PHOTOCHEMISTRY OF (η^5-C$_5$H$_5$)Mn(CO)$_2$[C(C$_6$H$_5$)$_2$]. GENERATION OF THE DIPHENYLCARBENE RADICAL ANION *

R.E. WRIGHT and A. VOGLER *

Universität Regensburg, Institut für Chemie, D-8400 Regensburg (B.R.D.)

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Summary

The electronic absorption spectrum of (η^5-C$_5$H$_5$)Mn(CO)$_2$[C(C$_6$H$_5$)$_2$] shows an intense maximum which is assigned to a MLCT transition in which the empty p_π orbital on the carbene carbon is populated. Upon irradiation of this band, the complex undergoes a decomposition with a disappearance quantum yield $\Phi = 0.10 \pm 0.01$ independent of solvent. In the CT excited state, the complex can be roughly described as containing d^5 Mn^{II} and a diphenylcarbene radical anion ligand C(C$_6$H$_5$)$_2^-$. Due to the kinetic lability, the complex decomposes producing a Mn^{II} species and the free carbene radical anion, which then undergoes secondary reactions. In addition, small amounts of substitution product are observed. It is proposed that prior to total decomposition of the excited state, a radical pair (η^5-C$_5$H$_5$)Mn(CO)$_2$S$^+$/C(C$_6$H$_5$)$_2^-$ forms (S = solvent). A back electron transfer from C(C$_6$H$_5$)$_2^-$ to the labile cation competes with decomposition to produce the substituted complex and free carbene.

Introduction

Since 1964, when the first transition metal carbene complex was prepared and characterized by Fischer and Maasböl [1], a great variety of new metal carbene complexes have been synthesized. The nature and reactivity of the metal—carbon bond in these carbene complexes has been extensively studied [2]. All the experimental evidence seems to indicate that reactions leading to a transformation of the carbene ligand do not involve the formation of a free carbene, but rather reaction at the coordinated ligand. Simple thermal substitutions in which a free carbene is generated do not occur. The reason for this inability to liberate the carbene ligand may be associated with the high electrophilic character of the coordinated carbene carbon. Ligands which would be

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able to substitute the carbene in the complex are nucleophilic molecules and apparently prefer to attack the electron deficient carbene. While this behavior is characteristic for the electronic ground state of carbene complexes, the reactivity of an electronically excited state may be quite different. We explored this possibility and selected for the present study the complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-$[C(C_6H_5)_2]$ which has been reported to be photosensitive [3].

Results

When solutions of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ are irradiated, the yellow color rapidly fades. The spectral changes associated with photolysis, Fig. 1, show that the most prominent feature in the absorption spectrum decreases, while a slight increase at longer wavelengths occurs. Similar changes occur in acetonitrile, chloroform, cyclohexane, ethanol and tetrahydrofuran with 1% t-butylisonitrile (t-BuNC) added. The quantum yield for disappearence of complex was 0.10 ± 0.01, independent of solvent.

The IR spectrum of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ consists of two bands in the CO stretching region located at 1910 and 1973 cm^{-1}. Irradiation of oxygen-free solutions of the carbene complex leads to the disappearence of both bands and the appearence of two broad bands at 1585 and 1480 cm^{-1}. These new bands are independent of solvent. Similar bands appear in the IR of the decomposition product from the air oxidation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$. Additional support that decomposition is occurring comes from the ESR results (see below)

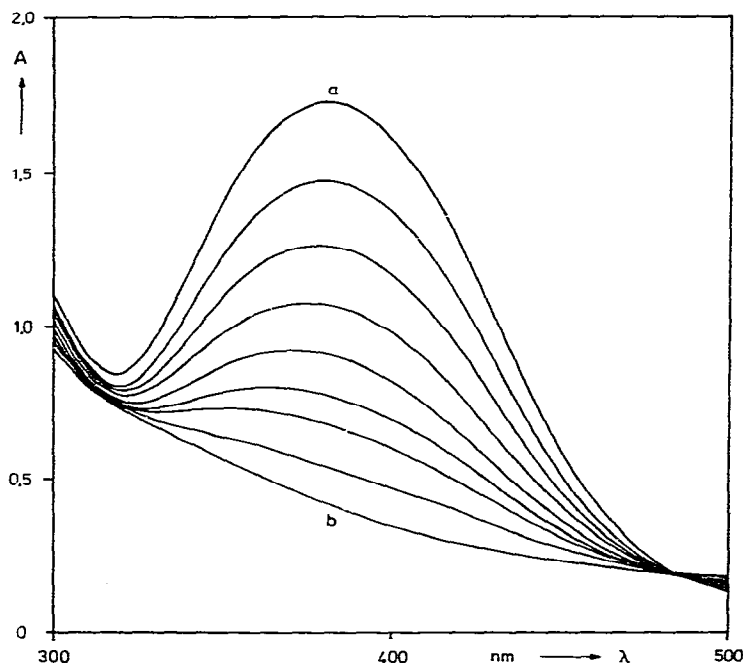Fig. 1. Spectral changes observed upon irradiating a 2.15×10^{-4} M solution of $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-$[C(C_6H_5)_2]$ in 2-MeTHF with $\lambda > 335$ nm. Cell length = 1 cm. Total irradiation time between (a) initial and (b) final is 4 min.

