Coordination Chemistry Reviews, 97 (1990) 167–178
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PHOTOCHEMICAL BEHAVIOR OF PHOSPHORUS LIGANDS-SUBSTITUTED DIMANGANASE CARBONYLS

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SUMMARY

Photochemistry of ax,ax-$L(OC)_4Mn$-$Mn(CO)_4L$ (L=$P(n\text{-}Bu)_3$) (S) in cyclohexane has been studied by means of laser photolysis with a uv-vis detection system. In addition to the transient absorption features due to the occurrence of primary processes, (1) Mn–Mn bond cleavage to give $Mn(CO)_4L$ (I), and (2) CO dissociation without metal-metal bond cleavage to give $Mn_2(CO)_7L_2$ (II). Two absorption features are observed: The one is attributed to the formation of a secondary intermediate (IV), whose structure is assigned to ax,eq-$L(OC)_4Mn$-$Mn(CO)_4L$, from the reaction of II with CO. The other appears to show the possibility of a third primary process (3) in the photolysis system of the disubstituted $L(OC)_4Mn$-$Mn(CO)_4L$. A whole photochemical reaction scheme is proposed in Scheme 2 and the nature of the intermediates, IV and unknown III, is discussed.

INTRODUCTION

When we encountered our first laser flash photolysis results (ref. 1) showing the existence of the second primary photochemical process in $Mn_2(CO)_{10}$ other than the metal-metal bond homolysis to give 17 electron radical fragments (Process 1) in hydrocarbon solvents, there were only a few reports (ref. 2,3) in which presence of a second photochemical process for $Mn_2(CO)_{10}$ system was implicated. Since this compound has been considered a prototype for photochemistry of di- and poly-nuclear metal carbonyls with single metal-metal bond (ref. 4), we aimed at elucidating the nature of the second primary process.

The clue for the second process was the appearance of the transient absorbance in the region from 430–600 nm (λmax 500 nm) in addition to the concurrent appearance of the other transient absorbance in the region over 700 nm (λmax 830 nm). The latter had been well documented to be due to the formation of $Mn(CO)_5$ via (Process 1) (ref. 5,6) and shows characteristic features of its very short life time, 2nd order decay kinetics, and the quenching effect of CCl_4 as well as no effect of added CO on the kinetics. Although the chemistry of the 17 electron species has been a very active research area (ref. 7), it is not referred here in detail.

For the intermediate giving rise to the second transient absorption (λmax 500 nm), we proposed $Mn_2(CO)_9$, which is formed by losing CO with retention of

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Mn-Mn bond (Process 2), from a certain amount of evidence including the decay kinetics under degassed or Ar atmospheric conditions (slower, 2nd order) and under 1 atmospheric pressure of CO (faster, pseudo 1st order), the existence of an isosbestic point in the transient spectral change of the CH_3CN added system whose final absorption spectrum was similar to that of $Mn_2(CO)_9(CH_3CN)$ giving ε_{500} (1000 M^{-1}) for $Mn_2(CO)_9$ (ref. 8). Rothberg et al reported that these two absorptions are observable even 25 ps after excitation and proposed formation of similar intermediate, $Mn_2(CO)_9(EtOH)$, in ethanol solution (ref. 9).

In addition, the associative nature of the substitution reaction on $Mn(CO)_5$ with L was verified for the first time by studying the additive effects of CH_3CN and $P(n\text{-}Bu)_3$ (ref. 8). A similar conclusion was reported almost concurrently by Hepp et al (ref. 10) using a low temperature photolysis technique in frozen and fluid media with IR detection by which presence of a bridging CO was shown. Dunkin et al (ref. 11) reported an asymmetric CO bridging for it by matrix experiments involving plane polarized lights. Bridging CO in $Mn_2(CO)_9$ was also detected in solution at room temperature by Church et al (ref. 12) using laser photolysis with fast IR detection. Walker et al and Herrick et al (ref. 13,14) also confirmed the existence of two primary processes for $Mn_2(CO)_{10}$ and some phosphines or phosphites disubstituted compounds by conventional flash photolysis with uv-vis detection. Thus, mechanistic study on $Mn_2(CO)_{10}$ photochemistry has been greatly developed in these years (ref. 16-18). In Scheme 1, the photochemical passes for $Mn_2(CO)_{10}$ are shown and in Table 1 the rate constants for the recombination reaction of $Mn(CO)_5$ (Reaction 5) and of $Mn_2(CO)_9$ with CO (Reaction 6) reported by these various laboratories. These kinetic data are in agreement with each other.

