The Reduction of some Cationic Hydrido Complexes of Iron(II). Pulse Radiolysis in Methanol

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An investigation into the reaction of solvated electron (e_s^-) with the two hydrido complexes trans-*$FeH\{P(OCH_3)_3\}(DPE)_2^+$ and* trans-*$FeH(CO)(DPE)_2^+$, where DPE = 1,2-bis(diphenylphosphino)ethane, in methanolic solution deaerated with argon has been carried out using the technique of pulse radiolysis. The reaction of e_s^- with both complexes occurs with a rate constant $k = (2.6 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1} and yields a reduced intermediate of general formula $FeH(L)(DPE)(DPE)_{sesqui}$, where $(DPE)_{sesqui}$ denotes a ring-opened DPE ligand. The conversion of one of the DPE from a bidentate to a monodentate form, upon reaction of the starting complex with e_s^-, is not distinguishable from the electron transfer; in fact only one process has been observed. The absorption spectra of the reduced species are stable over the 0.1 s/div. time scale of the instrument, and have been characterized over the range 300–650 nm. Their stability over a longer period of time has been checked using single pulse spectroscopy at high doses and continuous γ radiolysis. Formulation of $FeH(L)(DPE)(DPE)_{sesqui}$ as a pentacoordinated species with a monodentate DPE ligand is supported by electrochemical and spectroscopic result. The behaviour of these two complexes is compared with that of the analogous complexes having the same general formula but with L = organonitrile ligands, and an interpretation of this behaviour is suggested.*

Introduction

After the discovery of *trans*-$HPtCl(PEt_3)_2$ by Chatt *et al.* [1] rapid development of the chemistry of transition metal hydride complexes began with an increasing interest in these coordination compounds, not only for their importance in organometallic chemistry, but especially for their role as intermediates or catalysts in reactions such as hydroformylation, olefin isomerization, nitrogen fixation, and hydrogen exchange [2]. In spite of this interest, very little work has been done on the radiation chemistry of these complexes.

We have initiated a systematic investigation into the reduction of a series of hydrido complexes of the general formula *trans*-$FeH(L)(DPE)_2^+$ by steady-state γ and pulse radiolysis in methanolic solution [3] in order to study the reaction of e_s^- and the mechanism of the reduction process and to investigate the role and fate of the coordinated ligands.

In this paper we report the results obtained with the compounds *trans*-$FeH\{P(OCH_3)_3\}(DPE)_2^+$ and *trans*-$FeH(CO)(DPE)_2^+$ where DPE = 1,2-bis(diphenylphosphino)ethane. Analogous to the other hydrido complexes previously studied [3], these complexes exhibit characteristics so as to suggest the use of the pulse-radiolysis technique as an alternative or complementary approach to the electrochemical reduction of these compounds [4].

The radiolytic behaviour of liquid methanol has been widely investigated and well characterized [5–7]. The effect of radiation on methanol may be represented as follows:

$$CH_3OH \rightsquigarrow H\cdot,\ \cdot CH_2OH,\ CH_3O\cdot,\ e_s^-,\ CH_3OH_2^+,\ CH_3O^- \quad (1)$$

Any CH_3O^- which is formed by the irradiation is rapidly neutralized by the excess of $CH_3OH_2^+$ ($k = (7.1 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}) [8]. Hydrogen atoms and $CH_3O\cdot$ are very reactive and undergo quickly a reaction with the solvent ($t_{1/2}$ = 18 ns [9]