and the precipitation of a brown solid upon photolysis of the carbene complex in CH_3CN. The IR of the isolated solid shows two broad bands at 1585 and 1480 cm^{-1}. Based on this evidence, it was concluded that the major photochemical pathway leads to complex decomposition. In addition, two much weaker bands appear in the CO stretching region which are solvent dependent. These were identified as the solvent substituted dicarbonyl complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_2S$ by comparison to authentic samples prepared by photolyzing $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in the appropriate solvent. The formation of some substitution product accounts for the increase in absorption at long wavelengths in the visible spectrum. The IR spectral changes obtained upon photolysis of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ in THF are shown in Fig. 2. The THF substituted complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ absorbs at 1845 and 1919 cm^{-1}. When 1% t-BuNC is added to a THF solution of the carbene complex, significantly different changes occur upon irradiation. The bands assigned to the com-
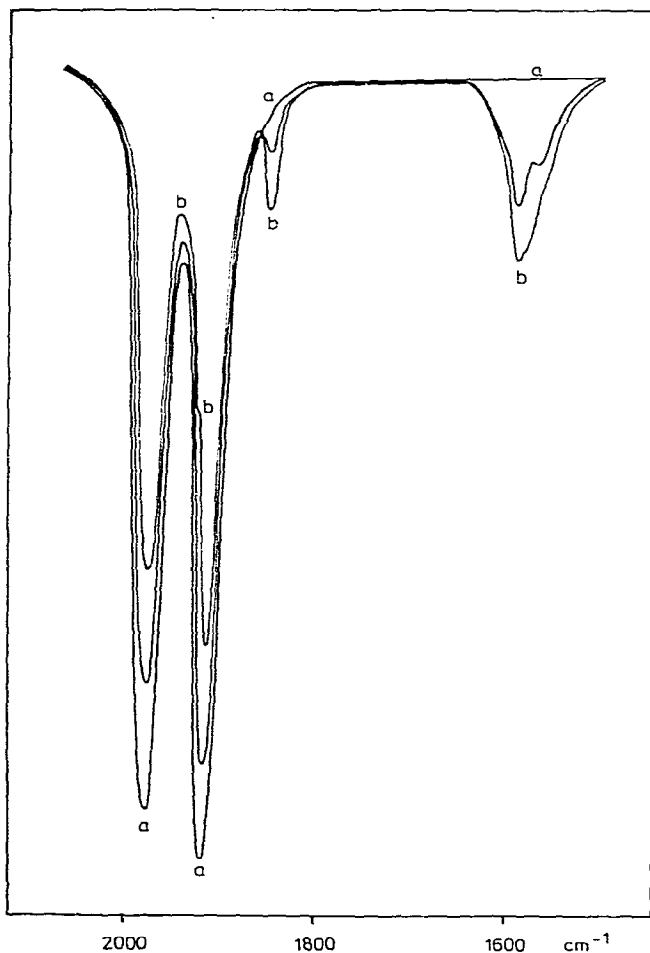

Fig. 2. IR spectral changes observed upon irradiating a 0.015 M solution of $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-$[C(C_6H_5)_2]$ in THF. Cell thickness = 0.200 mm. Spectrum (a) is initial, (b) after 2 min.

plex $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\text{t-BuNC})$ are much more intense indicating a much greater yield of substitution product. Much weaker bands due to the THF complex are also present. Photolysis of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in THF/1% t-BuNC produces an approximately equal amount of THF and t-BuNC substitition products. The much higher ratio of the t-BuNC to THF adduct from the photolysis of the carbene complex indicates that the reaction proceeds with a much higher selectivity than with the tricarbonyl complex. One other sharp band appears at 2019 cm^{-1} in the photolysis of the carbene complex in THF/1% t-BuNC. This is assigned to the diphenylketeneimine, the known product of diphenylcarbene with isonitriles [4].