This research has extended to manganese carbonyl compounds containing hetero metal-metal bond, Mn-Re (ref. 19-21), Fe-Mn and Mo-Mn (ref. 22,23), and also with Mn-non transition metal bond, Mn-Sn-Mn(ref. 24), Mn-Hg-Mn (ref. 25). In all these cases, the existence of the primary process of CO loss without metal-metal bond cleavage has been proved.

We observed a very long-lived absorption, in addition to two independent absorptions due to formation of $Mn(CO)_4L$ and CO lost intermediate without Hg-Mn bond homolysis, in the laser photolysis experiments of $Hg[Mn(CO)_4L]_2$ system. This led us to scrutinize the related system, $L(OC)_4Mn\text{-}Mn(CO)_4L$, although the properties of intermediates of the processes (1) and (2) were reported for some phosphorus ligands (ref. 13,14), and to find much composite photochemistry than that of $Mn_2(CO)_{10}$.

We describe a scheme for photochemistry of $L(OC)_4Mn\text{-}Mn(CO)_4L$ ($L=P(n\text{-}Bu)_3$) given chiefly from flash photolysis study with uv-vis detection.

SCHEME 1

Photochemical passes of $Mn_2(CO)_{10}$.

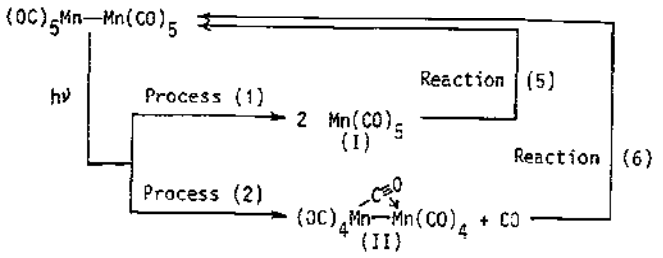


TABLE 1

Recombination rate constants of $Mn(CO)_4L$ and of $Mn_2(CO)_7L_2$ in cyclohexane at room temperature.

		Rate Constants($M^{-1}s^{-1}$)				Ref.
$Mn(CO)_4L$	L=CO	6×10^8[a]				5
		9.5×10^8				6,13
		9×10^8				8
		1×10^9[b], 7×10^8				12
	L=	$P(nBu)_3$	$P(iBu)_3$	$P(iPr)_3$		
		1×10^8	2×10^7	4×10^6		13
		2×10^8	7×10^7	3×10^6		27
$Mn_2(CO)_7L_2$	L=CO	1.2×10^5				8
		4.3×10^5[c]				15
		2.9×10^5[c]				14
		2.7×10^5[b], 5 12×10^5				12
	L=	$P(OiPr)_3$	$P(nBu)_3$	$P(iBu)_3$	$P(iPr)_3$	
		4.0×10^4	9.1×10^3	2.3×10^3	1.4×10^2	14
		3×10^4	9×10^3	2×10^3	2×10^2	27

[a]Observed in ethanol.
[b]Observed in n-heptane.
[c]Obtained from pseudo first order kinetics under 1 atmospheric pressure of CO.

METHOD

$Mn_2(CO)_8(P(n\text{-}Bu)_3)_2$ was prepared by the literature method (ref. 13). Tri-n-butylphosphine (Tokyo Kasei) and cyclohexane (Wako Pure Chemicals, spectrosol for fluorometry) were used as received.

Sample solutions were prepared in vacuo. Solvent stored on K-Na alloy was added in the sample compartrent after measuring its volume and the sample cells were hermetically sealed. Then, CO or Ar gas was admitted into them through a side arm with a teflon cock. Photocells of 1mm or 10 mm length were used.

The laser photolysis system (ref. 26) used in the present study is shown in Fig. 1. The third harmonics (355 nm, fwhm 20 ns, ca. 40 mJ/pulse) of the Q-switched Nd-YAG laser(J.K.Laser's Model HY 500) was used as excitation light source. A probe light source was a pulsed or continuous Xe lamp (Ushio UXL-150D, 150W). The transmitted light beam through a sample cell was led into a Ritsu monochromator (Model MC-20N), and the output from a photomultiplier attached to the exit slit of the monochromator was displayed on a Tektronix oscilloscope (Model 7904).

