

2. Aspinall, G. O.; McDonald, A. G.; Raju, T. S.; Pang, H.; Moran, A. P.; Penner, J. L. *Eur. J. Biochem.* **1993**, *213*, 1017.
3. Aspinall, G. O.; McDonald, A. G.; Raju, T. S.; Pang, H.; Kurjanczyk, L. A.; Penner, J. L.; Moran, A. P. *Eur. J. Biochem.* **1993**, *213*, 1029.
4. Aspinall, G. O.; McDonald, A. G.; Pang, H. *Carbohydr. Res.* **1992**, *231*, 13.
5. Richtmyer, N. K. *Methods in Carbohydr. Chem.*; Whistler, R. L.; Wolfrom, M. L., Ed.; Academic Press: 1962; Vol. I, p 108.
6. Baer, H. H.; Breton, R. L.; Shen, Y. *Carbohydr. Res.* **1990**, *200*, 377.
7. Mikami, T.; Katoh, A.; Mitsunobu, O. *Tetrahedron Lett.* **1990**, *31*, 539.
8. Aspinall, G. O.; McDonald, A. G.; Sood, R. K. *Can. J. Chem.* **1994**, *72*, 247.
9. Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
10. Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.
11. Paulsen, H.; Heume, M.; Györgydeak, Z.; Lebuhn, R. *Carbohydr. Res.* **1985**, *144*, 57.
12. Garegg, P. J.; Iversen, T.; Oscarson, S. *Carbohydr. Res.* **1976**, *50*, C12.
13. Lipták, A.; Jodál, I.; Nánási, P. *Carbohydr. Res.* **1975**, *44*, 1.
14. Garegg, P. J.; Hultberg, H.; Wallin, S. *Carbohydr. Res.* **1982**, *108*, 97.
15. Mikami, T.; Asano, H.; Mitsunobu, O. *Chem. Lett.* **1987**, 2033.
16. Chapleur, Y.; Boquel, P.; Chrétien, F. *J. Chem. Soc. Perkin Trans. I* **1989**, 703.
17. Chida, N.; Ohtsuka, M.; Nakazawa, K.; Ogawa, S. *J. Org. Chem.* **1991**, *56*, 2976.
18. Nilsson, S.; Lönn, H.; Norberg, T. *Glycoconjugate J.* **1991**, *8*, 9.
19. Oikawa, Y.; Yoshioka, T.; Yonemitsu, O. *Tetrahedron Lett.* **1982**, *23*, 885.
20. David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643.
21. Varma, A. J.; Schuerch, C. *J. Org. Chem.* **1981**, *46*, 799.
22. Mulzer, J.; Dehmlow, H. *J. Org. Chem.* **1992**, *57*, 3194.
23. Sato, S.; Ito, Y.; Nukada, T.; Nakahara, Y.; Ogawa, T. *Carbohydr. Res.* **1987**, *167*, 197.

Application of Cluster Distributions to Energy Transfer in Two-Dimensional Choleic Acid Crystals

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The cluster distributions for different concentrations of 1,4-dibromonaphthalene (DBN) in 4,4'-dibromobenzophenone (DBBP)/1,4-dibromonaphthalene (DBN) choleic acid were determined by a computer simulation in order to model the energy transfer dynamics. The results of the simulation indicate that long range interaction between molecules further apart than nearest does not occur and energy transfer efficiency is restricted by single range interaction. The results also demonstrate that the trapping is diffusion limited. The energy transfer rate is reduced by a factor of 15 in DBBP/DBN choleic acid relative to that in DBBP/DBN doped into polystyrene due to the larger distance between molecules.

