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# Vibrational spectroscopy at high pressures. XL. A Raman study of manganese rhenium decacarbonyl

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$\text{MnRe(CO)}_{10}$  undergoes two first-order phase transitions under hydrostatic pressures, at  $\sim 7$  and  $\sim 13$  kbar. The Raman spectra have been followed through these transitions and are interpreted in terms of a change of molecular geometry from staggered to eclipsed and back to staggered with increase of pressure. Comments are offered on the assignment of the vibrational spectra of this material.

## I. INTRODUCTION

We have discovered recently<sup>1,2</sup> that under modestly high hydrostatic pressures the metal carbonyls  $\text{M}_2(\text{CO})_{10}$ , ( $\text{M} = \text{Mn}, \text{Re}$ ) undergo a first-order phase transition in which the molecular geometry changes from staggered ( $D_{4d}$ ) to eclipsed ( $D_{4h}$ ). We now report on the remarkable behavior of  $\text{MnRe(CO)}_{10}$  under similar conditions.

## II. EXPERIMENTAL

The mixed-metal carbonyl was prepared from  $\text{Na[Mn(CO)}_5]$  and  $\text{Re(CO)}_5\text{Br}$  using the method of Nesmeyanov *et al.*<sup>3</sup> It was purified by repeated sublimation. Details of the high pressure technique have been given elsewhere.<sup>4</sup>  $\text{Kr}^+$  647 nm excitation was used to obtain Raman spectra. The sample was immersed in 4:1 methanol ethanol and the pressures estimated by the ruby  $R$ -line method. Pressures are given in kbar [ $1 \text{ kbar} = 10^8 \text{ Pa}$ ].

## III. RESULTS AND DISCUSSION

### A. The phase behavior

The data are shown in Figs. 1–3. Visual examination under the microscope of a sample of  $\text{MnRe(CO)}_{10}$  under nonhydrostatic pressure showed *two* Becke lines. A Becke line indicates coexistence of phases with different refractive indices and is associated, therefore, with a first-order phase transition (the refractive index varies continuously with pressure in a second-order change).

Both phase changes, which are at  $\sim 7$  and 13 kbar under hydrostatic compression, exhibit considerable hysteresis, a further classic indication that the transitions are of first order: accordingly, many spectra were obtained of I/II and II/III intergrowths. This behavior is in contrast to that of the parent carbonyls which each exhibit only one transition below 50 kbar.

Figure 1 shows typical spectra obtained in experiments in which the pressure was increased in steps from the ambient value. In Fig. 2 we give spectra obtained following pressure cycling: these show the

I/II phase transition more clearly. However, the combined data from all runs when plotted Fig. 3 give further evidence for both transitions. The first phase change lies between the pressures at which  $\text{Mn}_2(\text{CO})_{10}$  ( $\sim 8$  kbar) and  $\text{Re}_2(\text{CO})_{10}$  ( $\sim 5$  kbar) are restructured<sup>1,2</sup>; the second one is apparently unique to  $\text{MnRe(CO)}_{10}$ .

The most obvious changes with pressure are in the region  $< 200 \text{ cm}^{-1}$ . The spectra in this region of the parent carbonyls have been analyzed in detail on the basis of single-crystal spectra<sup>5,6</sup> and are known to consist of many overlapped deformational modes  $\delta(\text{CMC})$ ,  $\delta(\text{MMC})$ , and lattice modes. An analogous story must be obtained for  $\text{MnRe(CO)}_{10}$  although a full assignment cannot be given without single-crystal evidence. It is clear that the intense band initially at  $155 \text{ cm}^{-1}$  is due to  $\nu(\text{Mn-Re})$ . With increase of pressure a band(s) quickly develops in the gap immediately to lower frequency of  $\nu(\text{Mn-Re})$  at  $\sim 145 \text{ cm}^{-1}$ : at 7.1 kbar the new band is fully developed while the original  $\nu(\text{Mn-Re})$  has almost vanished. Concurrently, there are changes of intensity and shifts of several other bands which together modify the vibrational envelope in this region. Strong lattice modes appear in the new phase II near 7 kbar.

The spectrum remains largely unchanged, apart from some relative pressure shifts, until  $\sim 13$  kbar, whereupon a further discontinuous shift of  $\nu(\text{Mn-Re})$  occurs from  $152\text{--}160 \text{ cm}^{-1}$ , accompanied by other changes which significantly alter the vibrational envelope to lower frequency. This new phase III is stable to at least 40 kbar.

