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Redox and Mixed-Valence Chemistry of the Clusters $M_4(CO)_{11}(\mu_4\text{-}PR)_2$ with M = Fe and/or Ru and of Their Derivatives

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As expected, the unsaturated clusters $Fe_4(CO)_{11}(PR)_2$ (R = *t*-Bu, **3**; R = Ph, **4**) undergo two electrochemically reversible one-electron reductions, whereas their saturated counterpart $Fe_4(CO)_{12}(PPh)_2$ can be oxidized reversibly. The same holds true for the unsaturated $P(OMe)_3$ and *p*-Tol-NC derivatives of **4**, for $Ru_4(CO)_{11}(PPh)_2$, and for its $P(OMe)_3$ derivative. With cobaltocene as a reductant, stable salts of the cluster monoanions can be obtained for an extensive series of these unsaturated M_4 clusters, including the Fe_4, Fe_3Ru, Fe_2Ru_2, and Ru_4 parent compounds and mono-PX_3 and mono-RNC derivatives of the Fe_4 system as well as disubstituted RNC and RNC/PX_3 derivatives thereof. The ESR spectra of the cluster ions show strong spin–spin coupling with the μ_4-bridging PR units as well as with terminal PX_3 ligands. The double clusters $Fe_4(CO)_{10}(PPh)_2$–LL–$Fe_4(CO)_{10}(PPh)_2$ (LL = $(MeO)_2P–C_6H_4–P(OMe)_2$ or $CN–C_6H_4–NC$) and the triple cluster $Fe_4(CO)_{10}(PPh)_2$–LL–$Fe_4(CO)_9(PPh)_2$–LL–$Fe_4(CO)_{10}(PPh)_2$ (LL = $(MeO)_2P–C_6H_4–P(OMe)_2$) can be reduced chemically or electrochemically to stable mono- and dianions that can be isolated as their cobaltocenium salts. For the mixed-valence double-cluster monoanions, the IR spectra show localized spins whereas the cyclic voltammograms, the ESR spectra, and the near-IR spectra provide some evidence for an electronic interaction between the two redox centers which is strongest in the case of the *p*-phenylenebis(isonitrile)-bridged system.

Introduction

Ever since the seminal work by Strouse and Dahl on the nature of the unpaired electron in $SCo_3(CO)_9$,[2] it has been known that clusters capped by Lewis basic main-group elements are good candidates for oxidation and reduction producing paramagnetic cations or anions. Their elementary redox chemistry has been extensively investigated[3] and also used as the framework for studies of ETC catalyzed ligand substitutions.[4] Comparatively little work is published, however, on the isolation of paramagnetic derivatives of these clusters and their investigation with respect to physical properties,[3,5] attractive ones being mixed valence in linked clusters and associated electronic phenomena.[6]

An especially well-investigated group of Lewis base bridged clusters is the tetranuclear M_4E_2 type, of which the RP-bridged compounds are readily accessible and of which $Co_4(CO)_{10}(PPh)_2$ and $Fe_2Co_2(CO)_{11}(PPh)_2$ have been explored with respect to their electrochemistry and ETC-catalyzed ligand substitution.[7] In this class of compounds, the Fe_4P_2[8] and Ru_4P_2[9] systems are exceptional in that they exist in the unsaturated $M_4(CO)_{11}(PR)_2$ form as well as in the saturated $Fe_4(CO)_{12}(PR)_2$ and $Ru_4(CO)_{13}(PR)_2$ forms. This difference between the Fe_4/Ru_4 and the Co_4/Fe_2Co_2 systems can be accounted for in terms of EHMO considerations,[10] and the consequences for reactivity have been worked out in detail starting from $Fe_4(CO)_{11}(PPh)_2$.[11] The ease of chemical interconversions between the saturated and unsaturated forms allowed the prediction that the electron count would be equally easily changed by oxidation of the saturated or reduction of the unsaturated compounds.

This paper reports our observations on the redox chemistry of the Fe and Ru systems. When it became obvious that their radical anions are unusually stable, the investigations were extended to ligand-substituted derivatives whose radical ions were expected to provide further bonding information from their ESR spectra. And finally the Fe_4–Fe_4 double clusters described in the preceding paper[12] were included in the investigation in the hope that they might yield paramagnetic mixed-valence compounds suitable for the study of intervalence charge-transfer phenomena.

Experimental Section

All compounds under investigation were prepared according to the published procedures.[9,11,12] Prior to each measurement,

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the purity of all samples was checked by IR spectroscopy which proved to be essential for the radical ion salts. IR spectra were recorded in solution on a Perkin-Elmer PE 782 spectrometer, ESR spectra on a Varian E 104 and E 112 and on Bruker B-ER 420 machines, UV–vis spectra on a Perkin-Elmer PE 555 machine, and VIS–near-IR spectra on a Varian 2390 spectrometer.

Electrochemical Procedures. The electrochemical techniques employed direct current rotating disk electrode (RDE) and cyclic voltammetry as well as controlled potential coulometry. The potentiostat (Model Wenking PCA 72 L), the voltage scan generator (Model Wenking VSG 72), and the coulometer (Model Wenking SSI 70) were from Fa. G. Bank, Göttingen, FRG. All measurements were made under a nitrogen atmosphere in highly purified benzonitrile,[13,14] which was 0.1 M in recrystallized Bu_4NClO_4. The purity of the solvent system was checked by running a blank voltammogram before each measurement. Cluster concentrations were about 10^{-3} M.

