Electrochemical investigation of the electron-poor/precise ($n=5/6$) complexes $[Fe_2(CO)_n(\mu\text{-}PR_2)(\mu\text{-}PR'_2)]$ ($n=5$, $R=R'=Bu^t$; $n=6$, $R=R'=Ph$; $R=Bu^t$, $R'=Ph$; $R=Bu^t$, $R'=Cy$). EPR study of the radical anion $[Fe_2(\mu\text{-}PBu^t{}_2)_2(CO)_5]^{\bullet-}$

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Abstract

The redox behavior of the bis(phosphido)-bridged diiron carbonyl complexes $[Fe_2(CO)_n(\mu\text{-}PR_2)(\mu\text{-}PR'_2)]$ ($n=5$, $R=R'=Bu^t$; $n=6$, $R=R'=Ph$; $R=Bu^t$, $R'=Ph$; $R=Bu^t$, $R'=Cy$) has been studied electrochemically at a platinum electrode in THF (0.1 M in $Bu_4N[PF_6]$). The electron-poor complex ($n=5$, $R=R'=Bu^t$) shows two well-defined reduction steps at -1.34 and -2.35 V assigned to the formation of the radical anion $[Fe_2(CO)_5(\mu\text{-}PBu^t{}_2)]^{\bullet-}$ and the dianion $[Fe_2(CO)_5(\mu\text{-}PBu^t{}_2)_2]^{2-}$. The uninegative radical ion has been further investigated by EPR spectroscopy. The fluid as well as the rigid solution spectra indicate that the two phosphido bridges are linking the two iron centers in the same manner and that the unpaired electron is metal centered. The electron-precise complexes ($n=6$) are reduced at approximately the same potentials (-1.74 to -1.91 V) in two closely spaced one-electron steps. Molecular configurational changes accompany these reductions and make both processes, reduction and re-oxidation, quite slow.

Key words: Electrochemistry; Iron complexes; Carbonyl complexes; Phosphido complexes; Dinuclear complexes

Introduction

Recently, a new type of electron-poor bis(phosphido)-bridged diiron pentacarbonyl complex $[Fe_2(CO)_5(\mu\text{-}PBu^t{}_2)(\mu\text{-}PR_2)]$ (Fe=Fe) ($R=Bu^t$ [1, 2], Cy [3]) has been described. Contrary to the butterfly-shaped ($\theta=100.0$–$107.3°$ [4]) electron-precise diiron hexacarbonyl complexes $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]$ (except the exactly planar complex $[Fe_2(CO)_6(\mu\text{-}PBu^t{}_2)(\mu\text{-}PCy_2)]$ [3]) these electron-poor complexes are nearly planar ($\theta=176$, $R=Bu^t$; 166, Ph [1]; 169°, Cy [3]), the deviation from planarity being due to the bulky substituents on the phosphorus atoms. The short metal–metal distances ($R=Bu^t$ 2.484, Ph 2.462 [1], Cy 2.472 Å [3]) are in agreement with the occurrence of an iron–iron double bond as also expected by the electron count of 32 valence electrons. EHT calculations [1] on the model complex $[Fe_2(CO)_5(\mu\text{-}PH_2)_2]$ confirm both the π/π^* MOs to be the frontier orbitals and the planarity of the $Fe_2(\mu\text{-}P)_2$ core to be a precondition for a good overlap of the π orbital. From this bond description it is to be expected that this type of complex should be well suited for redox reactions, and indeed the complex with $R=Bu^t$ is rapidly reduced by sodium in THF, and the resulting anion is immediately re-oxidized by traces of air. In order to study these processes in more detail an electrochemical investigation of the electron-poor complex $[Fe_2(CO)_5(\mu\text{-}PBu^t{}_2)_2]$ (**1**) including an EPR spectroscopic study of the radical anion $\mathbf{1}^{\bullet-}$ has been performed. For the purpose of comparison the electron-precise complexes $[Fe_2(CO)_6(\mu\text{-}PR_2)(\mu\text{-}PR'_2)]$($R=R'=Ph$ (**2**); $R=Bu^t$, $R'=Ph$ (**3**); $R=Bu^t$, $R'=Cy$ (**4**)) have been included in this study.

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Experimental

Materials

The complexes investigated were prepared according to the literature methods: $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)_2]$ [1], $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$ [5], $[Fe_2(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}PPh_2)]$ [1], $[Fe_2(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)]$ [3]. $Bu_4N[PF_6]$ (Jansen Chimica p.a.) was used as received. Solvents were purified according to standard procedures. THF was distilled from $LiAlH_4$. Acetonitrile was distilled from CaH_2.