Irradiation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ in either a THF or EtOH glass at 77 K leads to a color change from yellow to red after several hours. This is accompanied by the appearence of a very weak emission. By focusing the light onto a 3—4 mm diameter area of the glass, a much quicker change occurs producing a distinct red spot from which a weak emission is observed. Presumably this increased rate of photolysis is due to local softening of the matrix [5]. The broad emission has a maximum near 550 nm with an excitation maximum at 335 nm. These features are the same as those of the diphenylmethyl radical [6]. Warming and recooling an extensively photolyzed glass results in complete loss of the emission signal, consistent with a reactive intermediate. Furthermore, the red color undergoes a rapid transition to a green color which can be maintained by recooling. The emission is unchanged by this process. Further warming causes the green color to turn a pale red-brown. None of the colored
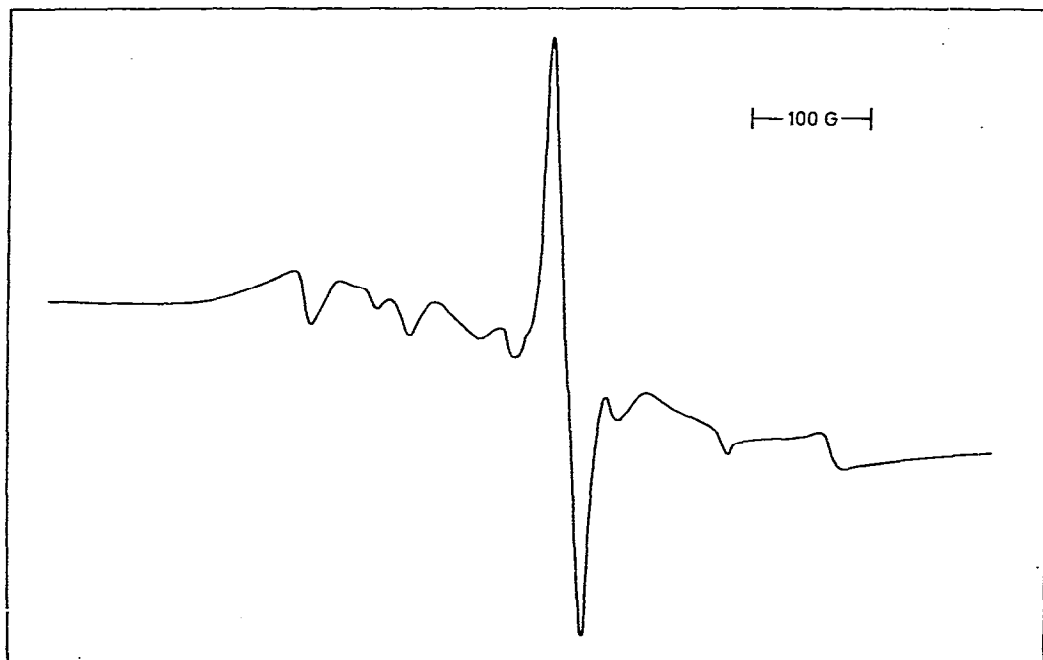

Fig. 3. ESR spectrum at 77 K following low temperature photolysis of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ in a 2-MeTHF matrix.

species could be positively identified, although the latter is most likely the manganese decomposition product. In addition, the initial red color is similar to that obtained after one electron oxidation of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ [7]. Thus it could be due to the cationic species.

