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Spin Trapping of Radicals Produced by Thermal Homolysis of $L_2Mn_2(CO)_8$

by

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Summary. The reaction of $L_2Mn_2(CO)_8$ (L = PPh_3, $P(OMe)_2Ph$, PEt_3, $PMePh_2$, $P(\underline{p}\text{-}CH_3C_6H_4)_3$, $P(\underline{m}\text{-}CH_3C_6H_4)_3$, $P(OEt)_3$, PEt_2Ph) with nitroso-t-butane at 23°C in a variety of solvents (dichloromethane, toluene, tetrahydrofuran, acetonitrile, acetone) in the dark produces stable nitroxide radicals which have been detected by electron spin resonance spectroscopy. The radicals are identified as the spin adducts $L(OC)_4MnN(O)C(CH_3)_3$. In pyridine solution substitution of the phosphine ligands of the radicals rapidly occurs so that the species trapped from $L_2Mn_2(CO)_8$ (L = PPh_3, PEt_3, $PPh(OMe)_2$, $AsPh_3$) is $(C_5H_5N)(OC)_4MnN(O)C(CH_3)_3$.

Introduction

Spin trapping by nitroso compounds, as well as by other molecules, has been used to study a number of organic radical producing reactions.[1] This technique has also been applied to the study of transition metal centered radicals, particularily pentacyanocobalt(II)[2] and radicals generated by the photochemical homolysis of metal-metal bonded organometallic dimers.[3]

We now report on the use of spin trapping experiments to detect the thermal homolysis of certain metal-metal bonds. In this case the spin trapping experiments offer a useful adjunct to direct esr observation of organometallic radicals produced by homolysis of metal-metal bonds (e.g., the case of $[(C_3H_5)Fe(CO)_3]_2$[4]). The reactions involved in the present systems are set out in eq 1 to 3. So long as the organometallic nitroxide produced in eq 2 is

1) $L_xM\text{-}ML_x \rightleftharpoons 2\ \cdot ML_x$

2) $R\text{-}N{=}O\ +\ \cdot ML_x \rightarrow R\text{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}\text{-}ML_x$

3) $R\text{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}\text{-}ML_x \rightarrow$ unidentified decomposition products.

stable, the technique is useful for probing situations in which the equilibrium of reaction 1 lies in favor of the metal-metal bonded dimer, since the combined effect of reaction 1 and 2 should result in the gradual increase in concentration of the nitroxide radical.

This article involves compounds of the class $[(R_3P)Mn(CO)_4]_2$. Although these species were originally formulated as paramagnetic monomers,[5] further studies have revealed their true dimeric nature.[6-10] The paramagnetism frequently observed in samples of these dimers has been ascribed to the presence of small quantities of Mn(II) impurities.[6,9] Thermal homolysis of $[Ph_3PMn(CO)_4]_2$ has previously been proposed to account for the formation of $Ph_3PMn(CO)_4I$ from the dimer and iodine at 25° in the dark[11] and to account for the kinetics of triphenylphosphite substitution of $[Ph_3PMn(CO)_4]_2$.[12]

Experimental

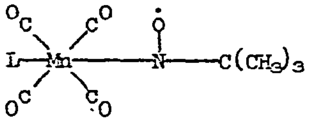
Commercial samples of $Mn_2(CO)_{10}$ (Strem) and nitroso-*t*-butane (Aldrich) were sublimed prior to use. Before use, triethylphosphite was distilled and triphenylphosphine was recrystallized. The other group V ligands were commercial samples that were used as received, except for dimethyl phenylphosphonite which was prepared by the reported procedure.[13] All operations were performed routinely under purified nitrogen using deoxygenated solvents. The complexes $[LMn(CO)_4]_2$ (L = PPh_3, PEt_3, PPh_2Me, PEt_2Ph, $P(OEt)_3$, $P(OPh)_3$ and $AsPh_3$) were prepared as previously described.[7,14] New complexes of this type were obtained by irradiation of solutions of $Mn_2(CO)_{10}$ and L in 1:2 ratio followed by solvent evaporation and recrystallization The following solvents were used: L = $PhP(OMe)_2$, irradiation-cyclohexane, recrystallization-methanol; L = $(p\text{-}CH_3C_6H_4)_3P$, irradiation-benzene, L = $(m\text{-}CH_3C_6H_4)_3P$

irradiation-benzene, recrystallization-benzene/pentane. The new products were identified by satisfactory elemental analysis and by their infrared spectra.