Introduction

It has been shown that the concepts of cluster distributions can describe energy transfer in multi-component systems.^{1,2} Cluster distributions for different concentrations of C₁₀H₈ and C₁₀D₈ in naphthalene choleic acid were determined by a computer simulation to test whether the experimentally observed change in the C₁₀H₈ triplet excitation energy transfer efficiency α is due to the cluster distribution of C₁₀H₈ molecules.³ The results of the simulation agree with the experiment indicating that the change in α with increasing C₁₀H₈ concentration is caused by the growth of clusters and then limited by the small number of sites visited during the lifetime of the excitation. The energy transfer rate is reduced by a factor of about 10⁵ in naphthalene choleic acid relative to that in naphthalene crystals due to the larger distance between

the molecules, and the energy transfer topology changes from two to one-dimensional due to the change in molecular orientations and the increasing spacing. In addition, a molecular face-to-edge interaction dominates for nearest neighbors in the naphthalene crystal, and a face-to-face interaction dominates over an edge-to-edge interaction in NCA.

Donor-acceptor energy transfer for 4,4'-dibromobenzophenone(DBBP)/1,4-dibromonaphthalene (DBN) doped into a polymer matrix (polystyrene) has been studied previously.⁴ The excitation energy at 386 nm populates the excited singlet state of DBBP (donor) without exciting DBN (acceptor). The lowest singlet absorption band of the donor molecule lies at lower energy than that of the lowest singlet absorption band of the acceptor at 280 nm. The lowest triplet state of DBBP, on the other hand, because of the small singlet-triplet splitting in carbonyl compounds, lies above the lowest

triplet state of DBN. Because of this particular arrangement of energy levels, it is possible to excite selectively the donor molecules to the singlet state and be quite sure that no significant excitation of acceptor molecules occurs. In aromatic carbonyl molecules, the quantum yield of intersystem crossing from the lowest excited singlet state to the lowest excited triplet state is very high, dominating over other decay processes.⁵ The excited triplet state of DBBP therefore is populated by intersystem crossing, and phosphorescence from this state is observed around 430 nm. Some of these donor molecules transfer the excitation energy to acceptor molecules *via* a triplet-triplet exchange interaction, and sensitized phosphorescence from the lowest excited triplet state of DBN can be observed around 500 nm. A systematic data analysis of the experiments demonstrated that the fraction of total phosphorescence that came from the acceptor appeared to be independent of the donor concentration when the donor concentration was less than 5% and the acceptor concentration was 10% or higher.^{4,5} This experimental result indicates that regime where donor-donor energy transfer is not significant.

Recently this system has been incorporated into a choleic acid crystal.⁶ Using deoxycholic acid (DCA) as a crystalline matrix makes it possible to change the orientations and separations of the DBBP and DBN molecules in the choleic acid crystal system. Direct donor-acceptor triplet excitation energy transfer was characterized in DBBP/DBN choleic acid crystals using DBBP as energy donor and DBN as energy acceptor by monitoring the phosphorescence spectra as a function of acceptor concentration. In these experiments DCA serves as energy transfer insulators. The energy transfer efficiency did not show an abrupt change unlike the case for a polystyrene host. This difference is attributed to the intrinsically larger intermolecular distances imposed by the choleic acid lattice.

The actual geometrical distribution of DBBP/DBN clusters also strongly influences the energy transport. For low concentrations, there will be many isolated members, as well as many clusters of two, three, or four members. As the concentration increases, the distribution will contain more and more large clusters until several large clusters coalesce into a maxicluster, *i.e.* a percolation cluster. In the system of DBBP/DBN doped into polystyrene, cluster percolation occurs at concentrations near the energy transfer critical concentration, *i.e.* where the energy transfer efficiency α changes abruptly.¹ For the case of choleic acid system, α increases as the concentration increases but does not show an abrupt change over the range 5-20 mol % acceptor. In this paper we report the results of computer simulations that were used to test whether no abrupt change in α is related to the cluster distribution and/or the orientation of guest molecules, and/or the large intermolecular separations.