Although the most dramatic changes are in the region  $< 200 \text{ cm}^{-1}$ , others are present. Thus, in the middle region [ $\nu(\text{M-C})$ ,  $\delta(\text{MCO})$ ] the I/II phase change is indicated by an increase of intensity  $\sim 498 \text{ cm}^{-1}$  and a corresponding loss of intensity from the band initially at  $479 \text{ cm}^{-1}$ . However, the situation is exactly reversed by the II/III transition, so that the spectra of phases I and III in the  $380\text{--}550 \text{ cm}^{-1}$  region are almost identical, apart from pressure shifts.

Similar behavior is found in that part of the  $\nu(\text{CO})$

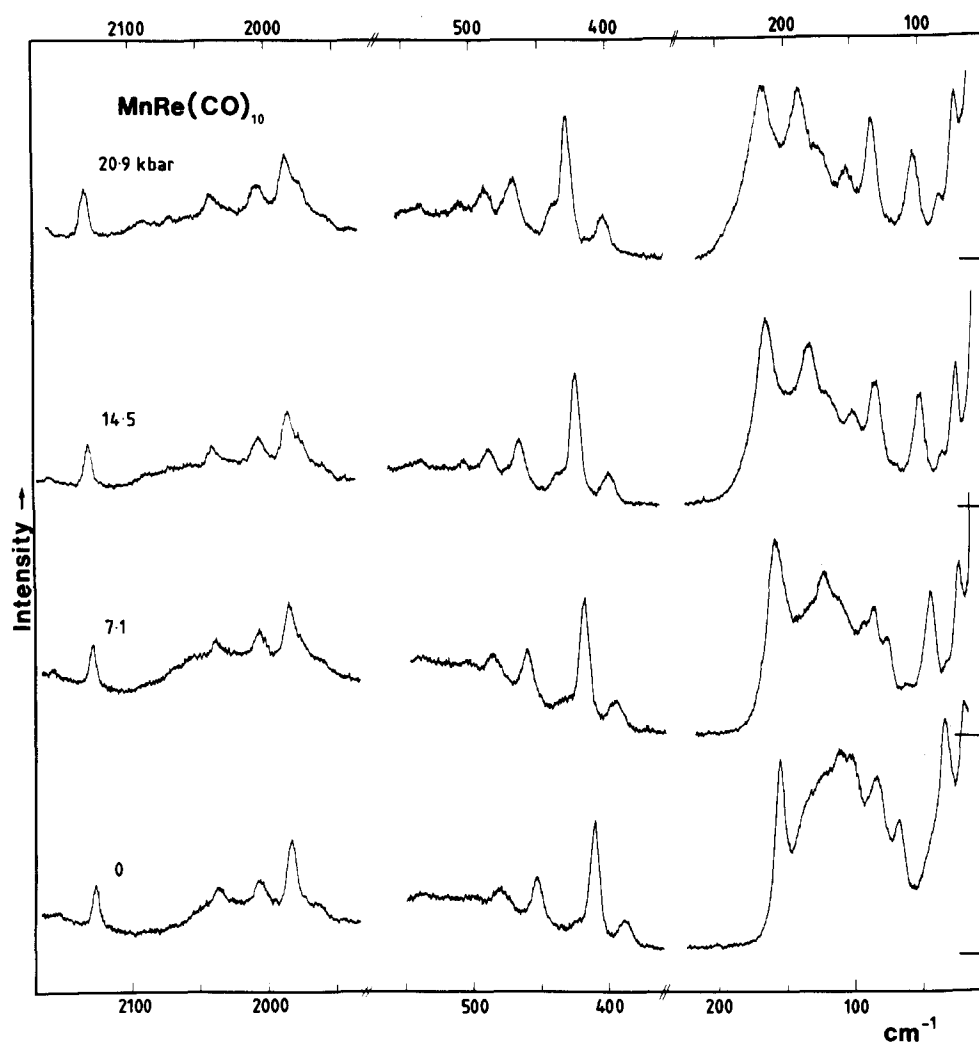


FIG. 1. Raman spectra of  $\text{MnRe}(\text{CO})_{10}$  at various pressures in a diamond anvil cell. The spectra shown were obtained during an initial excursion from ambient to successively higher pressures. 647 nm excitation,  $\sim 350$  mW. Spectral slit widths were generally  $2\text{ cm}^{-1} < 200\text{ cm}^{-1}$ ;  $2\text{ cm}^{-1}$  for 350 to  $550\text{ cm}^{-1}$ ; and  $3\text{ cm}^{-1}$  in the  $\nu(\text{CO})$  region. Base line levels are indicated on the right-hand side of the figure.