RESULTS AND DISCUSSION

General Feature of the Transient Absorption Spectra

The transient spectra of ax,ax-$L(OC)_4Mn\text{-}Mn(CO)_4L$ (L=$P(n\text{-}Bu)_3$) system under 1 atmospheric pressure of CO in cyclohexane after photolysis by excitation wavelength 355nm is shown in Fig. 2. Like the parent carbonyl (L=CO), the present compound S (L=$P(n\text{-}Bu)_3$ unless otherwise stated) shows the appearance of two absorbances in the range at 490-620 nm (λmax 530 nm) and in the range over 700 nm (λmax 830 nm) (ref. 13,14) immediately after excitation. These are due to the formation of $L(OC)_4Mn\text{-}Mn(CO)_3L$ (II) by Process (2) and to the formation of $Mn(CO)_4L$ (I) by Process (1), respectively. The decay kinetics and the effects of additives, Ar, CO and CCl_4 on them are in agreement with above assignment. The negative absorbance in the spectrum at 1 us after excitation can be undoubtedly ascribed to bleaching of ax,ax-$L(OC)_4Mn\text{-}Mn(CO)_4L$.

The absorbance around at 800 nm disappears by following second order kinetics under either Ar or CO atmosphere (Fig. 3a) and the decay changes into the pseudo-first order with addition of CCl_4. The one with λmax at 530 nm shows very long life under Ar atmosphere, whereas its decay becomes faster under 1 atmospheric pressure of CO to follow the first order kinetics (Fig. 3b). Addition of CCl_4 has no effect of its appearance and decay. This evidence shows that the two processes (1) and (2) also take place concurrently in this system (ref. 27). Recombination rate constants of $Mn(CO)_4L$ (I) (Reaction 5) and of $Mn_2(CO)_{7-2}$ (II) with CO (Reaction 6) for L=$P(n\text{-}Bu)_3$ and some other L are listed in Table 1. Steric effect of Ls on the rate of Reaction (6) is

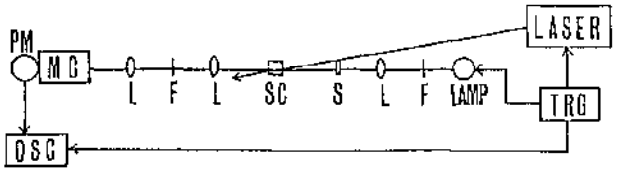


Fig. 1. Block diagram of time-resolved spectroscopy apparatus. TRG: trigger circuit, F: filter, L: lens, S: mechanical shutter, SC: sample cell, MC: monochromator, PM: photomulitiplier, OSC: oscilloscope.

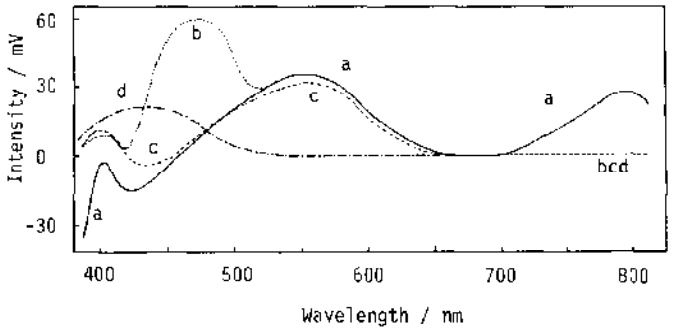


Fig. 2. Transient absorption spectra of $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$ in cyclohexane after the 355 nm laser pulse: a, at 1 μs; b, at 100 μs; c, at 2 ms; d, at 20 ms.

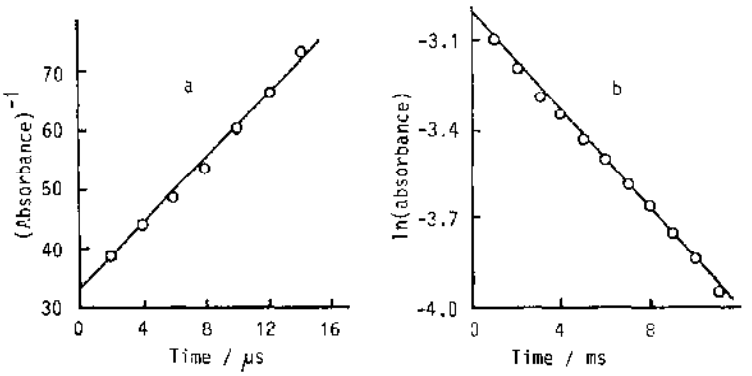


Fig. 3. Time dependence of absorption of $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$ under 1 atmospheric pressure of CO in cyclohexane after 355 nm excitation monitored at: a, 800 nm; b, 550 nm.