Energy Transfer Efficiency and the Cluster Distribution

For the choleic acid, the orthorhombic structure⁷⁻⁹ was used with two guest sites per unit cell with dimensions $27 \times 15 \times 14 \text{ \AA}^3$. We consider a two-dimensional lattice to determine the cluster distribution. In a two-dimensional system the percolation threshold is 0.59.^{1,10} For $p=1$, where p repre-

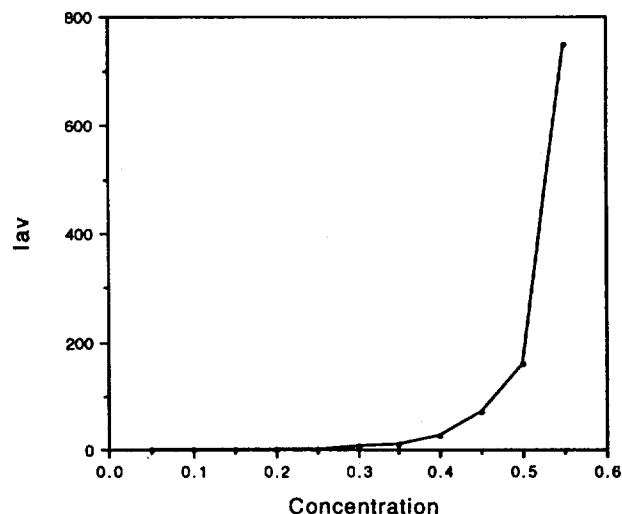


Figure 1. Average cluster size I_{AV} as a function of guest concentration for a square lattice with 10^6 sites. The percolation threshold is 0.59 in two dimension.

sents the probability that the lattice is occupied, all sites of the lattice are occupied by DBBP and DBN, and the whole lattice constitutes one single cluster. For every p smaller than unity, there will be choleic acid crystal with guest sites partially filled.⁶ The unoccupied spaces will produce a distribution of DBBP/DBN clusters. Figure 1 shows the average cluster size (I_{AV}) for a two-dimensional lattice as a function of concentration. The definition of the I_{AV} is^{1,11}

$$I_{AV} = \frac{\sum_m i_m m^2}{\sum_m i_m m} \quad (1)$$

where m is the size of a cluster and i_m is the frequency of the cluster size m . This I_{AV} increases monotonically with guest concentration C and diverges at the critical concentration.^{1,3} The results indicate that in two dimension percolating cluster is present for concentrations below unity. The cluster multiple labeling technique (CMLT)¹¹ was used to determine m and i_m . CMLT technique is based on the application of alternate labels to sites belonging to the same cluster. This technique is appropriate for the determination of the cluster distribution of a finite randomly mixed binary crystals. The practical algorithm is described in ref. 10.

Now consider diffusive exciton transfer. The formalism of exciton transfer in molecular solids has been described previously.^{1,2} The exciton generally is considered to be localized at one site at a time and to move from one guest site to the next. However, the exciton is confined within a cluster of size m and is excluded from visiting matrix (DCA) sites due to their higher energy. The probability of exciton creation inside a given cluster is proportional to the cluster size m . No energy transfer between donors is considered.^{4,5} When the exciton visits a trap site (DBN), it may be captured irreversibly. For small trap concentration ($\ll 1$), the trapping probability P , which is equivalent to α , of an exciton finding a trap site within the exciton lifetime τ_g is^{1,2,11} (assuming a trapping efficiency of unity)

$$P = \sum_m [1 - (1 - m/G)^{i_m}] m/G = 1 - \sum_m (1 - m/G)^{i_m} m/G \quad (2)$$

iff $1 \ll Z \ll G$

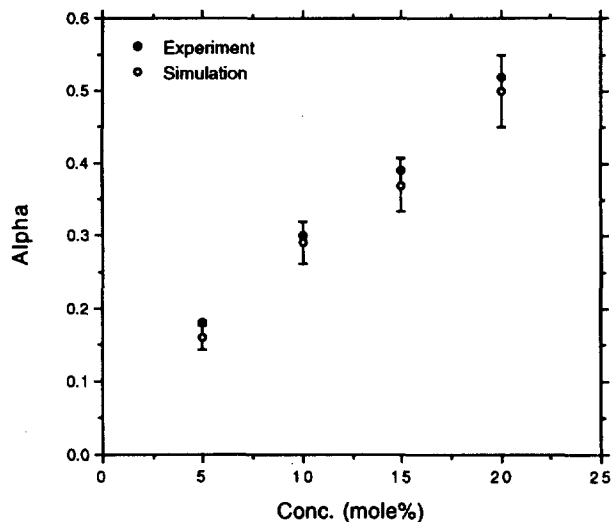


Figure 2. The energy transfer efficiency (α), which is the probability of a guest exciton being trapped, for different guest concentrations, as determined by both experiment and simulation.