Preparation of ESR Samples. A 10 ml round bottom flask equipped with a 5 mm od sidearm tube, which served as the esr sample holder, was charged with 1 x 10^{-5} mole of $Mn_2(CO)_8L_8$ and 4 x 10^{-5} mole of $[(CH_3)_3CNO]_2$. This flask was attached to a vacuum line *via* a stopcock and a standard taper joint. The assembly was evacuated and 1 to 2 ml of solvent, which had been previously dried and degassed, was distilled onto the sample. The sample solution was transferred to the sidearm for measurement of the esr spectrum. For the study of thermal reactions, the samples were prepared in a darkened room with the apparatus carefully wrapped with aluminum foil. Electron spin resonance spectra were measured on a Varian E-4 spectrometer, which was calibrated with Fremy´s salt.

Results

The esr spectrum obtained from a mixture of $Mn_2(CO)_8(PPh_3)_2$ and nitroso-*t*-butane in tetrahydrofuran solution is shown in Figure 1. The spectrum shows hyperfine coupling to one nitrogen nucleus (I = 1, 99.6% natural abundance), one manganese nucleus (I = 5/2, 100 % natural abundance), and one phosphorus nucleus (I = 1/2, 100% natural abundance). The radical is identified as the spin



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adduct **1** (L = PPh_3) which is produced by reaction 2. Similar spectra are observed in a variety of other solvents, except for pyridine (*vida infra*). The coupling constants obtained from these and other spectra are set out in Table I. One other feature of the spectrum in Figure 1 is noteworthy. The intensity of the spectrum continues to grow over at least a two hour period after the initial sample preparation. Eventually, however, the spectrum intensity begins to decay.

Other dimers, $Mn_2(CO)_8L_2$ where L = PEt_3, PPh_2Me, PEt_2Ph, P(*p*-$CH_3C_6H_4)_3$, P(*m*-$CH_3C_6H_4)_3$, $PPh(OMe)_2$ and $P(OEt)_3$, produce similar spectra with coupling to

Table I

ESR Parameters for Nitroxides, $L(CO)_4Mn-\overset{O\cdot}{\overset{|}{N}}-C(CH_3)_3$

Starting Complex	Solvent	a(N)[a]	a(Mn)[a]	a(P)[a]
$Mn_2(CO)_8(PPh_3)_2$	dichloromethane	19.44	11.33	3.86
	toluene	19.41	11.35	3.43
	tetrahydrofuran	19.41	11.35	3.43
	acetone	19.57	11.37	3.66
	pyridine	17.92	11.69	—[b]
$Mn_2(CO)_8(PEt_3)_2$	dichloromethane	18.80	10.90	4.62
	pyridine	17.92	11.69	—[b]
$Mn_2(CO)_8(PPh_2Me)_2$	dichloromethane	19.16	11.07	5.44
$Mn_2(CO)_8[P(\underline{p}-CH_3C_6H_4)_3]_2$	dichloromethane	19.37	11.30	3.95
$Mn_2(CO)_8[P(\underline{m}-CH_3C_6H_4)_3]_2$	dichloromethane	19.53	11.39	3.86
$Mn_2(CO)_8[PPh(OMe)_2]_2$	dichloromethane	19.24	10.77	6.09
	acetonitrile	19.30	10.80	5.97
	pyridine	17.92	11.69	—[b]
$Mn_2(CO)_8[P(OEt)_3]_2$	dichloromethane	19.17	10.97	6.62
$Mn_2(CO)_8(AsPh_3)_2$	dichloromethane	—[c]	—[c]	—[c]
	pyridine	17.92	11.69	—[b]
$Mn_2(CO)_8(PEt_2Ph)_2$	dichloromethane	19.17	11.11	5.58
$Mn(CO)_5^-$[d]		17.39	12.56	—

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[a] Coupling constant in Gauss (ave. values), reproducible to ± .05 G.

[b] No coupling to phosphorus, but coupling to pyridine, a(N) = 0.58 G.

[c] Too feeble in intensity for analysis.

[d] $(CO)_5Mn(O)NC(CH_3)_3$ obtained by oxidation with tropylium ion, data from reference 21

a single nitrogen, manganese and phosphorus detected in each case. As might be anticipated, changes in the substituents on the phosphorus ligands produce changes principally in the phosphorus coupling constant. These spectra also exhibit dynamic growth in intensity over at least a two hour period. Under similar conditions, $Mn_2(CO)_8(AsPh_3)_2$ produces a feeble spectrum whose intensity remains too weak to allow its analysis. No spectrum was obtained from either $Mn_2(CO)_{10}$ or $Mn_2(CO)_8[P(OPh)_3]_2$ under these conditions.

