

Photochemical Substitution and [4 + 2] Cycloadditions of a 1,1,1,1-Tetracarbonyl-2,3,1-diazaferrole Derivative with Triphenylphosphine, Diphenylacetylene, and 2,3-Dimethylbutadiene¹

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Abstract: The mechanism of the photochemical reactions of the 1,1,1,1-tetracarbonyl-2,3,1-diazaferrole derivative I, (L)-Fe(CO)₄, with triphenylphosphine (TPP), diphenylacetylene (DPA), and 2,3-dimethylbutadiene (DMB) is studied by measurement of quantum yields as a function of irradiation energy and ligand concentration, and by flash-photolysis experiments. It is shown that the excited state of I decays by loss of CO to form the coordinatively unsaturated species (L)Fe(CO)₃ ($\tau = 70$ ms), which reacts with CO ($k_3 = 2.1 \times 10^5$ l. mol⁻¹ s⁻¹) or TPP ($k_2(\text{TPP}) = 1.3 \times 10^6$ l. mol⁻¹ s⁻¹) to give (L)Fe(CO)₄ or (L)Fe(CO)₃TPP, with DPA by attack on a OC=Fe=C moiety in a stepwise [4 + 2] cycloaddition ($k_2(\text{DPA}) = 1.2 \times 10^3$ l. mol⁻¹ s⁻¹), and with DMB by the way of a stepwise Diels-Alder reaction with the cyclic C=C bond of the diazaferrole ring. DMB or DPA coordinates first to the metal before undergoing conversion into end products only photochemically in the case of the DMB reaction and thermally in the DPA addition.

The ability of a transition metal to change symmetry and energy restrictions imposed on pericyclic reactions is of great preparative and theoretical interest.⁴ Much of this new attention stems from the enormous impact of the Woodward-Hoffmann theory. In contrast to "purely" organic cycloadditions, the analogous reactions of coordinated ligands have not been as extensively studied. The role of the metal in these transformations is still a subject of controversy.^{4b} In addition, factors determining thermal or photochemical pathways of these "metal-assisted" cycloadditions are largely unknown. The observation that irradiation of the diazaferrole derivative I (Scheme I) in the presence of diphenylacetylene (DPA) or 2,3-dimethylbutadiene (DMB) affords cycloadducts III and IV prompted us to investigate the mechanism of these reactions. For comparison, simple photosubstitution by triphenylphosphine (TPP) was also studied.

Results

Irradiation ($\lambda \geq 290$ nm) of the 2,3,1-diazaferrole I in the presence of an equimolar amount of TPP affords red-violet crystals of the expected TPP derivative II (Scheme I). The appearance of three $\nu(\text{CO})$ bands in the ir spectrum (1978 vs, 1951 s, 1924 vs) does not allow an assignment of the sterical position of TPP by simple group theoretical procedures. However, by comparison with corresponding reactions of (1,4-heterodiene)M(CO)₄ complexes (M = Cr, Mo, W) and phosphines,⁵ it may be suggested that TPP is cis to the azo ligand. If the diazaferrole I is illuminated in the presence of a fourfold excess of DPA, complex III is obtained in 50% yield. The properties of III have been discussed in detail elsewhere;³ the structure is confirmed by x-ray analysis of the analogous complex IIIa (R = X = Ph, Scheme I).⁶

In connection with the formulation of a delocalized ground state for complex I,³ the reactivity of the C=C double bond in the diazaferrole ring has been investigated. It was of interest to determine if this bond would undergo usual olefin reactions such as [2 + 2] cycloadditions and the Diels-Alder reaction. Thus, 2,3-dimethylbutadiene was allowed to react thermally with I at various concentrations and temperatures (≤ 80 °C) but instead of the expected cycloaddition, only decomposition of complex I was observed. However, the desired Diels-Alder adduct can be easily obtained if the reaction is performed photochemically. The new complex IV is rather unstable and partially decomposes during its chromatographic separation,