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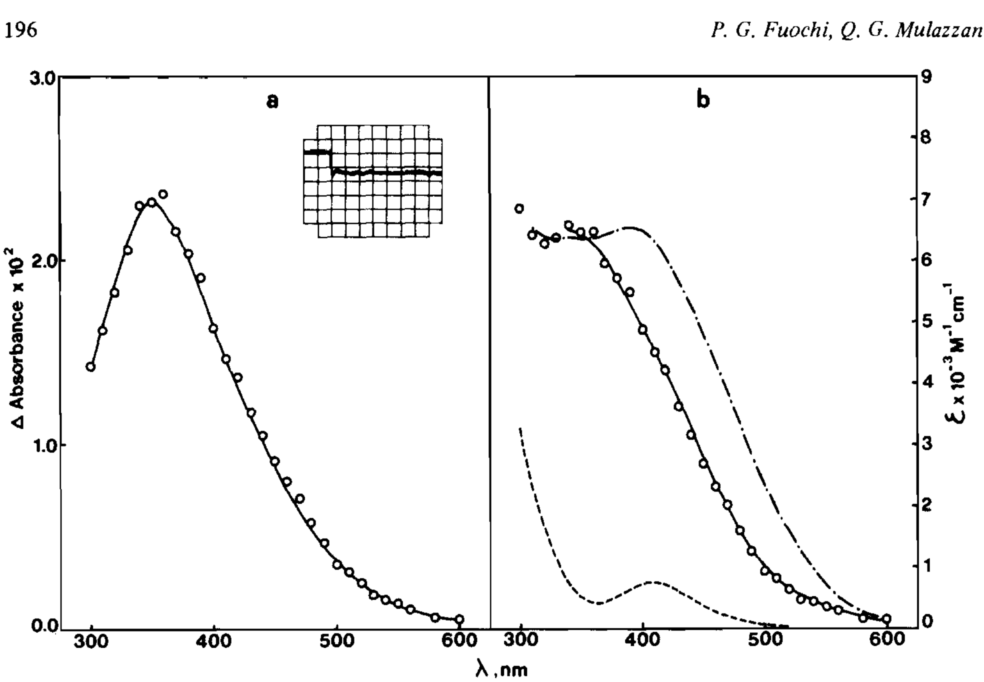

Fig. 1. Optical absorption spectrum obtained on pulse radiolysis of a 3.17 × 10^{-4} M $FeH\{P(OCH_3)_3\}(DPE)_2^+$ Ar-deaerated solution with a pulse dose of 6.95 × 10^{16} eV ml^{-1}, 2-cm optical cell: (a) absorption observed 5 μs after the pulse (○), inset: oscilloscopic trace obtained at 450 nm; abscissa 5 μs/div., ordinate 1.85% absorption/div.; (b) corrected spectrum obtained from the absorption observed 5 μs after the pulse (○) assuming $G[\text{-}FeH\{P(OCH_3)_3\}(DPE)_2^+] = 1.7$, (------) spectrum of $FeH\{P(OCH_3)_3\}(DPE)_2^+$ in methanol, (———) spectrum of $FeH\{P(OCH_3)_3\}(DPE)(DPE)_{sesqui}$ electrochemically generated from $FeH\{P(OCH_3)_3\}(DPE)_2^+$ in DME containing 0.2 M TBA_2^+ (– · – · –) spectrum of $FeH(DPE)_2$ obtained upon reduction of the complexes FeH(L)(DPE)P, where L = organonitrile [ref. 3].

and 106 ns [10] respectively at room temperature), in each case forming $\cdot CH_2OH$ (reactions (2) and (3)):

$$H\cdot + CH_3OH \rightarrow H_2 + \cdot CH_2OH \qquad (2)$$

$$CH_3O\cdot + CH_3OH \rightarrow CH_3OH + \cdot CH_2OH \qquad (3)$$

Reaction (4) represents the fate of free solvated electrons, e_s^-, in very pure methanol [11]

$$e_s^- + CH_3OH \rightarrow CH_3O^- + H\cdot \qquad (4)$$

and its decay at room temperature is comparatively slow ($k \leqslant 10^5\ M^{-1}\ s^{-1}$) [12]. The hydrogen atoms formed in reaction (4) disappear by reaction (2). Thus, the main reactive species which live long enough to react with a solute present in moderately low concentration ($\leqslant 10^{-3}$ M) are e_s^- and $\cdot CH_2OH$*.