Measurements

All experiments were performed in a glove-box in which a dry and oxygen-free dinitrogen atmosphere was maintained. A conventional three-electrode configuration was used with platinum working and auxiliary electrodes. The reference electrode consisted of a silver wire immersed in a 0.1 M solution of silver triflate. The reference compartment was separated from the electrolysis cell by a frit and a Luggin capillary, filled with the supporting electrolyte solution. All potentials are given versus the redox couple: $E_{1/2}$ ($Fc^{0/+1}$ in THF) $= -0.224$ V; $\Delta E_p = 72$ mV). Maximum *iR* compensation was applied. A PAR 273 potentiostat with PAR 270 electrochemical analysis software was used.

In situ electron spin resonance measurements

A two-electrode electrochemical EPR cell (SEERS cell) was constructed as published [6]. The working electrode was a gold helix (1 m length, 0.56 mm diameter) and the combined reference–auxiliary electrode was a platinum wire. A PAR 174A polarographic analyzer was used where both the reference and the auxiliary leads were connected to the platinum wire. Outside the EPR cavity a V_a–$E_{1/2}$ test line was made for the SEERS cell by the method published [7]. Here V_a is the maximum of the DPP voltammogram as obtained with this cell and $E_{1/2}$ is the half-wave potential as obtained from a normal three-electrode cell. Electron spin resonance spectra were measured on a Bruker ESR 300 spectrometer.

Results and discussion

The redox behavior of the bis(phosphido)-bridged diiron complexes **1**–**4** was studied electrochemically at a platinum electrode in THF and acetonitrile solutions (both 0.1 M in $Bu_4N[PF_6]$). In both solvents similar redox patterns were observed, but due to the better solubility of the compounds in THF and also the somewhat better resolution of the overlapping one-electron waves this study was mainly made in THF.

The electron-poor complex $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)_2]$ (1)

This compound exhibits two well-defined reduction steps at −1.34 and −2.35 V (Fig. 1) and a completely irreversible multi-electron oxidation step at +0.49 V. The data are assembled in Table 1. Exhaustive electrolysis (controlled potential electrolysis at −1.57 V) revealed that one electron is transferred in the first reduction process. A yellow–brown solution of the uninegative ion $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)_2]^{\bullet -}$ resulted. Both reduction steps are chemically as well as electrochemically reversible charge transfer processes, as can be concluded from the data: $E_{1/2}$ is constant over a wide scan rate region, as is i_b/i_f, and ΔE_p is about 70 mV, a value not uncommon for THF solutions. However, with increasing scan rates particularly the ΔE_p value of the second reduction step becomes rather large. The second reduction process is at the limit of the potential region of the solvent and therefore the i_b/i_f values are somewhat below one.

Thus, complex **1** undergoes the two reversible reductions, shown in eqn. (1), which mean, in the MO parlance, the stepwise population of the LUMO by one and two electrons and the decrease of the iron–iron bond order from 2 to 1.5 to 1. The stronger dependence

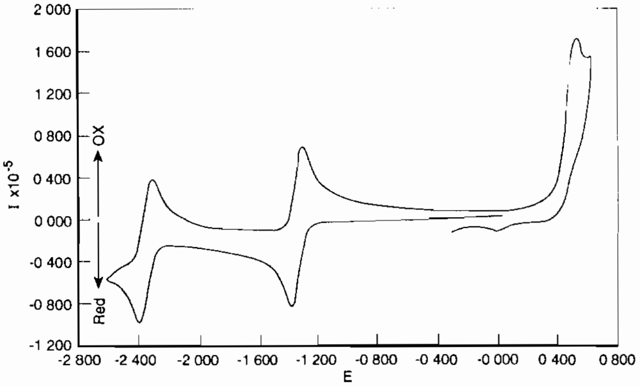

Fig. 1. Cyclic voltammogram of **1** in THF (0.1 M $Bu_4N[PF_6]$) with $v = 100$ mV/s. Potentials are in volts vs. the $Fc^{0/+1}$ redox couple.