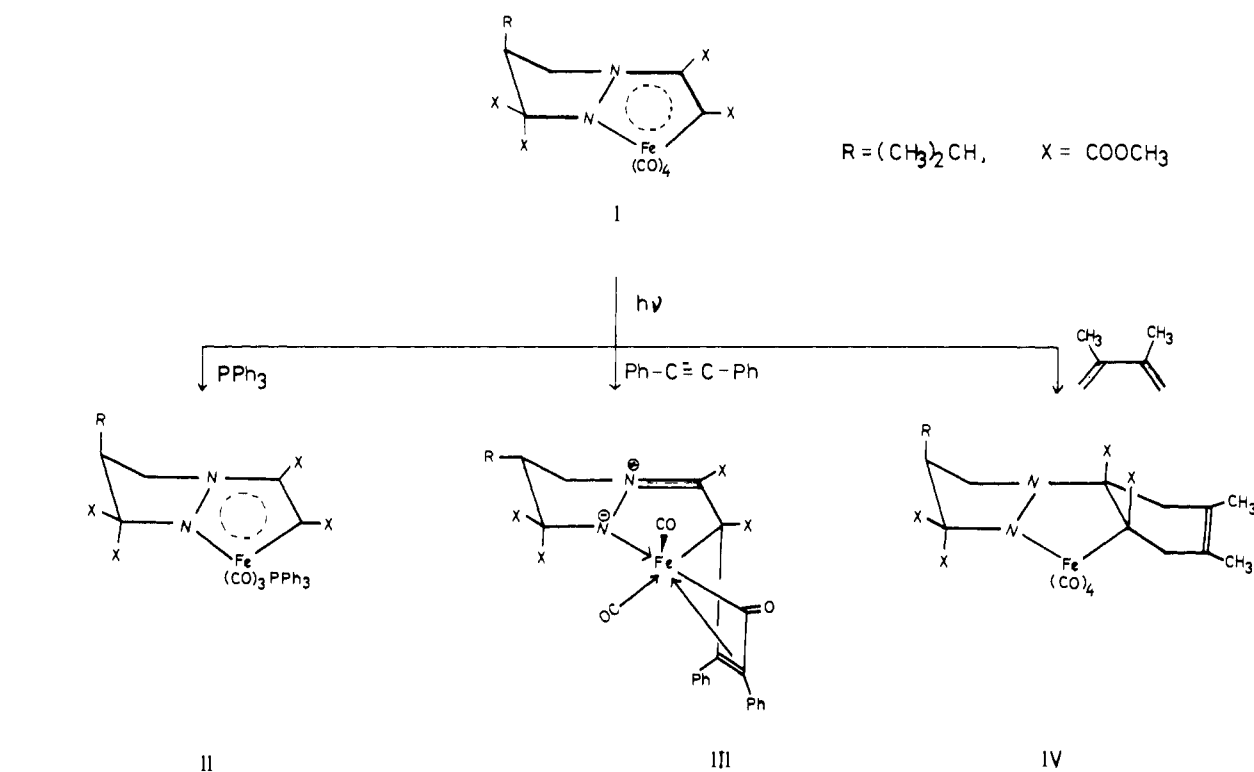
at -25 °C, into pyrazoline V, 1,2-bis(methoxycarbonyl)-4,5-dimethyl-1,4-cyclohexadiene (VI) and iron carbonyl fragments.

Repeated crystallization from *n*-hexane affords IV as brown crystals which give correct analytical data. The ¹H NMR spectrum demonstrates the asymmetry of the six-membered ring (τ_{CH_3} 8.7 and 8.56, τ_{CH_2} 7.45 and 7.4) and excludes the possibility that the C-N bond is already cleaved (according to Scheme II); the appearance of signals due to V and VI indicates that some decomposition occurs on dissolution in C₆D₆ (vide Experimental Section). The metal carbonyl absorptions show a pattern very similar to that of I except that all bands are shifted to lower wavenumbers by 10–20 cm⁻¹. This points to an Fe(CO)₄ group analogous to I but which is bound to a ligand with poorer acceptor properties such as the saturated N-N-C-C group of IV. The occurrence of two types of photoreactions in addition to simple substitution, and the presence of two well-resolved bands in the electronic absorption spectrum of I, prompted us to investigate the wavelength dependence of the reactions with TPP and DPA. These measurements could not be performed for the DMB reaction which is strongly intensity dependent and does not take place at all with the faint monochromatic light we used ($\approx 10^{-7}$ einstein/min). Figure 1 contains the electronic spectrum of I and quantum yields of product formation as a function of the irradiation energy. On lowering this energy, the quantum efficiency decreases and drops sharply on passing from the second to the first absorption band. It is noted that both reactions depend in the same manner on the energy of the absorbed light.

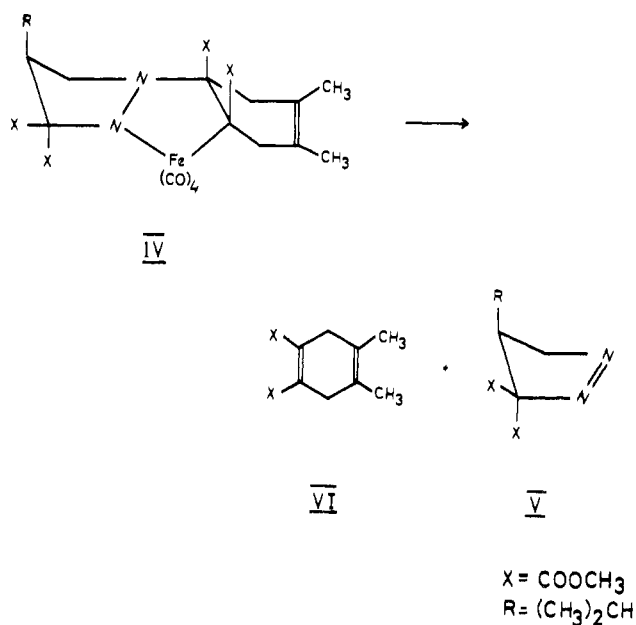
The effect of ligand concentration on these reactions in degassed and CO-saturated solutions is shown in Figure 2. The relative quantum yields of product formation are much less dependent on these variables for TPP substitution compared to DPA cycloaddition. The former reaction becomes independent of ligand and CO concentration at [TPP] ≥ 20 mM ([I] = 6.6 mM) while the latter is strongly dependent on both throughout the concentration range investigated.

The concentration dependence of the DMB reaction is similar to that of the DPA cycloaddition but exhibits a stronger CO inhibition (Figure 3a). However, the most distinctive feature of the DMB reaction is the strong dependence on the intensity of the exciting irradiation (Figure 3b). Low-intensity irradiation of degassed solutions of I in the presence of DMB results in a slow decomposition of I and little if any formation

Scheme I



Scheme II



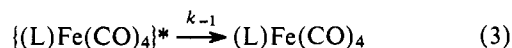
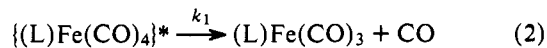
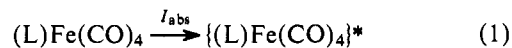
of the Diels-Alder adduct IV. No decomposition is observed in CO-saturated solution. This reaction therefore involves two or more photochemical reaction steps.