Experimental

Materials

The two complexes *trans*-$[FeH\{P(OCH_3)_3\}(DPE)_2](ClO_4)$ and *trans*-$[FeH(CO)(DPE)_2](ClO_4)$ were prepared and purified according to reported procedures [13, 14]. Their optical absorption spectra in methanol, where the complexes are moderately soluble and stable, are reported in Figs. 1 and 2. Methanol G. R. for analysis from E. Merck was purified by the method which Baxendale and Wardman [15] used for 2-propanol, and was stored in a quartz vessel under nitrogen atmosphere. The solvated electron half-life for the purified methanol deaerated with argon was ~3 μs using doses $\leqslant 3.1 \times 10^{16}$ eV ml^{-1}. Nitrous oxide was used after passing through a column of potassium hydroxide pellets followed by a trap cooled with a dry-ice/acetone mixture. All of the other gases used were of the purest grade commercially available and were used without further purification.

Radiation Techniques

Continuous radiolyses were carried out at room temperature on samples of solution contained in silica vessels fitted with Spectrosil optical cells of suitable path length on a side arm. Absorption spectra were

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*Ionising radiation is absorbed by matter in a non-selective way so that in methanol solution, for example, direct absorption of radiation by the solutes can be neglected when they constitute only a small fraction of the material present in the system. In practice direct effects can largely be ignored for solutions containing less than 1 M of a solute.

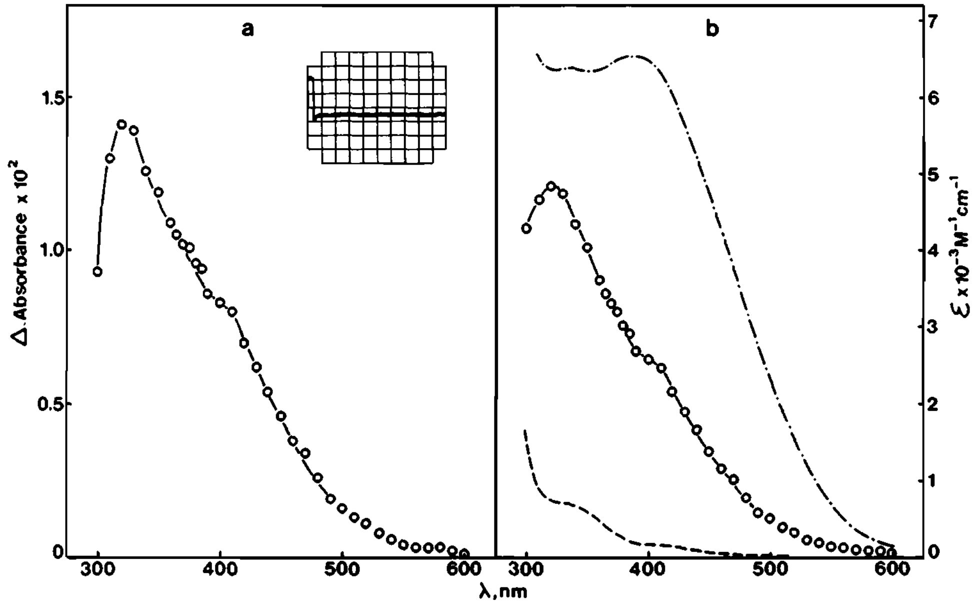

Fig. 2. Optical absorption spectrum obtained on pulse radiolysis of a 3.30 × 10^{-4} *M* $FeH(CO)(DPE)_2^+$ Ar-deaerated solution with a pulse dose of 6.15 × 10^{16} eV ml^{-1}, 2-cm optical cell: (a) absorption observed 5 μs after the pulse (○), inset: oscilloscopic trace obtained at 430 nm; abscissa 5 μs/div., ordinate 0.51% absorption/div.; (b) corrected spectrum obtained from the absorption observed 5 μs after the pulse (○) assuming $G[\text{-}FeH(CO)(DPE)_2^+] = 1.7$, (------) spectrum of $FeH(CO)(DPE)_2^+$ in methanol, (–·–·–) spectrum of $FeH(DPE)_2$ obtained upon reduction of the complexes $FeH(L)(DPE)_2^+$ where L = organonitrile [ref. 3].

recorded with a Perkin-Elmer Model 555 spectrophotometer. The absorbed dose from the $^{60}Co\gamma$ source was determined by the Fricke chemical dosimeter, assuming $G(Fe^{3+}) = 15.5$* and was corrected for the electron density of methanol. Its value was 7.2 × 10^{16} eV ml^{-1} min^{-1}.