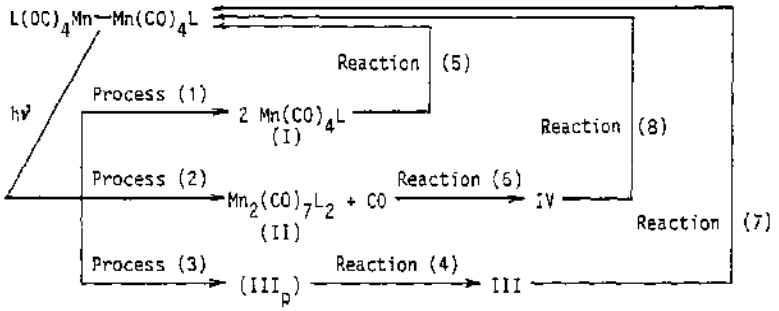
visualized in Fig. 4. The effects of L on rates of Reactions(5) and (6) have already been discussed for some Ls (ref. 13,14).

Fig. 2, however, suggests a more composite profile of the photochemistry of $L(OC)_4Mn\text{-}Mn(CO)_4L$ ($L=P(n\text{-}Bu)_3$). We have observed a growth and decay of new absorbance in the range of 430-510 nm (λmax 470 nm). The growth of absorbance at 470 nm is completed within 100 μs, which appears to be almost coincidental with the decay of $Mn(CO)_4L$ (I) at 780 nm and the absorbance at 470 nm disappears within 2 ms (Fig. 5a). In addition, a slow growth of another new absorbance in the range of 400-470 nm (λmax 430 nm) has been observed under CO atmosphere (Fig. 5b). The rise in absorbance at 420 nm is completed within 20 ms and corresponds well with the decrease of the absorbance at 550 nm (Fig. 5c). The absorbance at 400 nm and at 470nm have no change in the time range 2 - 20 ms showing there are isosbestic points at 400 nm and at 470 nm between these two absorptions.

Based on these spectral changes and following results and discussion, we propose Scheme 2 for the photochemistry of $L(OC)_4Mn\text{-}Mn(CO)_4L$, which is in contrast with the simple Scheme 1 for L=CO. This photolytic system is shown to be cleanly reversible to ax,ax-$Mn_2(CO)_8L_2$ under CO atmosphere from the IR spectroscopic analysis of the photolytic system with one shot of Xe flash (10 μs whfm) under complete absorption conditions at room temperature.

SCHEME 2

Photochemical reaction processes of $L(OC)_4Mn\text{-}Mn(CO)_4L$.



Occurrence of the secondary reaction (6) after the primary process (2)

In addition to the congruence of the growth of absorbance at 420 nm with the decrease of that at 550 nm under CO atmosphere, under Ar atmosphere no growth of absorbance in the range of 400-460 nm and no decrease of absorbance in the range of 500-600 nm has been observed in the time range 2-20 ms showing that a

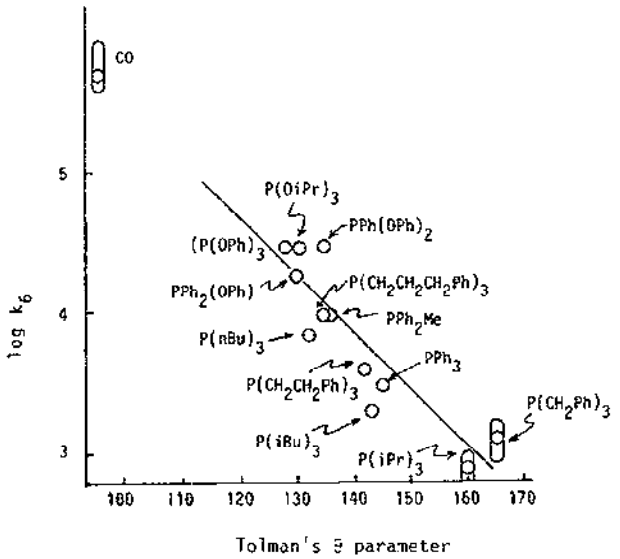


Fig. 4. Plots of the rate constants obtained with various L for the reaction (6) against Tolman's θ values (Ref. 28).