Flash photolysis experiments reveal that complex I is very photostable in degassed benzene solutions ($c = 0.1$ mM). No decomposition could be observed after 15 flashes. Only one, very long-lived transient is observed ($\tau = 70$ ms, $\lambda_{\text{max}} 17.8$ kK, Figure 4) which decays by a second-order rate law. In CO-saturated solution the same transient is observed and the rate law is now pseudo-first-order, $k_1 = 1.5 \times 10^3$ s $^{-1}$. Analogous experiments in the presence of TPP ($c = 0.01$ mM) again exhibit a pseudo-first-order decay of this transient accompanied by the growing-in of complex II; $k_2(\text{TPP}) = 1.3 \times 10^6$ l. mol $^{-1}$ s $^{-1}$. Flash irradiation of I, (L)Fe(CO) $_4$, in the presence of DPA

or DMB shows again the same transient, most probably (L)-Fe(CO) $_3$, from which a longer-lived species is formed showing a new absorption band at about 15.5 kK. No rate constants of product formation could be measured in these cases because of overlapping absorption bands. These long-lived species most probably are π -complexes of DPA or DMB with (L)Fe(CO) $_3$. This assumption is supported by low-temperature experiments. Irradiation of a toluene solution of I and DMB at -50 °C leads to a color change from orange-red to pink-red, corresponding to the appearance of a "tail-absorption" down to 15.6 kK in the electronic spectrum. Infrared analysis of this cold solution reveals the presence of a new complex, probably (L)Fe(CO) $_3(1,2-\eta\text{-DMB})$, exhibiting $\nu(\text{CO})$ bands of approximately equal intensities at 2072, 2040, and 2012 cm $^{-1}$ (I absorbs at 2057, 1992, and 1980 cm $^{-1}$). On prolonged irradiation the "tail-absorption" and new $\nu(\text{CO})$ bands vanish with concomitant production of ir bands due to IV. If the irradiation is interrupted and the solution warmed up to room temperature, the $\nu(\text{CO})$ bands of (L)Fe(CO) $_3(1,2-\eta\text{-DMB})$ disappear without production of metal carbonyl bands due to IV or any other iron carbonyl complex. Analogous low-temperature experiments with I and DPA reveal that also in this case an intermediate complex is formed, probably (L)Fe(CO) $_3(\text{DPA})$, as demonstrated by the appearance of a new $\nu(\text{CO})$ band at 2067 cm $^{-1}$. This complex is slowly transformed into III at -50 °C but converts very fast on warming up to room temperature without irradiating.

Discussion

The simplest scheme to account for the experimental results is the following (A refers to the entering ligand TPP or DPA):



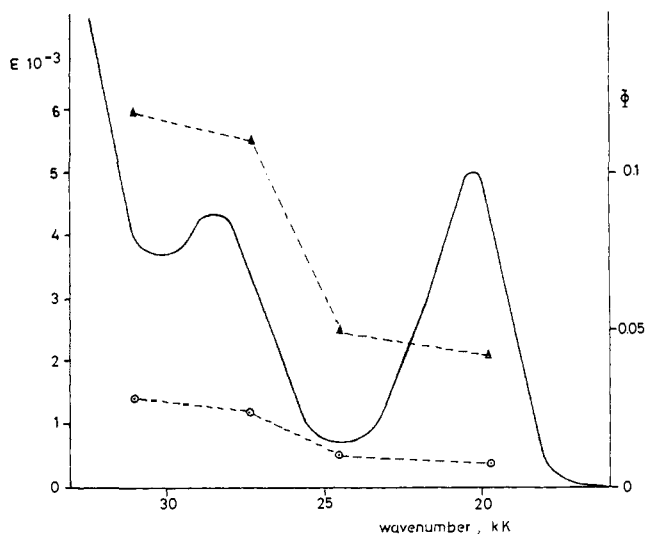


Figure 1. Electronic spectrum of complex I (—) and wavelength dependence of quantum yields of the reactions with TPP (Δ - - Δ) and DPA (\circ - - \circ); in degassed benzene solution, $[I] = 6.6$ mM, $[TPP] = [DPA] = 26.4$ mM.

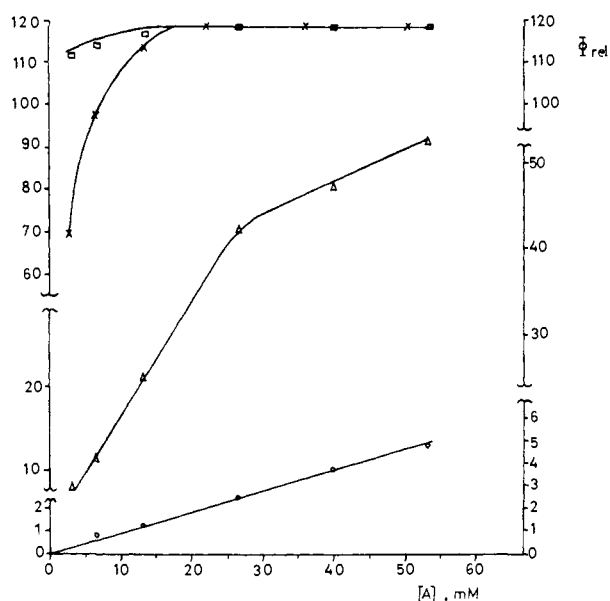
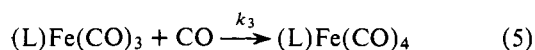
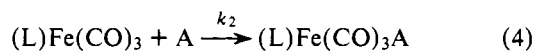


Figure 2. Dependence of relative quantum yields on ligand concentration for the reactions of I with DPA (\circ) CO-saturated, (Δ) degassed benzene solution) and with TPP (\times) CO saturated, (\square) degassed benzene solution).