Pulse radiolysis was performed using a 12 MeV Vickers linear accelerator as the source of pulsed electrons. The irradiations were done at room temperature on solutions contained in a Spectrosil cell of 2 cm path length. Changes in absorption following the pulse were monitored for each wavelength by a conventional system including a light source (Osram XBO 450 W xenon lamp), a monochromator, a photomultiplier (Hamamatsu R 955) and an oscilloscope (Tektronix 7633 with 7A16A plug-in). The optical detection system measured changes in absorption (ΔOD) relative to the unirradiated solutions. The radiation dose per pulse of electrons was monitored with a 0.1 *M* KSCN aqueous solution saturated with O_2 by using the value $G\epsilon = 2.15 \times 10^4$ at 500 nm [16]. Kinetic data analyses were performed with a Bradley 175 curve analyzer and a Hewlett-Packard 9830 A calculator. In order to avoid or minimize photolytic effects induced by the analyzing light, the solutions were exposed to the minimum amount of UV light through the use of a shutter and cut-off filters. In single pulse spectroscopy at high radiation doses used to check the stability of long-lived species, the sample was contained in a modified spectrophotometer cell and spectra were recorded in less than 1 min after the pulse of electrons on a Beckman ACTA CIII spectrophotometer.

The gases were introduced into the solution through a bubbler containing purified methanol to prevent evaporation of the solvent. All of the experiments were performed on freshly prepared solutions and the sample was irradiated with a single pulse.

Results and Discussion

Pulse Radiolysis

The reaction of e_s^- with Ar-deaerated methanol solutions of $FeH(L)(DPE)_2^+$, where L = $P(OCH_3)_3$ and CO, which yields the absorbance changes recorded in Figs. 1 and 2, was established by following the kinetics of the decay of the intense absorption of e_s^- at 600 nm [17] in the presence and in the absence of the compound. The decay of e_s^- is first order and proportional to the $FeH(L)(DPE)_2^+$ concentration, and from such measurements, a bimolecular rate

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*$G(x)$ denotes the number of molecules of species x formed or destroyed per 100 eV of energy absorbed by the solution.

constant of (2.6 ± 0.3) × 10^{10} M^{-1} s^{-1} is obtained for both compounds.

Since in radiolyzed methanol solution $\cdot CH_2OH$ radicals as well as e_s^- are reducing entities, we wished to confirm that the observed changes in absorption arise only from the reaction of e_s^- with the iron complexes. Solutions of $FeH(L)(DPE)_2^+$ were saturated with N_2O so that e_s^- is converted rapidly ($t_{1/2} \leqslant$ 1 ns) [18] into $\cdot CH_2OH$ according to the reaction (5).

$$N_2O + e_s^- \xrightarrow{CH_3OH_2^+} N_2 + H_2O + \cdot CH_2OH \quad (5)$$

Under these conditions the previously observed optical signals are eliminated.

The absorption spectra of the products formed from the reaction of e_s^- with $FeH(L)(DPE)_2^+$ were obtained by the measurement of the post-pulse absorption (300–650 nm) produced in $FeH(L)(DPE)_2^+$ solutions (~3 × 10^{-4} M); this absorption does not change over the course of ~1 s. This absorption can be due to: 1) formation of a reduced six-coordinate complex, or 2) formation of a reduced complex already pentacoordinated (the loss of one ligand being very fast ($k \geqslant 10^8$ s^{-1}) with respect to the reduction process).