The ESR spectrum of an irradiated glass of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ in 2-methyltetrahydrofuran (2-MeTHF) at 77 K is shown in Fig. 3. The presence of high-spin effective low-spin Mn^{II} is indicated by the six-line signal, $A(Mn) = 88$ G. A similar spectrum is observed in the photolysis of $Mn_2(CO)_{10}$ [8]. Expansion of the free radical region indicates the presence of two more paramagnetic species, one of which was identified as a solvent radical. At slightly
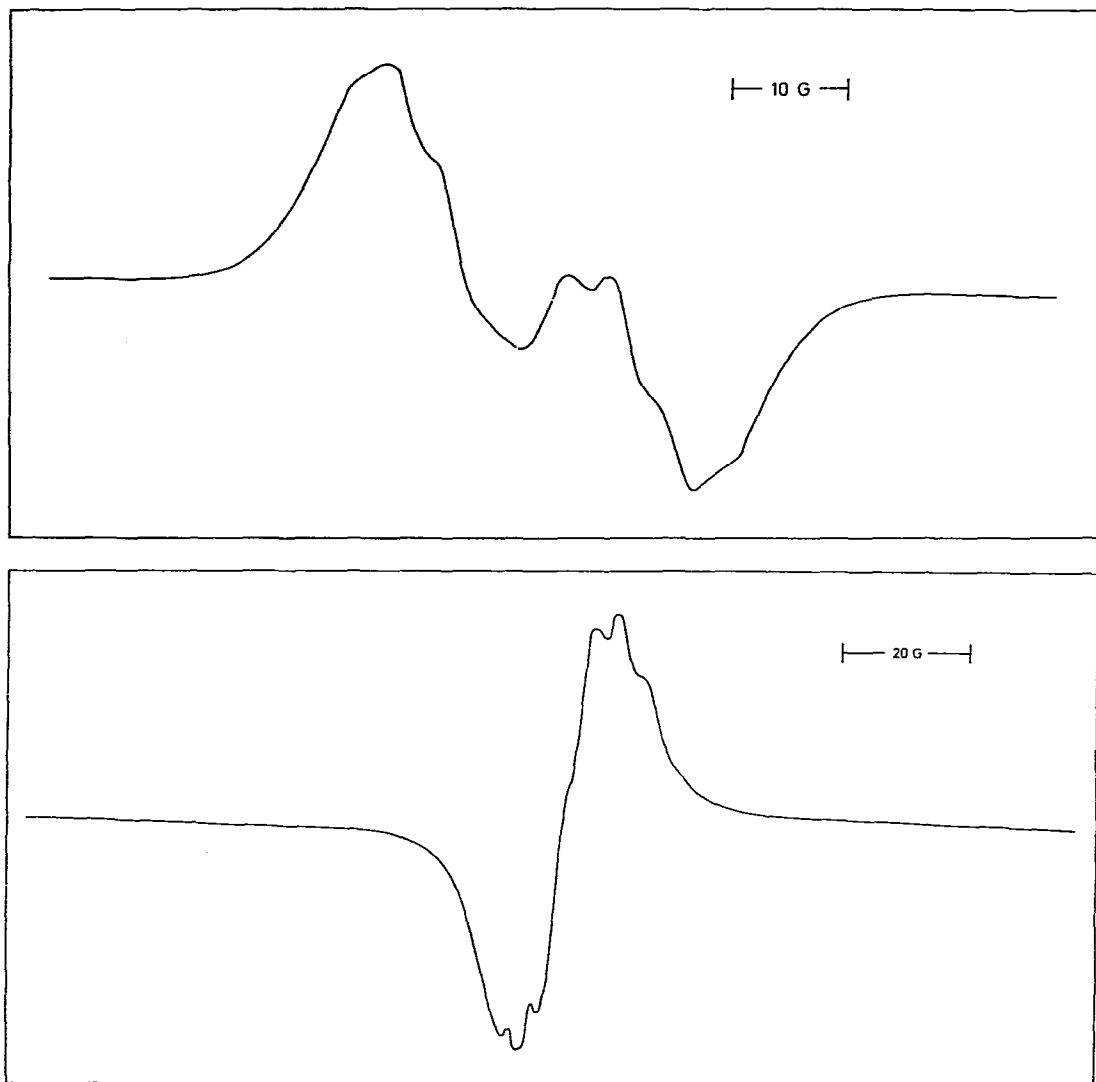

Fig. 4. Low temperature ESR spectra of free radical region following photolysis of $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-$[C(C_6H_5)_2]$ in (a) EtOH, $a_H = 18.7$ G, $g = 2.0017$ and (b) EtOD, $a_D = 2.87$ G (theoretical), $g = 2.0018$.

elevated temperatures, the solvent radical signal diminishes while the major radical component resolves into a doublet. Photolysis in an EtOH matrix is much cleaner and produces the radical signal shown in Fig. 4a. Mn^{II} is again clearly identified by its characteristic sextet (not shown). The doublet signal is consistent with a free electron on carbon coupled to an α-hydrogen. The hyperfine structure is due to coupling with the hydrogens on the phenyl.rings [9]. Since the precursor to a diphenylmethyl radical might add a hydrogen atom or a proton, the low temperature photolysis in EtOD was done. The result, shown in Fig. 4b, clearly shows that the acidic hydrogen is transferred from the solvent.