Equation 3 summarizes physical decay and any process, e.g., loss of (L), which destroys $\{(L)Fe(CO)_4\}^*$ without formation of $(L)Fe(CO)_3$. Applying the steady-state approximation for excited state and coordinatively unsaturated intermediate, the rate of product formation is given by:

$$\frac{d[(L)Fe(CO)_3A]}{dt} = \frac{k_1 k_2 I_{abs} [A]}{(k_1 + k_{-1})(k_2 [A] + k_3 [CO])} \quad (6)$$

Since the results were obtained at low conversions ($\leq 5\%$), the internal filter effects of products and intermediates can be neglected and the following simplified cases may be envisaged.

(a) $k_2 [A] \gg k_3 [CO]$; eq 6 becomes eq 7 and the quantum yield of product formation is given by eq 8

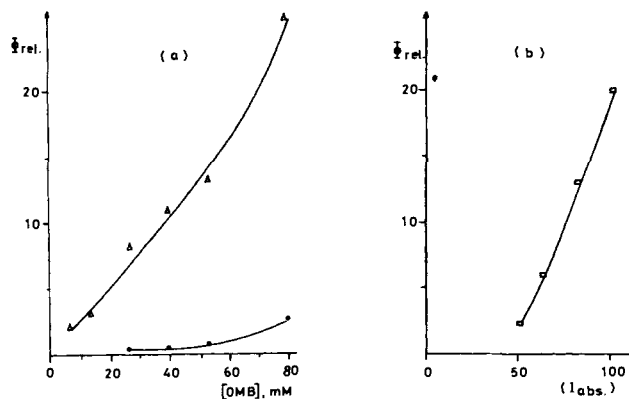


Figure 3. Dependence of the relative quantum yields of the reaction of I with DMB on: (a) DMB concentration in CO-saturated (\circ) and degassed (Δ) benzene solution ($[I] = 6.6$ mM); (b) irradiation intensity in degassed benzene solution, I_{abs} = irradiation intensity in arbitrary units.

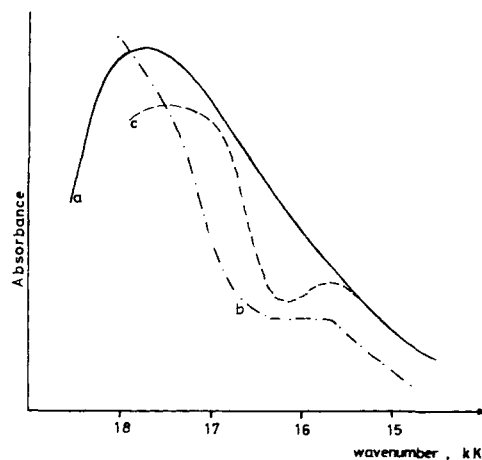


Figure 4. Electronic spectrum of transients formed by flash photolysis of I in benzene solutions ($[I] = 0.1$ mM): (a) complex I, 20 ms after flash; (b) I + DMB, 200 ms after flash (after 8 ms the spectrum is identical with a); (c) I + DPA, 200 ms after flash; $[DMB] = [DPA] = 10$ mM.

$$\frac{d[(L)Fe(CO)_3A]}{dt} = \frac{k_1}{k_1 + k_{-1}} I_{abs} \quad (7)$$

$$\Phi_a = \frac{k_1}{k_1 + k_{-1}} \quad (8)$$

This case applies to TPP photosubstitution where the quantum yield is almost independent of $[TPP]$ in degassed solutions (Figure 2). In CO-saturated solution, where $[CO] \approx 7 \times 10^{-3}$ M, the maximum value of Φ_a is reached with $[TPP] \approx 2.0 \times 10^{-2}$ M; thus, $k_2(TPP)$ should be larger than k_3 , but of the same order of magnitude. The values of $k_2(TPP) = 1.3 \times 10^6$ and $k_3 = k_1/[CO] = 2.1 \times 10^5$ l. mol $^{-1}$ s $^{-1}$, as determined by the flash photolysis experiments, are in good agreement with this conclusion. The ratio of k_1/k_{-1} is calculated from the quantum yields at 28 and 20 kK as 1/9 or 1/20 for irradiation into the second or first absorption band of $(L)Fe(CO)_4$, respectively.