By knowing the radiation dose delivered to the solution, a correction for the depletion of the substrate can be made so that ϵ of the new absorption can be evaluated (Figs. 1b and 2b) if a value of $G[\text{-}FeH(L)(DPE)_2^+] = 1.7$ is used. The aborption spectrum of the species formed upon reaction of $FeH\{P(OCH_3)_3\}(DPE)_2^+$ with e_s^- quantitatively matches the spectrum of the product electrochemically generated from the reduction of $FeH\{P(OCH_3)_3\}(DPE)_2^+$ in 1,2-dimethoxyethane (DME). This reduced species has not been definitely established, but the formulation as a complex already pentacoordinated with a DPE acting as monodentate ligand, $FeH\{P(OCH_3)_3\}(DPE)(DPE)_{sesqui}$*, can be substantiated by the recovery, in the electrochemical two-electron reduction of $FeH\{P(OCH_3)_3\}(DPE)_2^+$ in the presence of proton donors, of a product for which elemental analysis and IR data support the formulation *cis*-$H_2Fe\{P(OCH_3)_3\}(DPE)(DPE)_{sesqui}$ [4]. All this strongly suggests that even in the reduction of $FeH\{P(OCH_3)_3\}(DPE)_2^+$ by e_s^-, a very fast opening of one end of one DPE and the conversion from a bidentate to a monodentate form, upon reaction with e_s^-, is not distinguishable from the electron transfer; in fact only one process has been observed. The same considerations hold when L = CO even though the electrochemically reduced species, $FeH(CO)(DPE)(DPE)_{sesqui}$, cannot be isolated because the reduction process occurs in a two-electron step [4]. Nevertheless, studies at different temperatures and cyclic voltammetric scan rates are indicative of an ECE mechanism (*viz.* a chemical reaction interposed between two electron transfer reactions) similar to that found for the complex with L = $P(OCH_3)_3$ [4]. Moreover, even with $FeH(CO)(DPE)_2^+$ in the presence of proton donors, a two-electron reduction product is obtained for which the elemental analysis, IR spectrum, and its reaction with CCl_4 are typical for hydrides, suggesting its formulation as *cis*-$H_2Fe(CO)(DPE)(DPE)_{sesqui}$ [4]. We can also add the following observations as further support to the above conclusions: a) the possibility of the loss of the hydrogen ligand can be discarded on the basis of the electrochemical and spectroscopic results; b) the possibility of the release of the ligand L can also be excluded since the spectra of the reduced complexes are completely different from the spectrum of $FeH(DPE)_2$ obtained upon reduction of the analogous complexes having organonitrile as ligand L [3] (see Figs. 1b and 2b).

The observed value of $G[\text{-}FeH(L)(DPE)_2^+] = 1.7$ corresponds to the yield associated with reaction (6),

$$FeH(L)(DPE)_2^+ + e_s^- \rightarrow FeH(L)(DPE)(DPE)_{sesqui} \quad (6)$$

Because of the low solubility of the complexes examined in methanol, the concentrations of $FeH(L)(DPE)_2^+$ used ($\leqslant$3.2 × 10^{-4} M) are probably insufficient to effect the complete scavenging of e_s^-. Thus, the observed value of $G\text{-}[FeH(L)(DPE)_2^+]$ can be considered to be in good agreement with the value of $G(e_s^-) = 2.0 \pm 0.3$ in methanol reported previously [8, 19–21].