where m is the size of a cluster, i_m is the frequency of the cluster size m , G is the number of guests, and Z is the number of traps. P can be related to the kinetic rate constants and can be found experimentally by measuring the guest and trap phosphorescence intensities. The size of cluster (m) and the frequency of cluster m (i_m) for the different numbers of guests (G) are determined by computer simulation using CMLT. By applying values (m , i_m , G , Z) obtained from the computer simulation into eq. (2), values of α for different DBN concentrations can be obtained. Increasing the trap concentration by an order of magnitude has a significant effect on the critical concentration.¹ In the case of isotopically mixed naphthalene crystals, the critical concentrations are 0.12 and 0.08 for trap concentrations of 10^{-3} mole fraction and 10^{-2} mole fraction, respectively. For DBBP/DBN choleic acid, much higher trap concentrations (10^{-1} mole fraction) are used. Therefore, we expect sharp cut-off and significant decrease in the critical concentration. Figure 2, however, does not show this behavior. The results demonstrate that long range interaction between molecules further apart than nearest does not occur.

Distribution of Donors and Acceptors

For DBBP/DBN doped into polymer matrix, the energy transfer efficiency α approaches unity at 20% of DBN concentration, as shown in Figure 3. The distance between molecules is ≈ 7.2 Å and long range interaction between molecules further apart than nearest or next nearest neighbors occur by a superexchange interactions.^{2a,13-15} Some simple approximate analytical solutions have been given for the critical concentration C_c as a function of interaction range and have been verified by extensive simulation.¹ C_c decreases as the interaction range n increases, when n is defined as the maximum number of nearest neighbor bonds over which an interaction can occur. Experimentally, the critical concentration for an DBBP/DBN doped into polystyrene was deter-

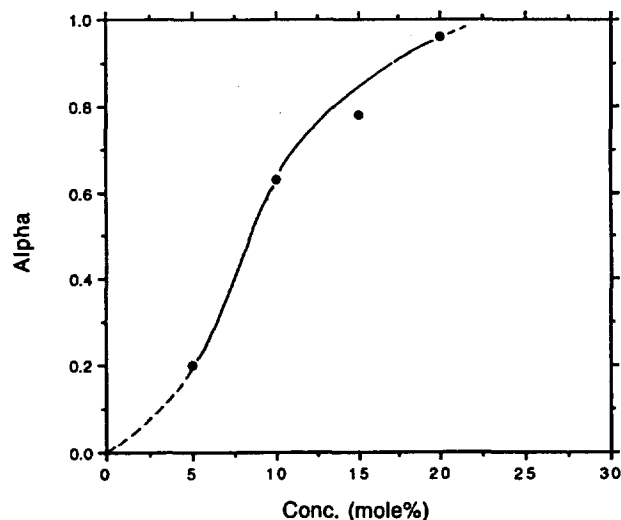


Figure 3. Fraction of phosphorescence from acceptor as a function of acceptor concentration (mole fraction) for DBBP/DBN doped into polystyrene.

mined to be 0.08.⁶

For stoichiometric DBN choleic acid crystal, every donor molecule has neighbors occupied by acceptor molecules. The experimental value of α for 20% DBN choleic acid crystals (with 2% DBBP) at 4.2 K was determined to be 0.52.⁶ For DBBP/DBN doped into polystyrene, α would equal 1. This much smaller value for DBBP/DBN choleic acid crystals implies that the probability of the excited donor find the acceptor in the nearest neighbor within donor's lifetime (2.75 ms)⁶ is much smaller than for the DBBP/DBN doped into polystyrene due presumably to differences of the molecular orientations and to the large distance between guest molecules since the hopping rate falls off exponentially with distance.