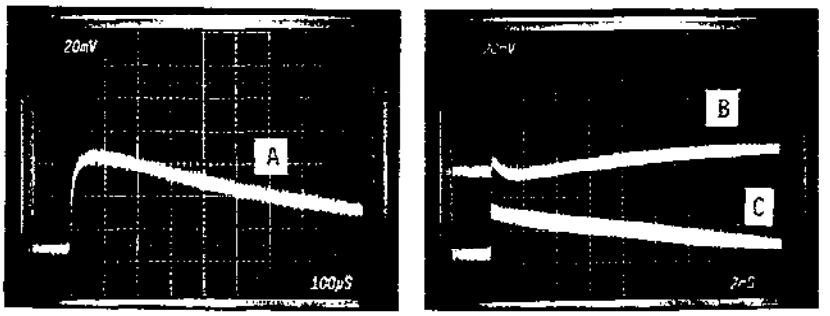


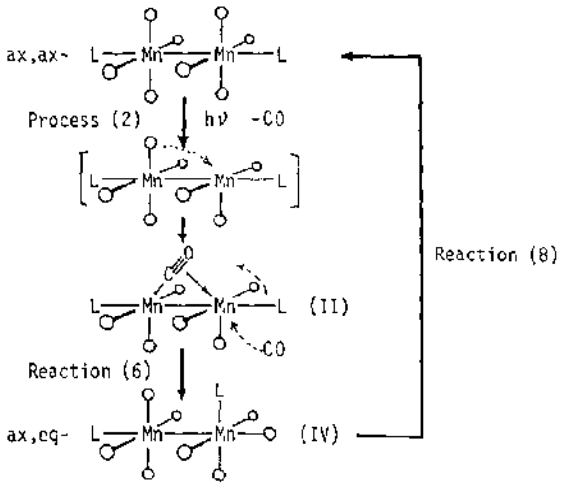
Fig. 5. Oscilloscope traces obtained from laser photolysis of $Mn_2(CO)_8L_2$: a, monitored at 470 nm; b, monitored at 420 nm; c, monitored at 550 nm; ordinate, 20 mV / 1 div.; abscissa, a, 100 μs / 1 div.; b and c, 2 ms / 1 div.

new intermediate (IV) responsible for the absorbance at around 420 nm is produced from the primary intermediate $Mn_2(CO)_7L_2$ (II) of Process (2) by reacting with CO (Reaction 6). Time dependence of the growth of 420 nm absorbance is shown in Fig. 6c.

IV most likely is to be ax,eq-L$(OC)_4$Mn-Mn$(CO)_4$L and the following reaction mechanism is postulated in Scheme 3:

SCHEME 3

Reaction mechanism of Reaction (6) after Process (2) to the starting compound.



The presence of IV leads us to a structure for II having bridging CO with two L being at diaxial position. Photoelimination of equatorial CO has been shown lately by Poliakoff et al in the photolysis of $Re_2(CO)_{10}$ in a rigid low temperature medium (ref. 29). The reversibility of the present photolysis system under CO atmosphere and no formation of $Mn_2(CO)_9L$ as a final product in the one Xe flash shot experiment mentioned above shows that only equatorial CO is eliminated in Process (2). A diaxial structure without CO bridging in which the equatorial position is kept vacant is eliminated since it may give directly the starting material by recombination with CO at the position.

As have been proven in $Mn_2(CO)_{10}$ (ref. 10-12) and $MnRe(CO)_{10}$ (ref. 19-21), the occurrence of bridging CO in II is reasonably conceivable. The incoming CO may attack the Mn atom from the opposite side to the bridging CO followed by shift of L from axial to equatorial position to give IV.

It has been reported that the ax,eq-L(OC)4Re-Re(CO)4L (L=P(n-Bu)$_3$) which show their uv-vis absorption in a longer wavelength region than those of

thermodynamically stable diax-isomers, and isomerize irto the diax-form within several hours at room temperature (ref. 30). The ax,eq-form is more congestive sterically in the manganese system than in the rhenium system and faster in isomerization to the final diaxial form.

Possibility of another primary process (3).

The intensity of absorbance at 470 nm stays constant in the time region later than 2 ms after excitation showing that this overlaps the component at this wavelength of the absorption with λmax 530 nm. The growth and decay of the absorption with λmax 470 nm obey the first order kinetics (Fig. 6a,b) and the rate constants are 4×10^4 s^{-1} and 2×10^3 s^{-1}, respectively. The bleach in absorbance at 380 nm recovers with three steps each of which corresponds to the Reaction (5), the decay of the absorbance at 470 nm, and Reaction (6) under CO atmosphere. This fact shows that this component decays back the starting compound directly.

