absorbs at 243 mμ [$\varepsilon = 11{,}150$]. Replacing methyl groups with chlorine atoms has little effect on the ultraviolet spectra (Table 3). The only other group which has so far been found to be effective in altering the band position is the vinyl group. Thus, 1,2-divinyltetramethyldisilane and 1,4-divinyloctamethyltetrasilane possess ultraviolet spectra with maximum absorption at 225 and 243.5 mμ, respectively.

From the foregoing discussion it can be seen that the unique spectral properties of polysilanes are due to the silicon–silicon bond acting as a chromophore, probably through the use of vacant *d*-orbitals of the silicon atom. Substituents such as phenyl and vinyl with their π-electron systems are apparently able to be conjugated with polysilane chains through suitable overlap of *d*- and π-orbitals.

The authors wish to express their sincere gratitude to Professor M. KUMADA for supplying purified samples of the permethylated polysilanes. This research was supported in part under Contract AF 33[616]-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Division, Wright-Patterson AFB, Ohio.

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J. Organometal. Chem., 2 (1964) 369–371

Received July 29th, 1964

Chemistry of the metal carbonyls

XXVII. The infrared spectra of organomanganese and organorhenium pentacarbonyls*

Recent interest in CO stretching modes in manganese[2–5], technetium[3] and rhenium[3] pentacarbonyls prompts us to report observations which appear to confirm a theoretical prediction[2]. Complexes of subgroup seven metals of type $LM(CO)_5$ should show three CO fundamental infrared bands, classified as two A_1 and one E stretching modes. The generality of this deduction has been confirmed experimentally[3,6], but it has been pointed out[2] that in addition to the normal frequencies, splitting of the intense E transition and appearance of a low intensity B_1 transition might be observed in the complexes if the ligand–metal group lacks axial symmetry.

Many manganese and rhenium complexes $LM(CO)_5$ (where L is an asymmetric fluorocarbon group) have been prepared[7]. We are currently measuring their infrared spectra under conditions of high resolution. When the organic group in the manganese pentacarbonyls is not axially symmetric, spectra in which the E band is split, such

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* For Part XXVI of this series, see ref. 1.

as the one shown in the fig. 1(a) have been observed. The magnitude of the splitting of the E band varies. As expected, manganese pentacarbonyls show the effect more strongly than the rhenium pentacarbonyls so that in the latter it is sometimes not seen [Fig. 1(b)]. Complexes which show a splitting of the E absorption and, in agreement with theory[2], simultaneous appearance of the B_1 mode in their infrared spectra (cyclohexane solution) include: $HCCl_2CF_2Mn(CO)_5$ (6 cm^{-1}), $HCCl_2CF_2Re(CO)_5$ (3 cm^{-1}), $C_2F_5COMn(CO)_5$ (5 cm^{-1}) and $C_6F_5COMn(CO)_5$ (12 cm^{-1}). The effect is not observed under similar conditions with more symmetrical compounds like $CH_3(CF_2)_4Re(CO)_5$, $C_6H_5Mn(CO)_5$, or $CH_3CF_2CF_2Mn(CO)_5$. In the *gas-phase* spectrum of $CH_3CF_2CF_2Mn(CO)_5$, however, an E band splitting of 2 cm^{-1} is just detectable.

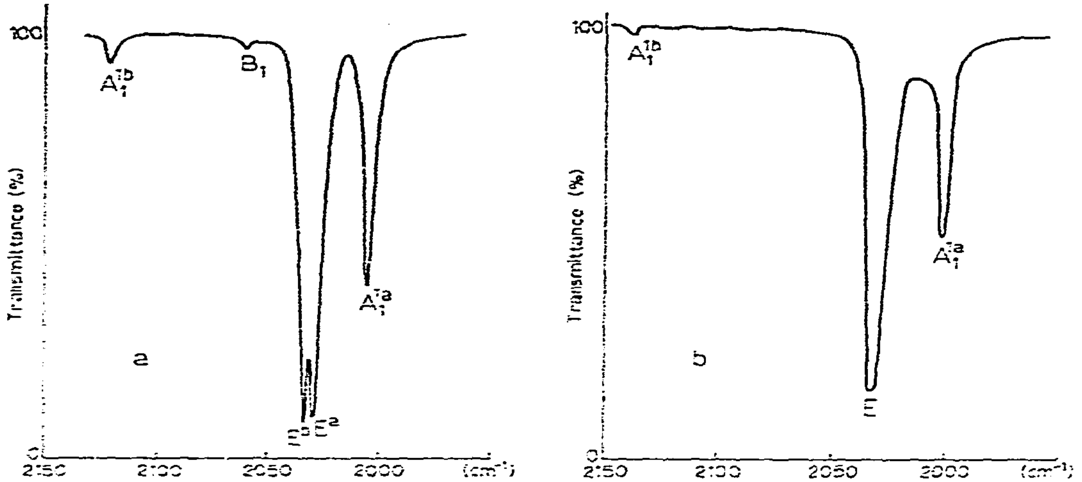

Fig. 1. Carbonyl stretching modes in the infrared spectrum (cyclohexane solution). (a), $HCFClCF_2Mn(CO)_5$, A_1^{1b} 2133; B_1, 2072; E^b, 2043; E^a, 2035; A_1^{1a}, 2014 cm^{-1}. (b), $HCFClCF_2Re(CO)_5$, A_1^{1b} 2147; E, 2038; A_1^{1a}, 2011 cm^{-1}. See ref. 3 for discussion of low intensities of A_1^{1b} bands observed in rhenium pentacarbonyls.

We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant for the support of this work. We thank the Department of Scientific and Industrial Research for the award of a studentship to J.B.W., and Dr. E. W. Abel for helpful discussions.

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Received June 18th, 1964