(b) $k_2 [A] \ll k_3 [CO]$; in this case eq 6 becomes eq 9

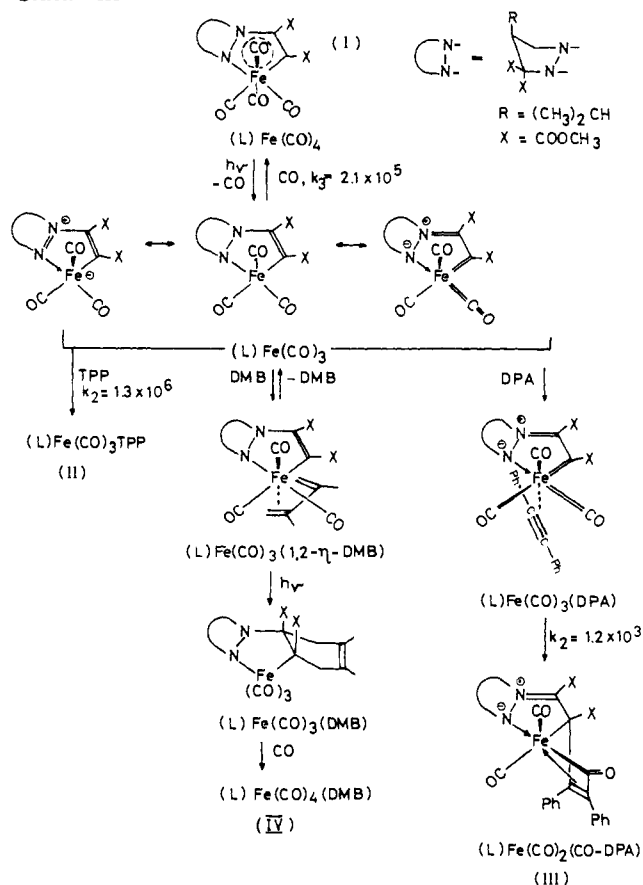
$$\frac{d[(L)Fe(CO)_3A]}{dt} = \frac{k_1 k_2 I_{abs} [A]}{(k_1 + k_{-1}) k_3 [CO]} \quad (9)$$

and under conditions where $[CO]$ and $[A]$ are assumed to be constant, the quantum yield can be expressed as

$$\Phi_b = \Phi_a \frac{k_2 [A]}{k_3 [CO]} \quad (10)$$

Equation 10 is in agreement with the linear increase of Φ_b with

Scheme III



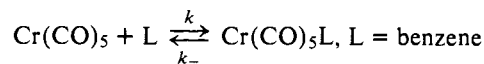
increasing $[A]$ as observed for the reaction with DPA in CO-saturated solutions (Figure 2). Using the values of Figure 2, the ratio of $k_2(DPA)/k_3$ is calculated from eq 10 as 5.8×10^{-3} . With the rate constant k_3 , which is known from the flash photolysis experiments ($2.1 \times 10^5 \text{ l. mol}^{-1} \text{ s}^{-1}$), $k_2(DPA)$ is obtained as $1.2 \times 10^3 \text{ l. mol}^{-1} \text{ s}^{-1}$.

(c) $k_2[A] \approx k_3[CO]$; in this case Φ_c depends on $[A]$ in a more complicated manner. For low values of $[A]$, Φ_c should grow with increasing $[A]$ as in case (b) but more rapidly because $[CO] \ll [CO]_{\text{saturated}}$. At higher values of $[A]$, Φ_c should approach the limiting value of Φ_a . The cycloaddition of DPA to I in degassed solutions is an example of this intermediate behavior.

The results obtained with the DMB cycloaddition cannot be rationalized by the kinetic scheme described. This agrees with the involvement of two or more photochemical reaction steps. The stronger CO inhibition suggests that CO competes for $(L)Fe(CO)_3$ more successfully with DMB than with DPA (Figure 3a). No reaction or decomposition of I is therefore observed on low-intensity irradiation in the presence of DMB in CO-saturated solutions.

Scheme III summarizes the results obtained in the present study. From the flash-photolysis experiments and the qualitatively same wavelength dependence it is concluded that all three reactions proceed through a common intermediate. In agreement with the many photochemical transformations of metal carbonyls,^{7,8} this intermediate, $(L)Fe(CO)_3$, is produced by loss of CO from the excited state $\{(L)Fe(CO)_4\}^*$. This coordinatively unsaturated complex ($\tau = 70 \text{ ms}$ in degassed benzene solutions) seems to gain some stability by accepting electrons from the diazaferrole ring as illustrated by the valence bond structures in Scheme III. It is not expected that benzene can stabilize this species remarkably and in fact the rate constant for recombination with CO, $k_3 = 2.1 \times 10^5 \text{ l. mol}^{-1} \text{ s}^{-1}$, is high (compare this with $k = 3 \times 10^6 \text{ l. mol}^{-1} \text{ s}^{-1}$

for $Cr(CO)_5 + CO \rightarrow Cr(CO)_6$ in cyclohexane⁹). However, the solvent molecules may interact weakly with the metal, as was demonstrated recently by detection of short-lived $Cr(CO)_5$ (solvent) complexes



$k = 7 \times 10^6 \text{ l. mol}^{-1} \text{ s}^{-1}$, $k_- = 2.1 \times 10^5 \text{ s}^{-1}$.¹⁰ Thus, it seems not unlikely that $(L)Fe(CO)_3$ forms a very short-lived ($\tau \leq 1 \mu\text{s}$) complex with benzene before undergoing further reactions. Preliminary results indicate that the rate of product formation is reduced in solvents like ether, capable of better stabilization.