region below  $2000\text{ cm}^{-1}$ . The strong band at  $1983\text{ cm}^{-1}$  is considerably reduced in intensity on entering phase II, while a weaker band initially at  $1965\text{ cm}^{-1}$  intensifies somewhat. This change is reversed at the II/III transition with the consequence that the  $\nu(\text{CO})$  spectra of phases I and III are very similar. However,  $\text{MnRe}(\text{CO})_{10}$  III has a shoulder  $\sim 1980\text{ cm}^{-1}$  which, although present under ambient conditions, is now more prominent.

In the parent carbonyls the molecular symmetry change from  $D_{4d}$  to  $D_{4h}$  alters the  $\nu(\text{CO})$  selection rules in a way that is of diagnostic value. The point group symmetry of  $\text{MnRe}(\text{CO})_{10}$  is  $C_{4v}$  in both staggered and eclipsed forms: accordingly no change in the number of bands is expected to accompany such a modification of geometry. The possibility of an internal rotation by some arbitrary value ( $\theta \neq 0, 45^\circ$ ) to give a structure of  $C_4$  symmetry must not be excluded although even this would make almost no difference to the Raman selection rules [the  $3A_2$  modes  $\delta(\text{MnCO})$ ,  $\delta(\text{ReCO})$ , and the torsion, which are inactive in  $C_{4v}$ , become allowed: otherwise there is no change in the number of Raman bands]. Since the selection rules are not helpful, our

structural deductions are necessarily based upon qualitative arguments.

### B. Assignment for $\text{MnRe}(\text{CO})_{10}$

The vibrational spectrum of this material has never been fully determined and assigned. IR spectra in solution and in KBr discs (ambient temperature) were reported and assigned by Flitcroft *et al.*,<sup>7</sup> and a Raman spectrum (ambient) obtained by Quicksall and Spiro.<sup>8</sup> Detailed assignments of the  $\nu(\text{CO})$  region have been attempted by two groups,<sup>9,10</sup> but considerable differences remain between their interpretations.<sup>11</sup> Our interest in the  $\nu(\text{CO})$  region centers on that part  $< 2000\text{ cm}^{-1}$ : unfortunately this is the chief region of dispute. Nevertheless, it is certain to contain the two  $A_1(\text{axial})$   $\nu(\text{CO})$  modes centered mainly on Mn and Re, respectively, and probably also one of the  $E$  modes (Mn centered). At the staggered-to-eclipsed transformation of  $\text{Re}_2(\text{CO})_{10}$ , there is increased interaction across the metal-metal bond, revealed by a substantially enlarged splitting between the  $A_1$  and  $B_2$  axial  $\nu(\text{MC})$  modes which is exhibited as a drop in the Raman-active  $A_1$  and a rise in IR-active  $B_2$  mode. In the Raman