Discussion

$(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ can be regarded as a pseudooctahedral complex with the central metal having an electronic configuration of d^6 Mn^I. This formalism is derived from the parent compound $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ which has an electronic structure similar to $Cr(CO)_6$. The lowest excited state of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $Cr(CO)_6$ is a ligand field (LF) state and is responsible for the photosubstitutions of these complexes [10].

$(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ shows a weak absorption at long wavelengths (625 nm, $\epsilon = 140$) which is of uncertain origin. A LF assignment does not seem appropriate due to the low energy of the band. The lowest LF band of the parent $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ has an absorption maximum at 329 nm. The most prominent feature of the carbene complex absorption spectrum is an intense band around 380 nm ($\epsilon \sim 7000$). The maximum shows a slight but definite solvent dependence as shown in Table 1, with the ordering typical of a metal to ligand charge transfer (MLCT) assignment [11]. The electronic transition must involve the removal of a d_π electron from the manganese and the population of the empty p_π orbital of the carbene carbon. This is in agreement with a previous assignment of other carbene complexes [12]. Theoretical considerations [13] as well as experimental evidence [14] support the assumption that the LUMO of a representative carbene complex is indeed centered on the carbene ligand. The electron distribution in the CT excited state can thus be roughly described as $(\eta^5\text{-}C_5H_5)(CO)_2Mn\text{—}\dot{C}(C_6H_5)_2$ containing d^5 Mn^{II} and a carbene radical anion ligand.

TABLE 1

SOLVENT EFFECT ON ABSORPTION MAXIMUM

| Solvent	λ_{max} (nm)
Acetonitrile	372
Acetone	375
Methanol	376
Ethyl acetate	378
Ethanol	379
Tetrahydrofuran	381
Chloroform	382
Cylcohexane	383

A simple photosubstitution of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ releasing CO or the diphenylcarbene ligand is neither expected in view of the nature of the excited state nor observed. A photodissociation producing free carbene would leave the $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ fragment which can be stabilized by THF. $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ was not observed as an important reaction product, whereas photolysis of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ produces exclusively the THF adduct. The high conversion to $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\text{t-BuNC})$ upon irradiation of the carbene complex in THF/1% t-BuNC requires special consideration (see below). In addition, the low temperature irradiation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ did not give any evidence for formation of the free carbene, a species which is stable under these conditions and can be identified by its ESR [15] and emission spectrum [16].

The release of CO in the primary photochemical step can also be ruled out. Only monosubstituted dicarbonyl complexes were identified. Particularly, the high yield of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\text{t-BuNC})$ upon irradiation in the presence of t-butylisonitrile is not consistent with the release of a CO ligand. The production of paramagnetic species, identified as products after low temperature photolysis, also argues against loss of CO.
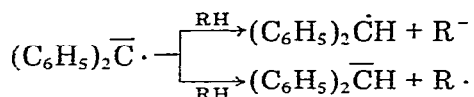
Having ruled out a simple photosubstitution, two mechanistic possibilities remain, which involve the participation of the carbene ligand in the photoreaction. Since the electron distribution in the CT excited state leaves an unpaired electron at the carbene carbon, radical reactions with solvent molecules may occur. If this is indeed the case, the reactivity should vary with the solvent. However, the quantum yield for disappearance of carbene complex was independent of the solvent. This observation is not consistent with a bimolecular reaction of the excited carbene complex with solvent molecules. A less reactive solvent would reduce the quantum yield by favoring the back electron transfer to regenerate the carbene complex. Additional evidence arguing against the photoreaction occurring due to the radical nature of the carbene in the excited state, is demonstrated by the low temperature stability of the one electron reduction products of similar carbene complexes [14]. Since the electron distribution at the carbene carbon is comparable in the two species, it seems unlikely that a reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ would occur during the lifetime of an excited state. Contrary to the results, the photolysis should not take place at low temperature if it occurs by such a mechanism.