The low quantum yields (0.13–0.01) suggest that decay processes (eq 3) of the excited state are more important than loss of CO and/or that $(L)Fe(CO)_3$ recombines very efficiently with CO (eq 5). Similar values of Φ have been measured for the substitution of CO in $Mn(NO)(CO)_4$ by TPP.¹¹ Loss of CO is apparently more efficient from the excited state reached by irradiation into the second absorption band of complex I; for both DPA and TPP reactions it is found that $\Phi(28.5 \text{ kK}) \approx 2\Phi(20.3 \text{ kK})$. This is consistent with the electronic transition at 28.5 kK being centered predominantly on the metal while the transition at 20.3 kK has some CT character involving charge transfer from the heterocyclic ligand to the iron carbonyl moiety (CTLM). Preliminary SCFF-MO calculations on the unsubstituted 1,1,1,1-tetracarbonyl-2,3,1-diazaferrole support this assumption.¹²

In the case of TPP substitution the relative quantum yields of product formation are independent of the concentration of TPP if $[TPP] \geq 3[I]$. Under these conditions the rate of the reaction is governed by the ratio $k_1/k_1 + k_{-1}$. At lower concentrations of TPP the rates of CO attack and TPP attack are comparable and the quantum yields depend on $[TPP]$. Thus the reaction may be viewed as a dissociative type of process. In contrast to TPP substitution in $Mn(CO)_4NO$ where the observation of an unstable intermediate, formulated as $Mn(CO)_4(NO)TPP$, indicates an associative mechanism,¹¹ there is no experimental evidence for a similar mechanism in the reactions of complex I with TPP. Concurrent dissociative and associative reaction paths were formulated for CO substitution by TPP or tri-*n*-butylphosphine in $Mn(CO)_4(NO)$,¹¹ $(\eta^3-C_3H_5)Co(CO)_3$,¹³ or $(\mu-PhC_2Pn)Co_2(CO)_6$.¹⁴ In the two latter cases only the ratio of the rate constants of CO recombination to attack of phosphine at the coordinatively unsaturated intermediate could be evaluated (2.1 or 2 for the binuclear or mononuclear cobalt carbonyl). In the present study the absolute rate constants of both reactions of the unsaturated $(L)Fe(CO)_3$ have been determined, and the corresponding ratio of k_3/k_2 (TPP) is found to be 0.16.

In contrast to substitution by TPP, the reaction with DPA is strongly influenced by the concentrations of CO and DPA, in agreement with the values of k_3 and k_2 (DPA). The reaction from $(L)Fe(CO)_3$ to end-product III (Scheme III) may be formally described as a stepwise $[4\pi + 2\pi]$ cycloaddition of the alkyne to the $-C=Fe=CO$ moiety, resembling the well-known "1,3-dipolar" cycloaddition. From the low-temperature and flash-photolysis experiments it seems well established that the alkyne coordinates first to the metal before undergoing C–C bond formation. The fact that in these experiments no intermediates could be observed for the conversion of $(L)Fe(CO)_3$ -(DPA) to III, supports the assumption that this step consists of a concerted cycloaddition. However, it cannot be completely ruled out that this reaction step may proceed by a different mechanism, and further experiments are necessary before making a final decision. Thus, the rate constant k_2 (DPA) is composed of two or more constants describing coordination of DPA and further reaction to end-product III.

Recently reported was the stepwise $[6\pi + 2\pi]$ cycloaddition of alkynes to tricarbonyl(cycloheptatriene)iron (VII). It was

suggested that irradiation of VII replaces one coordinated C=C bond by a solvent molecule, which is then thermally displaced by the alkyne, and that the last step consists of the thermal cycloaddition.¹⁵ However, it cannot be ruled out that also in this case the reaction may be initiated by loss of CO.

From the experimental results it is obvious that the "Diels-Alder" reaction does not proceed by direct attack of DMB on the cyclic C=C bond but in several distinct steps. This finding agrees with the formulation of a delocalized ground state for the diazaferrole I resulting in a low double bond character; this should be larger in the coordinatively unsaturated intermediate (L)Fe(CO)₃ which can accept the missing electron pair from the metallocyclic ring only by destroying its "aromatic character" (Scheme III). Coordination of DMB via one double bond to give (L)Fe(CO)₃(1,2- η -DMB) releases electron density from the metal carbonyls as demonstrated by the increase of $\nu(\text{CO})$ by 20–40 cm⁻¹ compared to I. The same effect should diminish "back-bonding" into the antibonding orbital of the cyclic C=C bond rendering it a better dienophile. The conversion of (L)Fe(CO)₃(1,2- η -DMB) to IV may be viewed as a photochemical "Diels-Alder" reaction of the coordinated diene with the cyclic double bond to yield the coordinatively unsaturated (L)Fe(CO)₃(DMB), which forms the end-product IV by up-take of carbon monoxide. This view is again supported by the low-temperature ir investigations and the flash-photolysis studies, which do not point to the involvement of intermediates during the conversion of (L)Fe(CO)₃(1,2- η -DMB) to the Diels-Alder adduct IV. However, as in the DPA reaction, from the experimental evidence it cannot be ruled out that this final step proceeds by a nonconcerted cycloaddition pathway.¹⁶ The end-product IV is very unstable in solution decomposing with cleavage of N-C, Fe-C, and Fe-N bonds, respectively (Scheme II). This instability of IV, where electron delocalization within the five-membered metallocycle is no longer possible, may be taken as chemical evidence for the significant contribution of this electronic effect to the stability of 2,3,1-diazaferroles.

Experimental Section

Complex I was synthesized according to ref 3 and repeatedly recrystallized from ether-hexane. Irradiations were performed with a Philips HPK 125 mercury lamp using Pyrex filter ($\lambda \geq 290$ nm). For general procedures see ref 3.