The experimental value of $\alpha=0.52$ means that 52% of the total number of excitons is trapped. A 10^6 site square lattice that filled with 20% acceptor and 2×10^4 randomly distributed donors was simulated. Cyclic boundary conditions were used. If trapping is assumed to be diffusion limited, i.e. the ratio of the number of reactive collisions to the number of total collisions is 1, the energy transfer efficiency α would be the ratio of the number of donors neighbored by acceptor to the number of total donors. The ratio was determined by CMLT. The results are shown in Figure 2 and compared with the experimental results. The values of α obtained by the computer simulation for two-dimension are in good agreement with the experimental values obtained experimentally.⁶ Therefore we conclude that trapping is diffusion limited.

For DBBP/DBN doped into polystyrene, a graph of α versus concentration exhibits an abrupt transition from $\alpha=0$ to $\alpha=1$ around a critical concentration of 0.08, as shown in Figure 3. This critical concentration is characteristic of cluster percolation and long range interaction, which is reflected in α because a DBBP excitation samples a large number of sites during its lifetime. In choleic acid only 52% is trapped, and α is restricted by single range interaction due to large distance between molecules.

Energy Transfer Dynamics

In the stoichiometric DBBP/DBN choleic acid, which is filled with DBN and a small amount (2% mole fraction) of DBN, only one species (DBBP) is excited. Instant trapping to the other species (DBN) is assumed. In the DBBP/DBN choleic acid, the exciton decays through one of the following processes: (1) unimolecular decay, (2) trapping, or (3) annihilation (*i.e.* meeting another exciton at the same site). This partitioning has a large effect on the yield of phosphorescence, sensitized phosphorescence, and delayed fluorescence. We neglect annihilation process since small number of donors are used.^{4,5}

DBBP transfer excitation to the nearest neighbor DBN molecules *via* an exchange interaction.¹⁶ The triplet exciton transfer rate between molecules at a distance r was found to be¹⁷

$$W(r) = k \exp[\gamma(d-r)] \quad (3)$$

where γ is spectral overlap between donor and acceptor, d is the critical distance. At low concentrations (up to 5 mol%), energy transfer is not very significant, due to the large intermolecular distances, and the depopulation of the excited state density is controlled mainly by the unimolecular decay process. Therefore the energy transfer efficiency α is similar for both the choleic acid and the polystyrene systems. As the concentration increases, the separation between molecules decreases and the energy transfer rate increases exponentially as a function of distance. For DBBP/DBN doped into polystyrene, the critical concentration (where $\alpha=0.5$) is found to be 0.08, and calculated critical distance is about 11 Å. These values compare with those found in other systems, *e.g.*, the critical concentrations are 0.03, 0.06-0.07, and 0.05 for benzene, naphthalene, and phenazine, respectively,¹⁸ and the critical distances are 11-18 Å for aromatic molecule systems.¹⁹

Computer simulation was carried out to determine the average distance between a donor and an acceptor at 20 mol% acceptor concentration in both the choleic acid and the polystyrene systems. In the simulation, molecules were generated in the model space and assigned random coordinates x_i, y_i, z_i . To satisfy the condition that molecules do not overlap each other, any separation, $[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}$, smaller than a molecular diameter was not allowed. The nearest-neighbor distance for each molecule was determined. Periodic boundary conditions were used. The average distance between neighbors was found to be 19.4 and 7.2 Å for the choleic acid and polystyrene systems, respectively. By using eq. (3) for DBBP/DBN doped into polymer, where the average neighbor distance is 7.2 Å, one calculates that during the lifetime of DBBP (2.75 ms),⁵ an excitation makes about 3 steps. It is not clear whether we can use it for the choleic acid crystal system. Using eq. (3) we get a transfer time of about 17.5 ms, giving about 0.15 steps within the triplet lifetime (2.75 ms). The result implies that energy transfer between molecules further apart than nearest is not allowed for the choleic acid. However this estimate, which neglects the orientation dependence of the interaction, is inconsistent with the experimental α value. The actual hopping time should be much faster. This may be a result of the particular geometry of the guest molecules

in the present system (effectively linear topology), or perhaps due to a different exciton-phonon interaction. It has been observed that the sensitized phosphorescence of acceptors containing a heavy atom is substantially stronger than the sensitized phosphorescence of acceptors of the same moiety without the heavy atom.²⁰⁻²² The dominant difference between DBBP/DBN doped into polymer and DBBP/DBN choleic acid crystals with respect to energy transfer therefore appears to be due to the increasing spacings and the orientation of the guest molecules.