TABLE 1. Electrochemical data[a] for $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)_2]$ (**1**)

Process	Scan rate (V/s)	$E_{1/2}$ (V)	ΔE_p (mV)	i_b/i_f
0/−1	0.10	−1.34	66	1.00
	0.50	−1.34	68	1.00
	1.00	−1.34	76	0.98
	5.00	−1.34	120	0.95
−1/−2	0.10	−2.35	74	0.92
	0.50	−2.35	96	0.93
	1.00	−2.36	112	0.98
	5.00	−2.37	170	0.94

[a] In THF (0.1 M $Bu_4N[PF_6]$); potentials vs. $Fc^{0/+1}$ redox couple.

of ΔE_p ($-1/-2$) from the scan rate may indicate a significant structural change on going from $\mathbf{1}^{\bullet -}$ to $\mathbf{1}^{2-}$.

$$\mathbf{1} \underset{-e}{\overset{+e}{\rightleftharpoons}} \mathbf{1}^{\bullet -} \underset{-e}{\overset{+e}{\rightleftharpoons}} \mathbf{1}^{2-} \tag{1}$$

Linear scan voltammetry at a low scan rate, 2 or 5 mV/s, applied to a 10^{-3} M solution of $[Fe_2(CO)_5(\mu\text{-}PBu^t{}_2)_2]$ in a SEERS cell [6] generated a sufficient concentration of the uninegative radical ion to record an EPR spectrum successfully.

The fluid solution EPR spectrum of the electrochemically generated radical anion $\mathbf{1}^{\bullet -}$ reveals a proper 1:2:1 triplet (Fig. 2) indicating the coupling of the unpaired electron with two equivalent phosphorus centers of the two $PBu^t{}_2$ bridges ($a(^{31}P) = 14.7(2)$ G). The isotropic g value ($g_{iso} = 2.037(2)$) is considerably larger than the free electron value of 2.0023. The rigid solution spectrum shows three distinct principal components of a rhombic $\boldsymbol{g}$ tensor ($g_1 = 2.054(2)$, $g_2 = 2.028(2)$, $g_3 = 2.002(2)$). g_1 and g_2 consist of triplets caused by the hyperfine coupling of the unpaired electron with two equivalent ^{31}P ($A_1(^{31}P) = 12.0(5)$ G, $A_2(^{31}P) = 15.5$ G). Hence, even at very low temperature the two phosphido bridges are linking the two Fe centers in the same manner.

The EPR data of the fluid as well as of the rigid solution spectra are in quite good accordance to other phosphido-bridged di- and trinuclear iron carbonyl radical anions [8–12]. The large isotropic g value as well as the rhombic $\boldsymbol{g}$ tensor indicate a metal centered unpaired electron which confirms the results from EHT calculations [1] showing the π,π^*-MO as frontier orbitals.

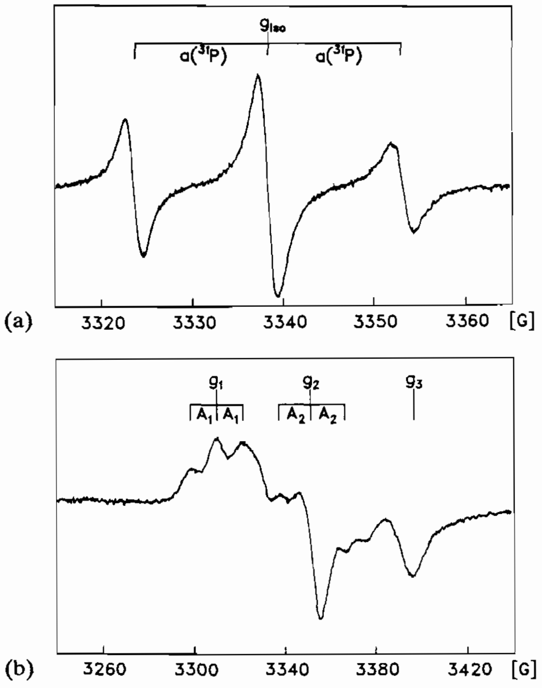

Fig. 2. Fluid (a) and rigid (b) solution EPR spectra of $\mathbf{1}^{\bullet -}$ generated *in situ* by means of electrochemical reduction (X-band, THF, (a): $T = 230$ K, (b): $T = 10$ K (for further details see text).