As pointed out above, $Mn_2(CO)_8(PPh_3)_2$ produces a distinctly different

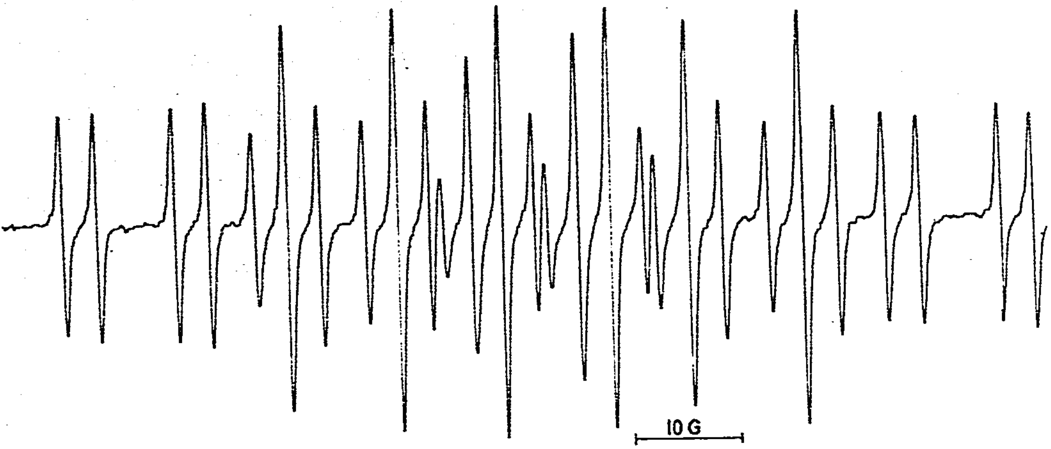


Fig. 1. Esr spectrum obtained from a mixture of $Mn_2(CO)_8(PPh_3)_2$ and nitroso-t-butane in tetrahydrofuran solution.

spectrum in pyridine solution. That spectrum is shown in Figure 2. The spectrum exhibits hyperfine coupling due to nitrogen and manganese. The coupling constants found for these two nuclei are similar in magnitude to the coupling constants obtained in other solvents. However, coupling due to phosphorus is lacking. In its place coupling to a second nitrogen is observed. This small coupling results in the splitting of each major line in the spectrum into a triplet. This smaller nitrogen coupling is readily seen in Figure 3 in which the three lowest field lines in the spectrum are displayed on an expanded scale. Exactly the same spectrum is obtained from $Mn_2(CO)_8(PEt_3)_2$ and from

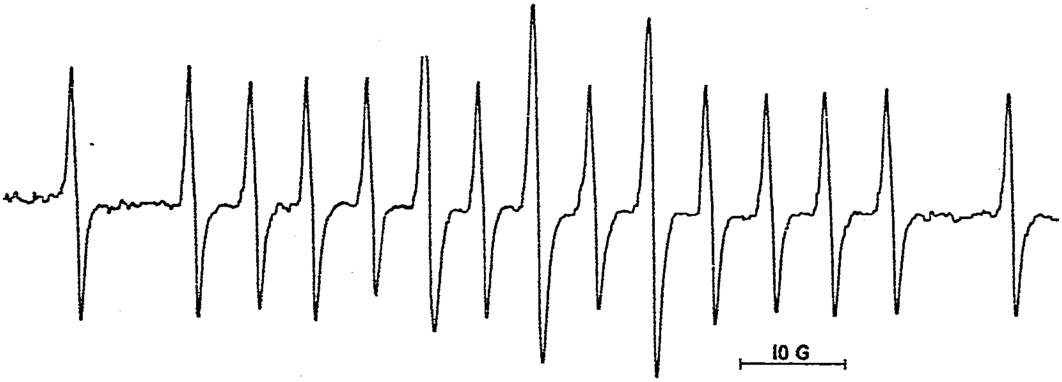


Fig. 2. Esr spectrum obtained from a mixture of $Mn_2(CO)_8(PPh_3)_2$ and nitroso-t-butane in pyridine solution.

Fig. 3. The three lowest field lines in the esr spectrum shown in Figure 2, displayed on an expanded scale.