Preparation of II. A degassed solution of 260 mg (0.5 mmol) of I and 125 mg (0.5 mmol) of TPP in 100 ml of toluene is irradiated for 8 h. Evaporation of the residue and chromatography with benzene-ethyl acetate (1:1) yields a red oil which is crystallized from acetone-hexane to give 250 mg (65% yield) of red-violet crystals of II, mp 180–183 °C. Anal. Calcd: C, 57.5, H, 4.79, N, 3.6, P, 4.02, Fe, 7.26. Found: C, 57.92; H, 5.28; N, 3.61; P, 3.88; Fe, 7.10. Ir (benzene): 1978 vs, 1951 s, 1924 vs, 1725 s, 1695 s, 1425 s. Uv (benzene): 19.4 kK (ϵ 3.08 \times 10³), 28.8 (sh, ϵ 7.75 \times 10³), 32.4 (sh, ϵ 1.09 \times 10⁴). NMR (C₆D₆): 2.5–3.12 m (τ , m = multiplet, phenyl protons); 6.73, 6.85, 6.98, 7.08, all s (s = singlet, ester methyl); 8.35 m, 9.3 d, 9.6 d (d = doublet, isopropyl group). Mass spectrum: no molecular peak (590), 482 (M⁺ - TPP - CO), 426 (M⁺ - TPP - 3CO).

Preparation of III. A degassed solution of 260 mg (0.5 mmol) of I and 360 mg (2 mmol) of DPA in 100 ml of toluene is irradiated for 12 h. Chromatographic workup (eluting with benzene and acetone) and crystallization from dichloromethane-methanol yields 180 mg (50% yield) of III. For physical data see ref 1.

Preparation of IV. A degassed solution of 530 mg (1 mmol) of I and 1.15 ml (10 mmol) of DMB in 100 ml of toluene is irradiated for 15 h. Evaporation of the solvent affords a red-brown oil which is chromatographed at -25 °C with benzene-ethyl acetate (4:1). Repeated crystallization from hexane yields 150 mg (25% yield) of deep-brown crystals of IV, mp 72–73. Anal. Calcd: C, 50.4; H, 5.16; N, 4.51; Fe, 9.03. Found: C, 50.9; H, 5.70; N, 4.42; Fe, 8.80. Ir (*n*-hexane): 2045 vs, 1973 vs, 1963 vs, 1725 s, 1685 s. Uv (*n*-hexane): 18.4 (sh, $\epsilon \approx 1.3 \times 10^2$), 21.5 ($\approx 6 \times 10^2$), 31.5 (sh, 4.3×10^2). NMR (C₆D₆): 6.77 s, 6.55 s, 6.44 (six protons) (four ester methyls); 8.7 s (broad, C-meth-

yls); 7.4 s (broad, methylene group); 9.47 d, 9.39 d (isopropyl group); as impurities are present pyrazoline V (ester methyls: τ 6.6 and 6.41)¹⁸ and the 1,4-cyclohexadiene derivative VI. The latter is isolated during the chromatographic separation of IV on further elution with benzene-ethyl acetate (1:1). The physical properties are identical with an authentic sample of VI synthesized from DMB and dimethyl acetylenedicarboxylate analogous to ref 19 (NMR: τ 6.5, 7.2, and 8.65 in C₆D₆).

Absolute Quantum Yields. In this and all following measurements the benzene used was distilled from sodium. Samples were degassed by repeated freeze, pump, and thaw cycles or by prolonged bubbling with argon. Quantum yields were determined using an optical bench fitted with a stabilized dc HBO 200 lamp, collimator lens and a cylindrical vessel ($\Phi = 2$ cm, $l = 10$ cm) containing 14 ml of solution which was stirred during irradiation.²⁰ Monochromatic light was obtained by means of precision Schott or Balzer interference filters. Light intensities were measured with a ferrioxalate actinometer.²¹ The amount of reagent consumption and product formation was evaluated by ir spectroscopy using the $\nu(\text{CO})$ bands at 2057, 2021, 1924, and 2045 cm⁻¹ for I, II, III, and IV, respectively. Small aliquots were withdrawn from the sample solution at various intervals and analyzed by ir. Validity of Beer's law and the absence of any effect of the components of the reaction mixture on the absorption of the $\nu(\text{CO})$ bands were tested for all experiments. In any case the conversion was kept lower than 5% in order to avoid light absorption by products.

Relative Quantum Yields. To a stock solution of complex I in benzene ($c = 6.6$ mM) were added solutions containing different amounts of ligand ($c = 3$ –80 mM). Irradiations were performed in a merry-go-round reactor: $\lambda \geq 360$ nm; Philips HPK 125-W lamp; GWCA-filter, Glaswerke Wertheim. No light was absorbed by the ligand. Concentrations of products were determined as described above.

Intensity Dependence of DMB Cycloaddition. These measurements were performed using a high transmittance filter ($290 \leq \lambda \leq 450$) which allowed an intensity of 6×10^{-6} einstein/min to reach the sample, [DMB] = 26.5 mM, [I] = 6.6 mM. Different intensities were generated by adding Balzer "neutral" filters.