The electron-precise complexes $[Fe_2(CO)_6(\mu\text{-}PR_2)(\mu\text{-}PR'_2)]$ ($R = R' = Ph$ (2); $R = Bu^t$, $R' = Ph$ (3); $R = Bu^t$, $R' = Cy$ (4))

Dessy *et al.* [10, 11] investigated the electrochemically reversible 2e reduction of $[Fe_2(CO)_6(\mu\text{-}PMe_2)_2]$ in 1,2-dimethoxyethane to give the appropriate dianion. They also found that an equilibrium mixture containing the uninegative radical anion is formed on reacting the dianion with the neutral parent [12]. Ginsburg *et al.* [13] found that the cyclic voltammogram of $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$ in acetonitrile at a mercury electrode exhibits a single reversible 2e reduction step. These authors also reported that the reduction is totally irreversible at a platinum electrode. In contrast to the results of Dessy *et al.* [10–12] on the bis(dimethylphosphido)-bridged complex, in the case of the bis(diphenylphosphido)-bridged complex no EPR detection of any paramagnetic species could be obtained upon mixing THF solutions of the dianion and the parent [13]. Complexes **2**–**4** could also be reduced at a platinum electrode in THF solutions, all at approximately the same potentials, −1.74 to −1.91 V, indicating that the substituents R and R′ on the phosphido ligands have only a minor influence on the redox potentials. The data are summarized in Table 2. Two closely spaced one-electron transfers were observed. For **4** indeed two separate waves were noted at low scan rates, like in the differential pulse voltammograms. For both complexes **3** and **4** in the backgoing oxidative scan also two separate waves were seen, whereas for **2** a large ΔE_p value was noted (Table 2). From the here assembled data and from earlier reported electrochemical and structural data [5, 12, 13] it can be concluded that these compounds can be reduced in two one-electron steps. In this reduction process the dinegative ion $[Fe_2(CO)_6(\mu\text{-}PR_2)(\mu\text{-}PR'_2)]^{2-}$ is formed, the existence of which is well established [13]. Molecular configurational changes accompany this reduction (the Fe–Fe bond is broken and the Fe_2P_2 unit flattens), which make the electrochemical processes, both reduction and re-oxidation, quite slow. This accounts for the large found ΔE_p values. The occurrence of the uninegative ion $[Fe_2(CO)_6(\mu\text{-}PR_2)(\mu\text{-}PR'_2)]^{\bullet -}$ is limited to a very small potential region. Thus, this anion readily disproportionates to the neutral and the dianionic species. Due to the resulting very low concentration EPR detection will be difficult [13].

Complexes **3** and **4** could be oxidized at nearly the same potential, 0.20 and 0.15 V, to give the unipositive ions $[Fe_2(CO)_6(\mu\text{-}PBu^t{}_2)(\mu\text{-}PR_2)]^{\bullet +}$. A comparison of

TABLE 2. Electrochemical data[a] for complexes **2**–**4**

Scan rate (V/s)	**2**				**3**				**4**			
	$E_{p,c}$ (V)	$E_{p,a}$ (V)	ΔE_p (mV)	i_b/i_f	$E_{p,c}$ (V)	$E_{p,a}(1)$ (V)	$E_{p,a}(2)$ (V)	i_b/i_f	$E_{p,c}$ (V)	$E_{p,a}(1)$ (V)	$E_{p,a}(2)$ (V)	i_b/i_f
Reductions: 0/−2												
0.10	−1.90	−1.68	220	0.87	−1.74	−1.67	−1.55	0.96	−1.82	−1.70	−1.00	0.71
0.50	−1.95	−1.64	310	0.88	−1.75	−1.66	−1.52	0.90	−1.88	−1.69	−1.56	0.73
1.00	−1.98	−1.61	370	0.91	−1.76	−1.64	−1.51	0.88	−1.92	−1.68	−1.57	0.67
5.00	−2.06	−1.56	500	0.81	−1.80	−1.62	−1.46	0.73	−2.02	−1.65	−1.48	0.46

Scan rate (V/s)	**2**	**3** $E_{1/2}$ (V)	**3** ΔE_p (mV)	**3** i_b/i_f	**4** $E_{1/2}$ (V)	**4** ΔE_p (mV)	**4** i_b/i_f
Oxidations: 0/+1							
0.10	$E_{p,a}=0.82$[b]	0.20	87	0.62	0.15	76	0.92
0.50		0.20	102	0.84	0.15	92	0.99
1.00		0.21	126	0.94	0.15	106	0.98
5.00					0.16	160	0.97

[a] In THF (0.1 M $Bu_4N[PF_6]$); potentials vs. $Fc^{0/+1}$ redox couple. [b] Irreversible multi-electron wave.

the current functions with those for the reductions shows that one electron is transferred. This oxidation process is chemically reversible at a scan rate of 1 V/s ($i_b/i_f=1$), but the electron transfer is a rather slow process as shown by the large ΔE_p values. In contrast with this, compound **2** exhibits only an irreversible oxidation wave in which the compound decomposes.

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