$Mn_2(CO)_8[PPh(OMe)_2]_2$ in pyridine solution. $Mn_2(CO)_8(AsPh_3)_2$, which in dichloromethane produces only a feeble spectrum, also produces this spectrum in pyridine. However, with $Mn_2(CO)_{10}$ and $Mn_2(CO)_8[P(OPh_3)_3]_2$ no spectrum is obtained in pyridine solution. The spectrum shown in Figures 2 and 3 is assigned to the radical $\underset{\sim}{1}$ (L = pyridine). The large nitrogen coupling constant is assigned to the nitroxide nitrogen while the small nitrogen coupling constant is assigned to the pyridine nitrogen. This radical is produced by substitution of pyridine for the group V ligand PPh_3, PEt_3, $PPh(OMe)_2$ or $AsPh_3$. Since evidence exists that substitution of $(Ph_3P)_2Mn_2(CO)_8$ occurs <u>via</u> initial homolysis,[12] the pyridine substitution probably occurs either with the radical intermediate $R_3PMn(CO)_4$ (a 17 electron species) or with the radical product $R_3P(OC)_4MnN(O)C(CH_3)_3$. We have not been able to distinguish between these two possibilities. The problem arises from the dynamic nature of our trapping experiments. Since the radical $R_3PMn(CO)_4$ is constantly being produced <u>via</u> reaction 1, it has not been possible to explore reaction of $R_3P(OC)_4MnN(O)C(CH_3)_3$ with pyridine in the absence of a flux of $R_3PMn(CO)_4$.

The electronic spectra of the $L_2Mn_2(CO)_8$ complexes are reported in Table II. The assignment of the two lowest energy transitions as $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ follows from previous study of the spectra of $Mn_2(CO)_{10}$ and some derivatives.[15] Here the σ and σ^* orbitals are the bonding and anti-bonding orbitals associated with the metal-metal bond. The weaker $d\pi \rightarrow \sigma^*$ transition appears as a shoulder on the strong $\sigma \rightarrow \sigma^*$ transition and the position of the weaker band is only approximate. Table II also contains a listing of the force constants for stretching of the equatorial carbon monoxide ligands.[7]

Table II

Electronic Spectral and Infrared Force Constant Data

	Electronic Spectra[a]				Force Constants[b]
Complex	$d\pi \rightarrow \sigma^*$, cm^{-1}	(ε)	$\sigma \rightarrow \sigma^*$, cm^{-1}	(ε)	$k_2(CO)$, mdyn/Å
$Mn_2(CO)_{10}$	26,300sh	(4800)	29,400	(20,500)	16.33[c]
$Mn_2(CO)_8[P(OPh)_3]_2$	24,700sh	(4770)	28,300	(29,200)	15.999
$Mn_2(CO)_8[P(OEt)_3]_2$	23,800sh		27,800		15.754
$Mn_2(CO)_8[P(\underline{m}\text{-}CH_3C_6H_4)_3]_2$	23,100sh		27,000		-
$Mn_2(CO)_8(PPh_3)_2$	22,900sh		27,000		15.626
$Mn_2(CO)_8(AsPh_3)_2$	22,300sh		26,900		15.620
$Mn_2(CO)_8(PPh_2Me)_2$	23,300sh	(3850)	27,500	(31,700)	-
$Mn_2(CO)_8(PEt_2Ph)_2$	23,600sh	(3490)	27,800	(27,300)	15.510
$Mn_2(CO)_8(PEt_3)_2$	23,800sh	(3000)	28,300	(22,600)	15.466

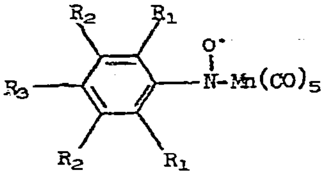
[a] Acetonitrile solution, this work.

[b] Carbon disulfide solution, reference 7.

[c] Carbon tetrachloride solution, reference 22.