Single Pulse Spectroscopy

Single pulse spectroscopy was carried out to check the stability of the long-lived species $FeH(L)(DPE)(DPE)_{sesqui}$ over a longer period of time and to see if $FeH\{P(OCH_3)_3\}(DPE)(DPE)_{sesqui}$ performed the ring-closure with elimination of the phosphite to give the final well-known $FeH(DPE)_2$ [3, 22] as established by polarographic studies [4]. Ar-purged samples of $FeH(L)(DPE)_2^+$, where L = $P(OCH_3)_3$ and CO, were irradiated with radiation doses per pulse $\geqslant$3 × 10^{17} eV ml^{-1} delivered by pulses of electrons having duration $\geqslant$0.2 μs. Such irradiated samples were analysed with a conventional spectrophotometer and the spectra recorded in less than 1 min after the pulse. The spectra thus recorded show no trace of the long-lived absorptions attributed to the intermediates $FeH(L)(DPE)(DPE)_{sesqui}$ and no changes compared to the spectra of the unirradiated solutions. It appears that once $FeH(L)(DPE)(DPE)_{sesqui}$ is formed it is oxidized back to $FeH(L)(DPE)_2^+$, predictably, according to a sequence of reactions similar to that proposed earlier [3, 22].

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*Where $(DPE)_{sesqui}$ denotes a monodentate DPE ligand.

Continuous Radiolysis

The spectra obtained after the continuous radiolysis (dose rate = 7.2 × 10^6 eV ml^{-1} min^{-1}) of Ar-purged or vacuum degassed solutions of FeH(L)-$(DPE)_2^+$ do not show the presence of FeH(L)(DPE)$(DPE)_{sesqui}$, but neither do they show the presence of $FeH(DPE)_2$, in agreement with the results reported previously [3]. It is plausible to consider that the intermediate FeH(L)(DPE)$(DPE)_{sesqui}$, produced upon reaction with e_s^-, disappears by reaction with the radicals generated in low steady-state concentration in the methanolic solution, forming different products not identified.

When solutions of FeH(L)$(DPE)_2^+$ with L = $P(OCH_3)_3$ and CO were saturated with N_2O, no variation of the optical absorption was detected upon continuous radiolysis. This fact further confirms that the only species reacting with these complexes is e_s^-.

Conclusions

The reaction of e_s^- with FeH(L)$(DPE)_2^+$ (L = P-$(OCH_3)_3$ and CO) yields in each case the long-lived absorption attributed to FeH(L)(DPE)$(DPE)_{sesqui}$ (Figs. 1 and 2). The rate constants for the formation of these absorptions are near those expected for diffusion-controlled processes and very close to the value found for the reactions of e_s^- with the other hydrido complexes of iron(II) [3]. In contrast, uncoordinated CO reacts more slowly with e_s^- (k = 1.0 × 10^9 M^{-1} s^{-1} in water) [23]* and no data are available for the reaction of $P(OCH_3)_3$ with e_s^-. Nevertheless, from the results reported by Venturi *et al.* [27] on PPh_3 (no evidence of reaction between e_s^- and PPh_3) and from von Sonntag *et al.* [28] on $OP(OCH_3)_3$ (k = 2.0 × 10^5 M^{-1} s^{-1} in water), it appears that e_s^- is not very reactive towards phosphorous compounds. These results are therefore compatible with the simple mechanism of direct electron addition to the iron center (reaction (7))

$$e_s^- + Fe(II)^{2+} \rightarrow Fe(I)^+ \qquad (7)$$

already reported for the analogous complexes of iron(II) with L = organonitrile [3]; the $Fe(I)^+$ intermediate would have the extra electron in a σ* molecular orbital. As expected, the lower oxidation state of Fe(I) is not stable with respect to the ligand configuration of Fe(II) so that dissociation of one end of one diphosphine ligand rapidly occurs.

The different behaviour upon reduction shown by complexes containing organonitriles and those with L = $P(OCH_3)_3$ and CO, could be accounted for by ligand field theory. The field strength of the hydride ligand would be dependent on its environment in the complex. Thus hydrogen behaves as a strong-field ligand when the ligand *trans* to itself is a good π-acceptor [2a, 2c], like $P(OCH_3)_3$ and CO [14]. In contrast, when the *trans*-L ligand is a poor π-acceptor, as organonitriles are [14], the hydrogen should carry a larger negative charge and hence exhibit a weaker ligand field strength [2a, 2c]. Consequently the nature of the L ligand *trans* to the hydrogen should influence the relative energies of the d_{z^2} and $d_{x^2-y^2}$ antibonding orbitals, thus dictating the site of reduction. As suggested in our previous work [4], according to which of the two orbitals d_{z^2} and $d_{x^2-y^2}$ the extra electron will enter, there will be the release of the ligand L (when L is an organonitrile) or the dissociation of one end of a DPE, respectively, in order to rearrange into a more stable configuration the intermediate d^7 formed upon reduction with e_s^-.