In DBBP/DBN doped into polystyrene, the energy transfer rate is 8.4×10^2 /sec. For the choleic acid system, the energy transfer rate is reduced by a factor of 15. Therefore a walker decays unimolecularly, if no trapping occurs.

Summary and Conclusions

Cluster distributions for different concentrations of DBN in DBBP/DBN choleic acid were determined by a computer simulation to test whether the experimentally observed change in the triplet excitation energy transfer efficiency α is due to the cluster distribution of the molecules. The results of the simulation demonstrate that the trapping is diffusion limited and long range interaction between molecules further apart than nearest does not occur. The energy transfer rate is reduced by a factor of about 15 in DBBP/DBN choleic acid relative to that in DBBP/DBN doped into polystyrene due to the larger distance between the molecules, and the energy transfer topology changes from three to two-dimensional due to the change in molecular orientations and spacing.

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References

- Francis, A. H.; Kopelman, R. In *Topics in Applied Physics*; Yen, W. M., Selzer, P.M., Eds.; Springer-Verlag: Berlin Heidelberg, New York, 1981; vol 49, p 241.
- (a) Kopelman, R.; Monberg, E. M.; Ochs, F. W. *Chem. phys.* **1977**, *21*, 373. (b) Kopelman, R. *J. Phys. Chem.* **1976**, *80*, 2191. (c) Kopelman, R. In *Topics in Applied Physics*; Fong, F. K., Ed.; Springer: Berlin, 1976; vol 15, ch 5. (d) Hoshen, J.; Kopelman, R.; Monberg, E. M. *J. Stat. Phys.* **1978**, *19*, 219.
- Kook, S.-K.; Hanson, D. M.; Kopelman, R. *J. Phys. Chem.* **1993**, *97*, 12339.
- Lin, Y.; Hanson, D. M. *J. Phys. Chem.* **1987**, *91*, 2279.
- Lin, Y. Ph.D. Dissertation, Department of Physics, State University of New York at Stony Brook, 1987.
- Kook, S. K.; Hanson, D. M. *J. Phys. Chem.* **1993**, *97*, 9578.
- Giglio, E. *J. Mol. Struct.* **1981**, *75*, 39.
- Ferro, D.; Quagliata, C.; Giglio, E.; Piacente, V. *J. Chem. Eng. Data* **1981**, *26*, 192.
- Herndon, W. C. *J. Chem. Educ.* **1967**, *44*, 724.
- Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London and Philadelphia, 1985; p 52.
- Hoshen, J.; Kopelman, R. *J. Chem. Phys.* **1976**, *65*, 2817.

12. Hoshen, J.; Kopelman, R. *Phys. Rev.* 1976, B14, 3438.
13. Allgren, D. C.; Monberg, E. M.; Kopelman, R. *Chem. Phys. Lett.* 1979, 64, 122.
14. Sternlicht, H.; Nieman, G. C.; Robinson, G. W. *J. Chem. Phys.* 1963, 38, 1326.
15. Hong, H-K; Kopelman, R. *J. Chem. Phys.* 1971, 55, 724.
16. Craig, D. P.; Walmsley, S. H. *Excitons in Molecular Crystals*; Benjamin: New York, 1968.
17. Dexter, L. *J. Chem. Phys.* 1953, 21, 836.
18. Blumen, A.; Silbey, J. *Chem. Phys.* 1979, 70, 3707.
19. Strambini, G. B.; Galley, C. *Chem. Phys. Lett.* 1976, 39, 257.
20. Gobov, G. V.; Konashenko, V. I. *Opt. Spectrosc.* 1977, 43, 622.
21. Gobov, G. V.; Surin, N. M. *Vibronic Spectra of Aromatic Compounds*; Smolensk: Moscow, 1978; p 31.
22. Gobov, G. V.; Yudnikov, V. V.; Yurchenko, A. I. *Present-Day Aspects of Fine-Structure and Selective Spectroscopy*; Smoleusk: Moscow, 1984; p 199.