Discussion

The ability to successfully detect spin trapped radicals depends on the stability of the nitroxide product. The photolysis of $Mn_2(CO)_{10}$ has been shown, by synthetic and physical studies, to produce $Mn(CO)_5$ radicals.[11] The identity of a long-lived radical produced by photolysis of $Mn_2(CO)_{10}$ in tetrahydrofuran solution has been the subject of considerable controversy.[16-20] The $Mn(CO)_5$ radical, produced by photolysis of $Mn_2(CO)_{10}$, has been trapped at -30°C using nitrosodurene[2] or 2,4,6-tri-*t*-butylnitrosobenzene.[20] However, these radicals rapidly decompose. We have been able to observe the spin adduct 2 only during direct photolysis at -35°C. This radical rapidly decays when photolysis ceases. In the case of 3, it is reported that warming causes the radical to transform into a new species which is claimed to result from insertion of carbon monoxide into the M-N bond. In



2 $R_1 = R_2 = CH_3$, $R_3 = H$

3 $R_1 = R_3 = C(CH_3)_3$, $R_2 = H$

contrast, we find that the organometallic radicals trapped with nitroso-*t*-butane are stable enough to accumulate to readily detectable concentrations at room temperature. Since these solutions of organometallics and nitroso-*t*-butane are extremely light sensitive, all of our samples have been carefully shielded from light. The radical $(CH_3)_3CN(O)Mn(CO)_5$ has also been detected in experiments in which $Mn(CO)_5^-$ is oxidized by the tropylium cation.[21]

Our observations verify the suspicions of others that certain substituted derivatives of $Mn_2(CO)_{10}$ undergo thermal homolysis under mild conditions. The identification of these radicals is inferred from the hyperfine couplings present in the spectra and by the dynamic growth of the spectral intensity with time.

There has been some controversy over the initial product produced by photolysis of $Mn_2(CO)_{10}$ in pyridine solution. Since the final product $[Mn(py)_6][Mn(CO)_5]_2$ results from disproportionation of the dimer, it has been suggested that photolysis in polar solvents, particularly pyridine, results in initial heterolysis of the metal-metal bond.[22] Our results with $Mn_2(CO)_8L_2$ indicate that thermal homolytic cleavage occurs in solvents of varying polarity, including pyridine. We suspect that disproportionation in $Mn_2(CO)_{10}$ and related species could occur after the initial homolysis (by either thermal or photochemical activation) produces a substitutionally labile 17 electron radical, $Mn(CO)_4L$.

Homolysis of the manganese complexes results from an electronic effect. The phosphine substituents occupy the axial coordination sites and should produce little steric strain about the metal-metal bond. On the other hand, it appears that increasing the σ electron donation of these axial ligands while weakening their ability to act as π acceptors does weaken the metal-metal bond and lower the activation energy for metal-metal bond cleavage. We have attempted to correlate our observations with two sets of other spectroscopic observations on these compounds. We suspect that the inability to observe radicals from either $Mn_2(CO)_{10}$ or $[(PhO)_3P]_2Mn_2(CO)_8$ at 23°C in the dark results because of a greater activation energy required to cleave the metal-metal bond in these cases. Of course, the failure to detect the radical could also be due to the lack of reaction 2 or to rapid decomposition of the product, reaction 3. Since no radical is observed in either inert solvents or pyridine where we know that 1 (L = pyridine) would be stable, it is highly likely that radicals are not observed because reaction 1 is slow when the axial ligands are CO or $P(OPh)_3$.

From the data in Table II it can be seen that $Mn_2(CO)_{10}$ and $[(PhO)_3P]_2Mn_2(CO)_8$ have the highest equatorial carbonyl stretching force constants of all the manganese dimers listed.[7] It may be argued that increasing the electron density at manganese can lead to weakening the Mn-Mn bond. Particularily, increasing the electron density in the Mn $d\pi$ orbitals should lead to increased repulsion between these filled orbitals on the two metals.[15] Consequently, from the force constant data, the high carbonyl force constants in $Mn_2(CO)_{10}$ and $[(PhO)_3P]_2Mn_2(CO)_8$ reflect a lower electron density in the $d\pi$ orbitals and less repulsion between the two Mn centers.

It has also been argued that the position of the intense electronic transition which has been assigned as a $\sigma \rightarrow \sigma^*$ transition of the metal-metal bond of these complexes may reflect the strength of the metal-metal bond.[15] The position of this band has been correlated with the activation energies for a series of reactions which are believed to occur by initial metal-metal homolysis.[12] However, in the present case a correlation between the observation of radicals and the position of this electronic transition does not exist. In particular, for both $[(PhO)_3P]_2Mn_2(CO)_8$ and $(Et_3P)_2Mn_2(CO)_8$ this electronic transition occurs at 28,300 cm^{-1} but only in the case of $(Et_3P)_2Mn_2(CO)_8$ is a radical trapped. It also should be noted that the energies of the assigned $\sigma \rightarrow \sigma^*$ transitions and the value of k_2 in Table II do not correlate with one another.

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