Rates of the growth and disappearance of the absorbance at 470 nm are not influenced by additives (Ar and CO as covering gas, and P(n-Bu)3) at all, and are little influenced by solvents (cyclohexane, benzene, 2-methyltetrahydrofuran). Observed effects of additives and solvents strongly suggest that an intermediate III, to which the absorbance is attributed, is a non-ionic species with no ligand loss.

To understand the origin of III, the possibility of III being a secondary product from I must be first taken into consideration because of the rather coincident growth of III with that of the decay of I although the order of the rate expressions is different. Another observation which is not inconsistent with this possibility is a dependence of peak intensity and growth time of the absorbance at 470 nm on the concentration of the added CCl_4. The profile shown in Fig. 3a is not altered at low concentration range of 5×10^{-3} M, whereas in the range of 2×10^{-2} M the timing of growth becomes shorter and the intensity decreases with increase of CCl_4 concentration although decay of the absorbance suffers no change. At the concentration of 1×10^{-1} M only absorbance due to II remains from the first.

However, the possibility of radical origin may be ruled out from the following arguments: 1) In the photolysis system of the present compound with 266 nm excitation laser light, the formation of III together with II could be observed, whereas the formation of I was not detected. 2) The appearance of III depends on the nature of the phosphorus L as is shown in Table 2. ax,ax-$L(OC)_4Mn$-$Mn(CO)_4L$ gives I and II by excitation with 355 nm laser light for all L. However it does not form III when L is bulky phosphines, PPh_3, $P(i\text{-}Pr)_3$, and $P(Cyclohexyl)_3$. And 3) The corresponding absorbance around 470

nm does not appear in the photolysis system of $(OC)_5Mn\text{-}Mn(CO)_4L$ (L=$P(n\text{-}Bu)_3$, PPh_2Me), mono-substituted analogues, although the occurrence of both processes (1) and (2) is evident in these systems too.

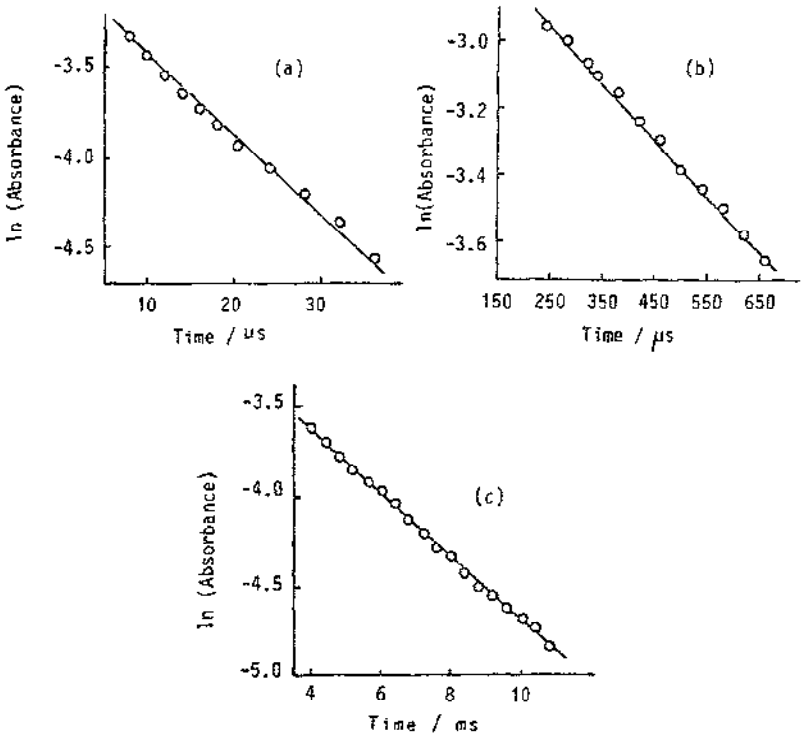


Fig. 6. Time dependence of absorbance of the system: a, growth at 470 nm; b, decay at 470 nm; c, growth at 420 nm.

TABLE 2

Dependence of the formation of III on the nature of L in $L(OC)_4Mn\text{-}Mn(CO)_4L$.