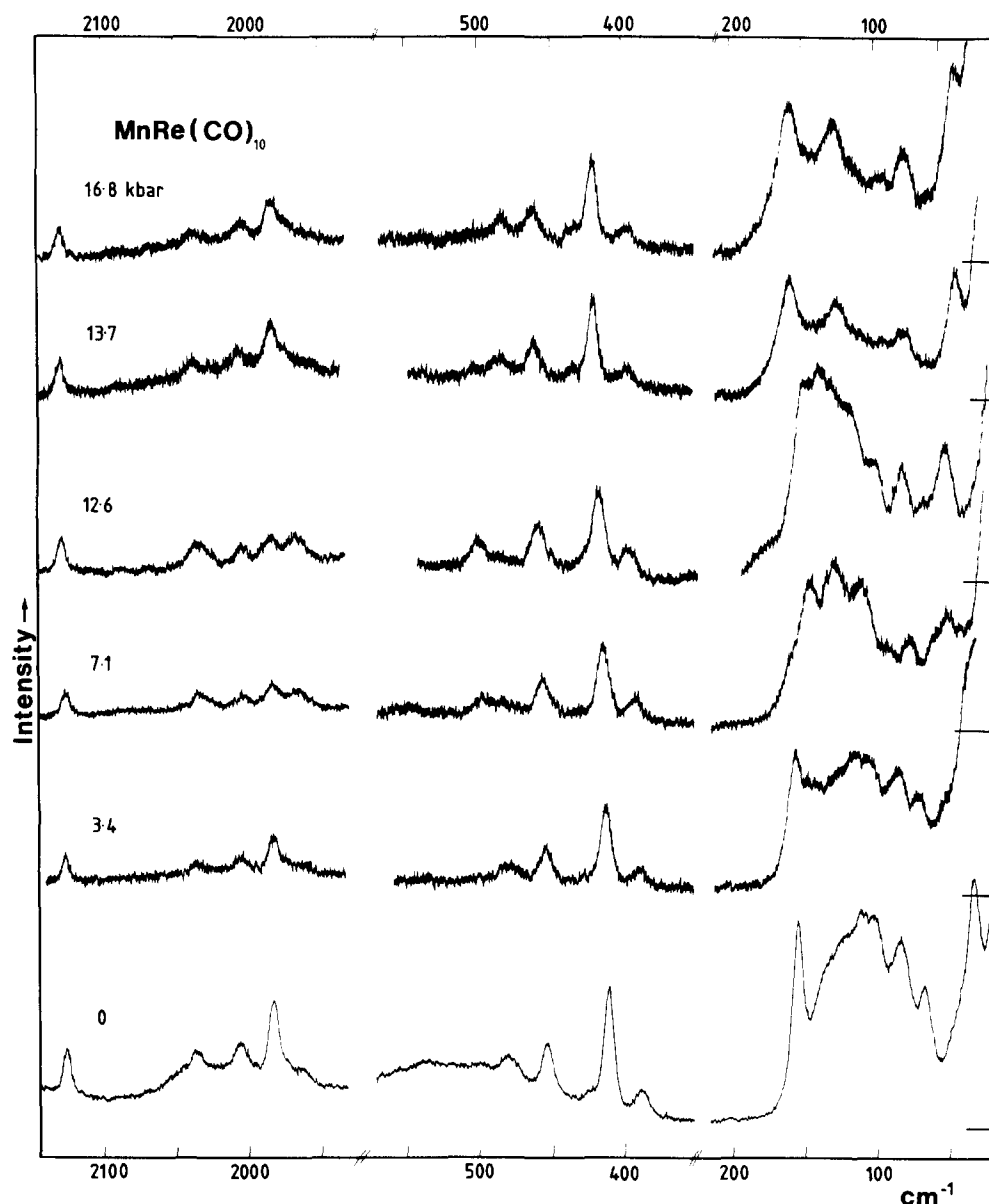


FIG. 2. Raman spectra of  $\text{MnRe}(\text{CO})_{10}$  at various pressures. The spectra were obtained following pressure cycling to induce the phase transition(s). Conditions as for Fig. 1, except that at 7.1, 12.6, and 13.7 kbar all spectral slit widths were  $\sim 0.5 \text{ cm}^{-1}$  higher than in Fig. 1.

spectrum of  $\text{MnRe}(\text{CO})_{10}$ , one of the  $A_1$  modes ( $1986 \text{ cm}^{-1}$ ) is more intense than the other in the ambient phase: on entering phase II these intensities are more nearly equalized, which is the result to be expected if there is increased interaction across the Mn-Re bond, leading to energy and intensity sharing. The data are, therefore, consistent with the proposed geometrical change.

In the  $350\text{--}700 \text{ cm}^{-1}$  range we are primarily interested in the provenance of the bands  $\sim 478$  and  $495 \text{ cm}^{-1}$  which vary in intensity at the phase transitions. Unfortunately, the highest  $\nu(\text{M-C})$  modes in  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$  are at  $486$  and  $479 \text{ cm}^{-1}$ , respectively<sup>12</sup>: assignment of our two bands is therefore equivocal, although the higher of the two is likely to be  $\delta(\text{MCO})$  in type. Table II gives new data but the assignment must wait further evidence.