An alternative mechanism involving the site of reduction appears also feasible for a qualitative rationalization of the behaviour upon reduction of the complexes of iron(II) so far studied by us. Contrary to the above proposed mechanism, the extra electron is assumed to always enter the $d_{x^2-y^2}$ orbital with rapid dissociation of one end of a DPE. Thus all of the intermediate species formed in Ar-purged solutions from the reaction of e_s^- with the complexes of general formula *trans*-FeH(L)$(DPE)_2^+$, where L = CH_3CN, CH_3CH_2CN, C_6H_5CN, p-$CH_3C_6H_4CN$, $P(OCH_3)_3$, and CO, should now be considered as reduced species FeH(L)(DPE)-$(DPE)_{sesqui}$ already pentacoordinated with a DPE acting as a monodentate ligand. The transients FeH(L)(DPE)$(DPE)_{sesqui}$ perform, then, rearrangement resulting in the DPE ring-closure and the simultaneous release of the ligand L according to a first-order kinetics [3, 4] giving the product $FeH(DPE)_2$. For the compound containing $P(OCH_3)_3$ it has been proposed that the ring-closure of the dangling diphosphine occurs through a six-coordinate transition state in which the $P(OCH_3)_3$ ligand is now *cis* to H; it is likely that the same process occurs also for all of the complexes containing organonitriles. The rate constants for the overall process are dependent on the nature of the ligand L and are presented in Table I. From the values reported in Table I it is possible to understand why the release of the organonitrile ligands could not be observed by cyclic voltammetry: this process is too fast to be observed by this technique, while the release of

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*When the value of a rate constant for a given reaction in an alcohol is not available, the value for the corresponding reaction in water is frequently used inasmuch as it has been proved that the rate constants for the same reaction in various polar solvents with quite comparable solvation energies, as it is for methanol and water [24, 25] are very similar [24, 26].

TABLE I. Rate Constants for the Process FeH(L)(DPE)(DPE)$_{sesqui}$ → FeH(DPE)$_2$ + L

L	k, s^{-1}
CH_3CN	$(1.6 \pm 0.2) \times 10^5$ [a]
CH_3CH_2CN	$(1.1 \pm 0.2) \times 10^5$ [a]
C_6H_5CN	$(2.5 \pm 0.3) \times 10^4$ [a]
p-$CH_3C_6H_4CN$	$(1.8 \pm 0.2) \times 10^4$ [a]
$P(OCH_3)_3$	4.5×10^{-4} [b]

[a] Obtained by pulse radiolysis at room temperature [ref. 3].
[b] Obtained by amperometric measurements at 40 °C in DME [ref. 4].

$P(OCH_3)_3$ is a process too slow to be observed by pulse radiolysis.

The excellent π-bonding ability of CO should suggest a half-life for the intermediate FeH(CO)(DPE)(DPE)$_{sesqui}$ much longer than that for FeH{$P(OCH_3)_3$}(DPE)(DPE)$_{sesqui}$. The occurrence of a single two-electron charge transfer reaction for the complex FeH(CO)(DPE)$_2^+$ prevented us from supporting this statement by polarographic studies [4].

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11 It has been reported that in pure methanol at low doses e_s^- disappears primarily by reaction (4) whereas at high doses it reacts predominantly with $CH_3OH_2^+$ and $\cdot CH_2OH$ by reactions

$$e_s^- + CH_3OH_2^+ \rightarrow CH_3OH + H\cdot \qquad (4')$$

$$e_s^- + \cdot CH_2OH \rightarrow CH_3O^- \qquad (4'')$$

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