The experimental results indicate that the major photochemical pathway leads to decomposition of the complex with the formation of a high-spin Mn^{II} species and the diphenylcarbene radical anion:

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2] \xrightarrow{h\nu} Mn^{II} + C(C_6H_5)_2^-$$
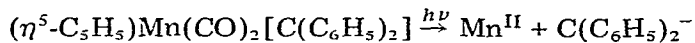
The formation of Mn^{II} is not only indicated by the ESR results of the low temperature photolyses but also by the observation that irradiation at room temperature leads almost completely to complex decomposition. Although the evidence for $C(C_6H_5)_2^-$ is only indirect, the results are only consistent with the intermediate formation of this species. This carbene radical anion has been suggested to be produced by electrochemical reduction of diphenyldiazomethane [17]. Such a radical anion could add a proton to give a diphenylmethyl radical

or abstract a hydrogen atom to give a diphenylmethyl carbanion.

$$(C_6H_5)_2\overline{C} \cdot \underset{\overline{RH}}{\overset{RH}{\longrightarrow}} \begin{array}{l} (C_6H_5)_2\dot{C}H + R^- \\ (C_6H_5)_2\overline{C}H + R \cdot \end{array}$$

In protic solvents, such as EtOH, formation of diphenylmethyl radical should dominate. The experimental results confirm this, the identification of the diphenylmethyl radical being made by ESR and emission spectroscopy following low temperature irradiation. Further evidence for proton transfer was obtained by photolyzing in EtOD. The ESR clearly showed no α-H coupling, as expected for $(C_6H_5)_2\dot{C}D$. If H-abstraction had occurred, the resulting ethanol radical would have been easily observed in the ESR. In aprotic solvents, such as THF, the diphenylmethyl radical is still the predominent radical. In addition, the observation of radicals derived from THF shows that a competing H-abstraction occurs.

The photoreactivity of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ can be explained by considering the electron distribution at the central metal in the CT excited state, d^5 Mn^{II}. This is expected to be kinetically very labile. It has been shown that the oxidation of related carbonyl complexes of Cr$^0(d^6)$ leads inevitably to unstable products [18].

The formation of small amounts of $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ in THF and large amounts of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(t\text{-}BuNC)$ in THF containing 1% t-BuNC remains to be explained. The invariance of the quantum yields suggests that the complex decomposition and formation of these substitution products have a common precursor. It is possible that the first reaction step is not a complete decomposition of the carbene complex but rather a formation of a $(\eta^5\text{-}C_5H_5)Mn(CO)_2S^+/C(C_6H_5)_2^-$ radical pair (S = solvent). The subsequent decomposition of the labile $(\eta^5\text{-}C_5H_5)Mn(CO)_2S^+$ may compete with a back electron transfer from the carbene radical anion producing stable $(\eta^5\text{-}C_5H_5)$-Mn(CO)$_2$S and the free carbene. The higher yield of $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-(t-BuNC) may reflect the greater stability of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(t\text{-}BuNC)^+$. Whereas the Group VI hexacarbonyls can not be oxidized to the cationic species, the corresponding isonitrile complexes $M(CNR)_6^+$ are relatively stable [19]. The fate of the free carbene which would be produced by this scheme was not investigated in detail. However, the IR spectrum of the photolyzed solution containing isonitrile shows a new absorption at 2019 cm^{-1}, consistent with the formation of the ketenimine, the known reaction product of carbenes with isonitrile [4].

Experimental

All photolyses were carried out under a nitrogen atmosphere using standard procedures for handling air-sensitive compounds. Solvents were dried and distilled under nitrogen. Solutions for UV/VIS spectroscopy were typically 10^{-4} M in complex while solutions for IR, ESR and emission measurements were 10^{-2}—10^{-3} M.

The quantum yield for disappearence of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ in THF was determined by irradiating a 10^{-2} M solution of complex in a 1.0 mm

cylindrical cell at 366 nm. The intensity of the CO stretching frequency at $1973 \ cm^{-1}$ was recorded before and after irradiation, from which the percent change could be calculated. Light intensity was determined by ferrioxalate actinometry [20]. Quantum yields in EtOH, cyclohexane, CH_3CN, $CHCl_3$, and THF/1% t-BuNC were obtained by photolyzing equimolar solutions of the complex and measuring the change in the electronic spectrum at 370 and 420 nm after equal irradiation times. Comparision with the behavior of a THF solution of $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ allowed relative quantum yields to be calculted. In all cases, they were within 10% of the value found in THF.

Low temperature photolyses were done in small diameter quartz tubes using the focused output of a 1000 W Xenon lamp. A Corning WG-335 cut-off filter was used to eliminate UV irradiation. The emission was monitored on an Aminco—Bowman spectrofluorimeter using a Corning WG-375 filter in front of the photomultiplier to eliminate scatter. ESR spectra were recorded either on a Varian E9 or a Bruker 420 ESR spectrophotometer. UV/VIS spectra were recorded on a Varian Super Scan 3 spectrophotometer while IR spectra were taken on a Beckman Acculab 6.

Acknowledgement

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