Flash Photolysis Experiments. The apparatus used was described previously.²² The exciting light comes from a solidex discharge lamp filled with Ar (flash half-duration ≤ 3 μ s); spectroscopic source is a Xe-high-pressure lamp Osram XBO 150 W-1. The cell-length is 13 cm. Spectra were recorded by the point by point method at intervals of 10 nm; [I] = 0.1 mM (in benzene). Only one transient is observed in degassed or CO-saturated solutions decaying by a pseudo-first-order rate law. The corresponding rate constants were obtained by plotting $\log A$ vs. time; $A = \log(I_0/I_t)$; I_0 , I_t being light intensity through the cell before or after (at time t) flashing. For systems where formation of a product is measured ("grow in"), $\log[\log(I_t/I_\infty)]$, is plotted against time; I_∞ is light intensity through cell after product formation has completed.

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Carbon-Hydrogen Bond Activation by Transition Metal Complexes. Oxidative Addition of Alkyl Methacrylate to Ruthenium. The Structure of Hydrido(2-*n*-butoxycarbonylpropenyl-*C*¹,*O*)tris(triphenylphosphine)ruthenium(II)

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Abstract: Alkyl methacrylate reacts with dihydrotetrakis(triphenylphosphine)ruthenium(II) via vinylic C-H bond cleavage to give hydrido(2-alkoxycarbonylpropenyl-*C*¹,*O*)tris(triphenylphosphine)ruthenium(II), RuH(CH=C(CH₃)C(O)OR)-(PPh₃)₃, accompanied by formation of an equimolar amount of alkyl isobutyrate per mole of the dihydrido complex. A hydridoalkenyl-type structure for the complex was proposed on the basis of chemical reactions, such as the formation of methyl *cis*- β -deuteriomethacrylate on treatment of the complex with DCl, and methylation at the β -position of alkyl methacrylate on treatment with methyl iodide. The low ν (C=O) band (~ 1580 cm⁻¹) in its ir spectrum, the presence of a hydride signal in the ¹H NMR spectrum, and the ³¹P{¹H} NMR spectrum characteristic of meridional octahedral configuration support the proposed structure. An x-ray study confirmed the structure of hydrido(2-*n*-butoxycarbonylpropenyl-*C*¹,*O*)tris(triphenylphosphine)ruthenium(II). This compound crystallizes from tetrahydrofuran-diethyl ether in the space group C_{2h}⁶-C₂/c with *a* = 29.691 (8) Å, *b* = 21.865 (5) Å, *c* = 21.245 (6) Å, β = 122.26 (1)°, and *Z* = 8. Based on 4801 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ full-matrix, least-squares refinement led to agreement indices (on *F*) of *R* = 0.067 and *R_w* = 0.111. The structure consists of discrete molecules of the complex in which the ruthenium atom is six-coordinate with distorted octahedral geometry. Three coordination sites are occupied by the phosphine ligands in a meridional arrangement. The alkyl methacrylate ligand is bidentate, bonded to the ruthenium atom via the vinylic carbon and the carboxyl oxygen atoms forming a Ru-C-C-C-O five-membered ring. The vinyl carbon atom is trans to a phosphine ligand and the oxygen atom is trans to the hydrido ligand. The terminal three carbon atoms of the *n*-butyl group of the *n*-butyl methacrylate ligand are disordered making a satisfactory description of their positions difficult. Some relevant metric parameters in the complex are: Ru-C(1), 2.061 (10) Å; Ru-O(1), 2.246 (7) Å; C(1)-C(2), 1.368 (15) Å; C(2)-C(4), 1.442 (15) Å; C(4)-O(1), 1.254 (12) Å; O(1)-Ru-C(1), 75.6 (4)°; Ru-C(1)-C(2), 117.8 (8)°; C(1)-C(2)-C(4), 113.4 (10)°; C(2)-C(4)-O(1), 121.2 (11)°; and C(4)-O(1)-Ru, 111.6 (7)°.

Activation of a C-H bond by a transition metal complex is attracting increasing interest because of its potential utility in synthetic organic chemistry. Oxidative additions involving C-H bond cleavage have been postulated in ethylene dimerization,^{2,3} oxidative substitution of an olefin assisted by palladium compounds,⁴⁻⁷ and in H-D exchange in aliphatic and/or aromatic hydrocarbons catalyzed by tantalum, niobium, iridium,^{8,9} platinum,¹⁰⁻¹³ titanium,^{14,15} rhodium,¹⁶ cobalt,¹⁷ and rhenium compounds.¹⁸ However, unequivocal examples of isolation of the product of oxidative addition involving C-H bond cleavage are relatively limited, except for a few examples of orthometalation and its analogous reactions in which C-H bond cleavage of a coordinated ligand is involved.¹⁹⁻³² Metalation of a vinylic carbon atom to form metal-sp²-carbon σ -bonds has been reported for platinum,³³ rhodium,³⁴ and

iridium,³⁵ all of which involve nitrogen as a donor atom. In the course of our systematic studies on the reaction of dihydrotetrakis(triphenylphosphine)ruthenium (1) with various substituted olefins, we found that alkyl methacrylate reacts with 1 via vinylic C-H bond activation to yield hydrido-2-alkoxycarbonylpropenyl-type complexes. The present paper reports in detail the preparation and characterization of these novel compounds with a series of ester-alkyl groups, and the crystallographic determination of the structure of one of these complexes, hydrido(2-*n*-butoxycarbonylpropenyl-*C*¹,*O*)tris(triphenylphosphine)ruthenium(II). A preliminary account has been published elsewhere.³⁶ Isolation of the hydrido carbon-to-metal σ -complexes by the direct oxidative addition involving C-H bond cleavage has also been reported for naphthalene,¹⁹⁻²¹ benzene,^{37,39-45} *p*-xylene and mesitylene,³⁸