### C. The pressure shifts

The relative pressure shifts  $d \ln \tilde{\nu}_i / dP$  shown in Table I can be converted to mode Grüneisen parameters  $\gamma_i$  by division by the isothermal compressibility  $\chi_T$ . The value of  $\chi_T$  is not known, but for most molecular crystals it is  $\sim 1 \times 10^{-2} \text{ kbar}^{-1}$ . Using this value, the relative pressure shifts become numerically equal to the  $\gamma_i$ .

All the  $d \ln \tilde{\nu}_i / dP$  values for bands from  $84 \text{ cm}^{-1}$  upwards are typical of those found for internal molecular modes, except for the band initially at  $111 \text{ cm}^{-1}$  which shifts at a rate more usually associated with lattice modes. The large values shown by the 20, 34, and  $68 \text{ cm}^{-1}$  bands are consistent with their assignment as lattice modes, but the  $50 \text{ cm}^{-1}$  band could be due to an admixture of internal and lattice motions, and

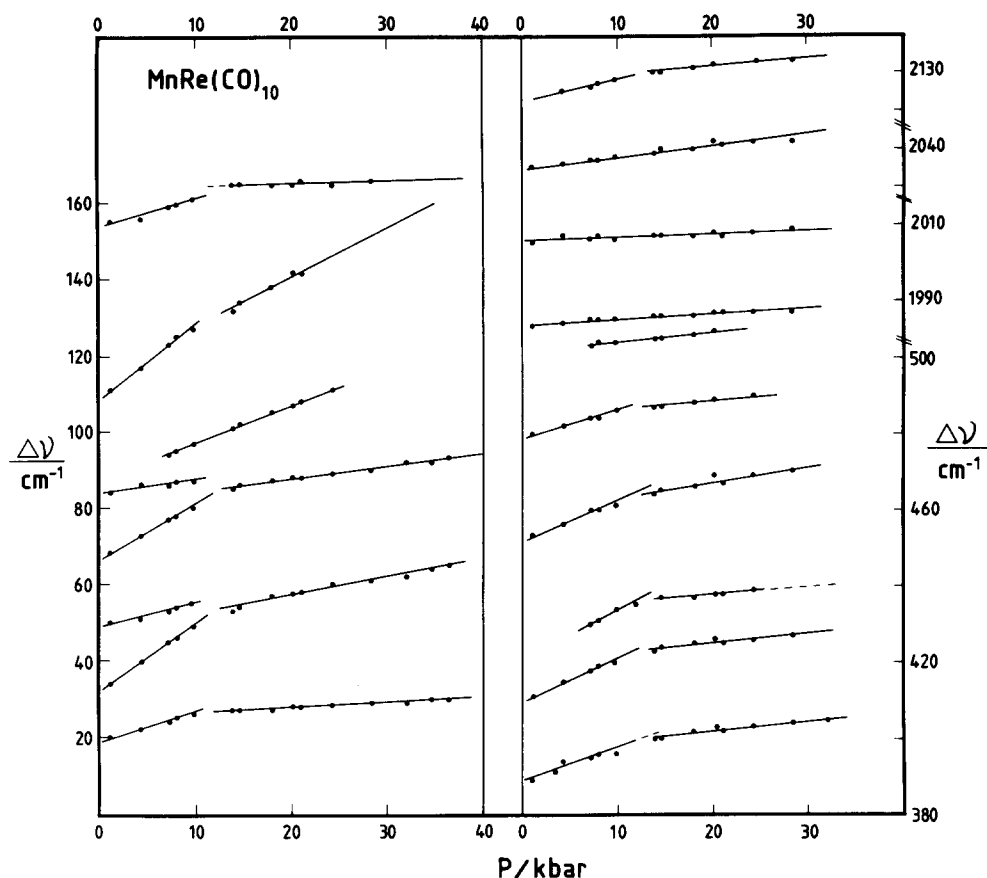


FIG. 3. Variation of the vibrational frequencies (wave numbers/cm<sup>-1</sup>) of MnRe(CO)<sub>10</sub> with pressure.

TABLE I. Raman bands (shift/cm<sup>-1</sup>) and their pressure sensitivities for MnRe(CO)<sub>10</sub>.