Synthesis and Characterization of Air Stable σ -Bonded *ortho*-carborane Manganese Metal Complexes 1-[Mn(CO)₅]-2-R-1,2-closo-(σ -C₂B₁₀H₁₀) and Their Conversion to the Stable *ortho*-carborane Substituted Fischer-type Carbene Complexes 1-[(CO)₄Mn=C(OCH₃)(CH₃)]-2-R-1,2-closo-C₂B₁₀H₁₀ (R=CH₃, C₆H₅)

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The metal-carbon σ -bond cluster complexes 1-Mn(CO)₅-2-R-1,2-C₂B₁₀H₁₀ (R=CH₃ **Ia**, C₆H₅ **Ib**) have been prepared in good yields from readily available carboranyl lithium complexes, 1-Li⁺-2-R-1,2-C₂B₁₀H₁₀⁻ (R=CH₃, C₆H₅), by direct reaction with (CO)₅MnBr. These manganese metal complexes are rapidly converted to the corresponding manganese metal carbene complexes, 1-[(CO)₄Mn=C(OCH₃)(CH₃)]-2-R-1,2-C₂B₁₀H₁₀ (R=CH₃ **IIIa**, C₆H₅ **IIIb**), via alkylation with methyllithium followed by O-methylation with CF₃SO₃CH₃. The crystal structure of **IIIb** was determined by X-ray diffraction. Thus, complex **IIIb** crystallizes in the orthorhombic space group P2₁2₁2₁ with cell parameters $a=15.5537(5)$, $b=19.0697(5)$, $c=7.4286(3)$ Å, $V=2203.4(1)$ Å³, and $Z=4$. Of the reflections measured a total of 3805 unique reflections with $F^2 > 3\sigma(F^2)$ was used during subsequent structure refinement. Refinement converged to $R_1=0.053$ and $R_2=0.091$. Structural studies showed that the manganese atom had a slightly distorted pseudo-octahedral configuration about the metal center with the carbene and *ortho*-carborane occupying the equatorial plane *cis*-orientation to each other.

Introduction

A series of extremely stable anionic chelated *ortho*-carborane-transition metal complexes containing unusually stable carbon-metal σ -bonds has been reported.¹⁻⁵ Previous study⁵ indicated that an extensive series of stable neutral manganese(I) carborane complexes incorporating the 1,2-C₂B₁₀H₁₁⁻, 1,10-C₂B₈H₉⁻, and 1,10-C₂B₈H₈²⁻ ligands through metal-carbon σ -bonds could be prepared. We now wish to report a compilation of results obtained on carborane 1-R-1,2-C₂B₁₀H₁₁ containing manganese(I)-carbon σ bonds and further conversion to a corresponding metal carbene species.

Thus, metal carbene complexes in which a carboranyl group is directly attached to the manganese metal in a σ -bonded fashion adjacent to the metal carbene moiety are now to be studied. Cluster complexes of transition-metals in which the metal atoms are directly bound are of interest

for the evidence they provide the ability of cluster to transmit its influence to the metal. Recent study⁶ of carboranyl metal carbene system in which metal and carborane are separated by one atom, have shown that some metal-carborane interaction occurs in such compounds.

In this paper we wish to report on progress made towards the syntheses of σ -bonded *ortho*-carborane manganese metal complexes and the formation of new manganese carbene complexes is discussed. Due to our interest in the structural features of manganese carbene complexes a single crystal X-ray diffraction determination of 1-[(CO)₄Mn=C(OCH₃)(CH₃)]-2-C₆H₅-1,2-C₂B₁₀H₁₀ **IIIb** was carried out.

Experimental Section

Methods and Materials. The majority of solvents were of reagent grade and were used without further purification.