toluene.

(13) The $Mn(CO)_5Br$ obtained in the cleavage reaction also indicates that under our reaction conditions <5% scrambling of CO on $Mn(CO)_5Re({}^{13}CO)_5$ had occurred prior to reaction with $Br_2$.

(14) Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822.

(15) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.

(16) Our labeling study suggests that a dissociative reaction occurring at Re (Scheme I(ii)) cannot be ruled out.

(17) Firth, S.; Hodges, P. M.; Poliakoff, M.; Turner, J. J.; Therien, M. J. *J. Organomet. Chem.* **1987**, *331*, 347.