Ligands which give III	Ligands which do not give III
PEt_3 $P(n\text{-}Bu)_3$ $P(i\text{-}Bu)_3$ PPh_2Et $PPhEt_2$ PPh_2Me $P(CH_2Ph)_3$ $P(CH_2CH_2Ph)_3$	$P(i\text{-}Pr)_3$ $P(Cyclohexyl)_3$ PPh_3 CO

Thus, the absorption with λmax 470 nm may show the existence of another primary process (3) in the present laser photolysis system. The rather slow appearance of III requires an unknown primary intermediate III_p to be considered as a precursor for III which can compete with the other two processes. However no evidence for III_p has been obtained spectroscopically so far. III_p must be quenched by CCl_4 (see above). $ClMn(CO)_4L$ may be a consequence of the quenching since the final product of the photolysis system in the presence of excess amount of CCl_4 has been proved to be $ClMn(CO)_4L$ by the one Xe flash experiment with IR detection.

We tentatively propose a bis-CO bridged form (ref. 3) for III which may arise from an vibrationally activated ground state III_p with unknown structure. The dependence of the occurrence of III on the nature of L (Table 2) may be a very important clue for understanding this chemistry. The secondary reaction (6) effect of L on its rate and behavior and the possibility of another process will be published elsewhere (ref. 31).

REFERENCES

1 H. Yesaka, T. Kobayashi, K. Yasufuku and S. Nagakura, Laser photolysis of dimanganese decacarbonyl, Reza Kagaku Kenkyu, 3 (1981) 97-99.
2 J.L. Hughey, IV, C.P. Anderson and T.J. Meyer, Photochemistry of $Mn_2(CO)_{10}$, J. Organometal. Chem., 125 (1977) C49-C52.
3 A. Fox and A. Poe, Nonradical intermediates in the photolysis of decacarbonyldimanganese, J. Am. Chem. Soc., 102 (1980) 2497-2499.
4 G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.
5 W.L. Waltz, O. Hackelberg, L.M. Dorfmann and A. Wojcicki, Pulse radiolysis studies of decacarbonyldimanganese(0) and halopentacarbonylmanganese(I). The pentacarbonylmanganese(0) radical, J. Am. Chem. Soc., 100 (1978) 7259-7264.
6 R.W. Wegman, R.J. Olsen, D.R. Gard, L.R. Faulkner and T.L. Brown, A flash photolysis study of the metal-metal bond homolysis in dimanganese decacarbonyl and dirhenium decacarbonyl, J. Am. Chem. Soc., 103 (1981) 6089-6092.
7 M.C. Baird, Seventeen-electron metal-centered radicals, Chem. Rev., 88 (1988) 1217-1227; and references therein.
8 H. Yesaka, T. Kobayashi, K. Yasufuku and S. Nagakura, Laser photolysis study of the photosubstitution in dimanganese decacarbonyl, J. Am. Chem. Soc., 105 (1983) 6249-6252; Presented at 10th Int. Conference on Organometallic Chemistry, Toronto, Canada, Aug 9-14, 1981.
9 L.J. Rothberg, N.J. Cooper, K.S. Peters and V. Vaida, Picosecond dynamics of solution phase photofragmentation of $[Mn_2(CO)_{10}]$, J. Am. Chem. Soc., 104 (1982) 3536-3537.
10 A.F. Hepp and M.S. Wrighton, Relative importance of metal-metal bond scission and loss of carbon monoxide from photoexcited dimanganese decacarbonyl: Unsaturated, CO-bridged dinuclear species in low-temperature alkane matrices, J. Am. Chem. Soc., 105 (1983) 5934-5935.
11 I.R. Dunkin, P. Haerter and C.J. Shields, Recognition of a semibridging carbonyl group in $Mn_2(CO)_9$ from plane-polarized photolysis of $Mn_2(CO)_{10}$ in Ar matrices at 12 K, J. Am. Chem. Soc., 106 (1984) 7248-7249.
12 S.P. Church, H. Hermann, F.W. Grevels and K. Schaffner, The primary photoproducts of $Mn_2(CO)_{10}$: Direct I.R. observation and delay kinetics of $Mn(CO)_5$ and $Mn_2(CO)_9$ in hydrocarbon solution at room temperature, J. Chem. Soc. Chem. Commun., (1984) 785-786.