$\tilde{\nu}_i^0$	$\frac{\Delta\tilde{\nu}_i}{\Delta P}$ (cm <sup>-1</sup> kbar <sup>-1</sup> )	$\frac{1}{\tilde{\nu}_i^0} \frac{\Delta\tilde{\nu}_i}{\Delta P}$ (10 <sup>2</sup> kbar <sup>-1</sup> )	$\frac{\Delta\tilde{\nu}_i^a}{\Delta P}$ (cm <sup>-1</sup> kbar <sup>-1</sup> )
2125	0.60	0.028	0.204
2035	0.33	0.016	
2005	0.10	0.005	
1983	0.16	0.008	
503 <sup>b</sup>	0.26	0.052	
479.5	0.75	0.156	0.221
453	1.11	0.245	0.408
430 <sup>b</sup>	1.30	0.302	0.262
411	1.16	0.282	0.280
389	0.89	0.229	0.275
155	0.74	0.474	0.089
111	1.97	1.775	1.290
94 <sup>b</sup>	0.28	0.300	
84	0.36	0.425	
68	1.49	2.19	0.333
50	0.63	1.25	
34	1.78	5.24	0.472
20	0.78	3.91	0.139

<sup>a</sup>Slope of line after II/III transition. No entry indicates that the slope was unchanged or that the band could no longer be observed.

<sup>b</sup>Not in phase I.

a similar explanation could hold for the band at 111 cm<sup>-1</sup>. Translatory modes would not be as high as 111 cm<sup>-1</sup>: it follows that any lattice mode contribution at 111 cm<sup>-1</sup> must be libratory in type. However, we cannot neglect the possibility that we may be seeing

TABLE II. Vibrational modes (frequency/cm<sup>-1</sup>) for solid MnRe(CO)<sub>10</sub> in the  $\nu$ (M-C),  $\delta$ (MCO) region.

IR (~100 K)	Raman (ambient)
667 vs	
~657 sh	
653 vs	
~645 sh	
590 vs	~588 vv
556 w	
537 w	538 w
518 vv	
502 vv	
~483 sh	
477 s	480 m
455 w	453 m
428 vw	426 w
413 m	411 vs
387 s	388 m
350 w	

the  $B_1$ ,  $\nu_{10}$  torsional mode, which is allowed to become active by virtue of the site and correlation fields. Molecular crystals should have lattice mode Grüneisens  $\sim 3.5$ .<sup>13</sup> The average of the Grüneisens for the four lowest modes is 3.15, but this rises to 3.78 if the  $50\text{ cm}^{-1}$  band is excluded (it may be an internal mode). While the details remain in doubt, it is clear that the compressibility of  $\text{MnRe}(\text{CO})_{10}$  cannot be far from  $1 \times 10^{-2}\text{ kbar}^{-1}$ .

#### D. Structural deductions

The numbers of Raman bands shown by each phase are similar, suggesting that the primitive cell occupancy remains the same throughout: (the parent phase is monoclinic  $I2/a$  with  $z=2$  in the primitive cell).<sup>14</sup> Since the transitions are apparently first order in type no direct symmetry relationships between the phases can be deduced without knowledge of the unit cell symmetries.

As with the parent carbonyls, the changes found in all three spectral regions of  $\text{MnRe}(\text{CO})_{10}$  at the I/II transition imply a change of molecular geometry: by analogy with them, a staggered to eclipsed transition is proposed. The remarkable similarities, again in all three regions, between the spectra of phases I and III suggest similar molecular structures. We therefore propose that at the II/III phase change the molecules revert to the staggered form. Implicit in this scheme is the belief that the energy difference between the staggered and eclipsed forms is slight. Indeed, in the vapor state,  $\text{Mn}_2(\text{CO})_{10}$  is staggered<sup>15</sup> but  $\text{Re}_2(\text{CO})_{10}$  is apparently eclipsed.<sup>16</sup> Hence as the unit cell is compressed and repulsive intermolecular interactions increase, the situation may be relieved (at both transition pressures) by a change of molecular geometry which assists repacking in a denser form. The tapered-cylindrical shape of  $\text{MnRe}(\text{CO})_{10}$ , as opposed to that of

$\text{M}_2(\text{CO})_{10}$ , must be implicated in the occurrence of the II/III change, which has no analogue for the homonuclear carbonyls.

#### ACKNOWLEDGMENT

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