13 H.W. Walker, R.S. Herrick, R.J. Olsen and T.L. Brown, Flash photolysis studies of dinuclear manganese carbonyl compounds, Inorg. Chem., 23 (1984) 3748-3752.
14 R.S. Herrick and T.L. Brown, Flash photolytic investigation of photoinduced carbon monoxide dissociation from dinuclear manganese carbonyl compounds, Inorg. Chem., 23 (1984) 4550-4553.
15 K. Yasufuku, H. Noda, J-I. Iwai, H. Ohtani and T. Kobayashi, Laser flash photolysis of dinuclear metal carbonyls, Sci. Papers I. P. C. R., 78 (1984) 193-197.
16 T. Kobayashi, K. Yasufuku, J-I. Iwai, H. Yesaka, H. Noda and H. Ohtani, Laser photolysis study on the photosubstitution in dimanganese- and dirhenium-decacarbonyls, Coord. Chem. Rev., 64 (1985) 1-19.
17 T.J. Meyer and J.V. Casper, Photochemistry of metal-metal bonds, Chem. Rev., 85 (1985) 187-218.
18 R.S. Herrick, Flash photolysis studies of dinuclear manganese carbonyl compounds, Rev. Inorg. Chem., 8 (1986) (1,2) 1-29.
19 S. Firth, P.M. Hodges, M. Poliakoff and J.J. Turner, Comparative matrix isolation and time-resolved infrared studies on the photochemistry of $MnRe(CO)_{10}$, Inorg. Chem., 25 (1986) 4608-4610.
20 S. Firth, P.M. Hodges, M. Poliakoff, J.J. Turner and M.J. Therien, Selective loss of CO in photochemistry of $MnRe(CO)_{10}$: a study using matrix isolation and time-resolved infrared spectroscopy, J. Organometal. Chem., 331 (1987) 347-355.
21 T.J. Oyer and M.S. Wrighton, Photochemistry of $MnRe(CO)_{10}$: Selective loss of CO from manganese and net substitution to yield $Mn(CO)_4(PPh_3)Re(CO)_5$, Inorg. Chem., 27 (1988) 3689-3697.
22 K.R. Pope and M.S. Wrighton, Low-temperature photochemistry of $(\eta^5-C_5R_5)Fe(CO)_2Mn(CO)_5$ (R=H,Me): Substitution by P-donor ligands and kinetics of thermal Fe-Mn bond homolysis, J. Am. Chem. Soc., 109 (1987) 4545-4552.
23 K.R. Pope and M.S. Wrighton, Low-temperature photochemistry of $(\eta^5-C_5H_5)Mo(CO)_3Mn(CO)_5$: Identification of an unexpectedly stable coodinatively unsaturated heterodinuclear carbonyl complex, Inorg. Chem., 26 (1987) 2321-2325.
24 K. Yasufuku, H. Noda, S. Onaka and T. Kobayashi, Photoreaction mechanism of dimethyltin-bis(pentacarbonylmanganese), 2(Sn-Mn), J. Chem. Soc. Jap., (1989) (8) 1403-1405.
25 K. Yasufuku, N. Hiraga, Y. Yamamoto, H. Noda, S. Teratani, S. Onaka and T. Kobayashi, Photochemistry of bis(phosphinetetracarbonylmanganese)mercury, 2(Hg-Mn) and related compounds, Proc. 34th Symposium on Organometallic Chemistry Japan, Kyoto, Japan, November 13-14 1987, p. 43-45; in preparation.
26 S. Yamamoto, M. Hoshino, K. Yasufuku and M. Imamura, Wavelength-dependent photochemical reaction of (u tetraphenylporphinato)bis[dicarbonylrhodium(I)]. Locking of metal ion into ligand, Inorg. Chem., 23 (1984) 195-198.
27 K. Yasufuku, N. Hiraga, K. Ichimura and T. Kobayashi, Laser flash photolysis of phosphine-substituted dimanganese carbonyl compounds, Proc. 7th Int. symposium, Photochemistry and Photophysics of coordination compounds, Elmau, West Germany, March 29-April 2 1987, Springer-Verlag, Berlin, 1987, p.271-274.
28 C.A. Tolman, steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis, Chem. Rev., 77 (1977) 313-348.
29 S. Firth, W.E. Klotzbuecher, M. Poliakoff and J.J. Turner, Generation of $Re_2(CO)_9(N_2)$ from $Re_2(CO)_{10}$: Identification of photochemical intermediates by matrix isolation and liquid-noble-gas techniques, Inorg. Chem., 26 (1987) 3370-3375.
30 P.O. Nubel and T.L. Brown, Photolysis of $Re_2(CO)_{10}$ in the presence of simple olefins. Thermal reactivity of (u-hydrido)(u-alkenyl)dirhenium octacarbonyl compounds, J. Am. Chem. Soc., 106 (1984) 644-652.
31 In preparation.