All the experiments employed a conventional three-electrode configuration with a platinum spiral wire auxiliary electrode and a reference electrode comprising a AgCl-coated Ag wire dipped in 0.1 M solution of Bu_4NClO_4 in benzonitrile and separated from the electrolyte solution by a fine frit. All quoted potentials are referenced to the standard Ag/AgCl electrode and were obtained by assuming a $E°$ relative to the standard Ag/AgCl electrode of −743 mV for the $[\text{cobaltocene}]^{+/0}$ couple in benzonitrile;[15] an internal calibration of the reference electrode was made with Cp_2CoClO_4 added after each measurement. The working electrode was a platinum disk electrode (0.013 cm^2) which was rotated at 600 rpm for the RDE voltammograms. Its surface was polished by using Cr_2O_3 until no scratches were observed at tenfold magnification. Before being inserted into the solution, the electrode was rinsed with acetone and distilled water and dried with a heat-gun. No compensation for iR drop losses was made. Under these conditions the $[\text{cobaltocene}]^{+/0}$ couple gave a peak separation, ΔE_p, of 70 mV at a scan rate of 50 mV s^{-1}. For the coulometric measurements the platinum disk electrode was replaced with a platinum foil (2–3 cm^2) and the solution stirred. Low-temperature experiments were performed by cooling the voltammetry cell with ice–acetone slushes; temperature control was of the order of ±2 °C. A summary of the essential electrochemical results is presented in Table I. Electrolyses in the cavity of the ESR spectrometer were performed with a three-electrode cell designed[16] for combined ESR and CV measurements under vacuum by using 0.1 M Bu_4NClO_4 in rigorously dried 1,2-dimethoxyethane.

Degradation of $Fe_4(CO)_{11}(PPh)_2$ with I_2. 4 (135 mg, 0.18 mol) in benzene (50 mL) was treated dropwise with a solution of I_2 (23 mg, 0.09 mmol) in benzene (20 mL). After 2 h of stirring the color of the solution had changed from black to dark orange. After evaporation to dryness, chromatography with benzene/hexane (1:10) over a 2 × 40 cm silica gel column yielded $Fe_3(CO)_9(PPh)_2$ (92 mg, 82%) as the only elutable band.

Preparation of the Paramagnetic Cluster Salts. All reductions were carried out at room temperature under argon in THF which was freshly distilled from natrium benzophenone ketyl. The cobaltocene used was freshly sublimed. A general reaction procedure is given, and the details for each specific case are contained in Table II: To a THF solution of the starting compound was added, under stirring, an equimolar amount of $CoCp_2$ dissolved in THF. An immediate decoloration indicated a quantitative reaction. The solution was filtered through a G4 frit and treated dropwise with oxygen-free pentane until the first signs of cloudiness occurred. Crystallization took place within 1 or 2 h at room temperature, or if necessary at 0 °C. The solvent was removed by filtration or, for small amounts of product, with a syringe. The product was washed with a small amount of pentane and dried under vacuum. Table III gives the characterization of the products. The amounts obtained of **2a**, **5a**, and **6a** were too small for analytical characterization; **20b** and **21b** could not be obtained analytically pure. All Fe_4 cluster salts are dark red in solution and black in the crystalline state; with increasing ruthenium content their color brightens and changes toward purple.

Table I. Electrochemical Data[a] for Compounds 1, 3, 4, 7, 9, 10, 14, 20, and 21[b]

compd	redox step	n^c	E_{pc}	E_{pa}	$(E_{pc} + E_{pa})^d/2$	i_{pa}/i_{pc}
1	reductn	1	−0.65			irrev
	oxidatn	1	+0.85	+0.95	+0.90	1.0
	oxidatn	>2		+1.61		irrev
3	reductn	1	−0.06	+0.02	−0.02	1.0
	reductn	1	−1.13	−1.03	−1.08	1.0
	oxidatn	from +0.7 V current–voltage curve badly defined				
4	reductn	(0.84)	+0.05	+0.13	+0.09	1.0
	reductn	1	−0.79	−0.67	−0.73	1.0
	oxidatn	1		+0.75		irrev
7	reductn (268 K)	1	−0.44	−0.34	−0.39	1.0
	reductn (268 K)	1	−1.01	−0.81	−0.90	1.0
	reductn (268 K)	1	−1.49			irrev
	oxidatn	from +1.2 V current–voltage curve badly defined				
9	reductn	1	−0.14	−0.06	−0.10	1.0
	reductn	1	−0.95	−0.75	−0.85	1.0
	oxidatn	from +0.5 V current–voltage curve badly defined				
10	reductn	1	−0.17	−0.09	−0.13	1.0
	reductn	1	−0.98	−0.88	−0.93	1.0
	oxidatn	from +0.5 V current–voltage curve badly defined				
14	reductn	1	−0.65	−0.57	−0.61	1.0
	reductn	1	−1.29	−1.03	(−1.16)	0.3
	oxidatn	from +1.0 V current–voltage curve badly defined				
20	reductn	(1.84)	−0.20	−0.06	−0.13	1.0
	reductn	2	−1.20			irrev
	oxidatn	from +1.0 V current–voltage curve badly defined				
21	reductn	1	−0.05	+0.05	±0.00	1.0
	reductn	1	−0.14	−0.04	−0.09	1.0
	reductn	1	−0.99			irrev
	reductn	1	−1.35			irrev
	oxidatn	from +0.5 V current–voltage curve badly defined				

[a] CV data in C_6H_5CN (0.1 M in TBAP, ~10^{-3} M in compound) at 293 K and 200 mV s^{-1} unless stated otherwise. Pt electrode. Potentials in V vs Ag/AgCl. [b] See text for compound numbering scheme. [c] Number of electrons transferred determined by comparison of limiting currents from RDE voltammograms. Values in parentheses determined coulometrically. [d] Roughly corresponding to $E_{1/2}$. The value in parentheses is a true $E_{1/2}$ from an RDE experiment.

Results and Discussion

All neutral cluster compounds used for this investigation have previously been reported by us.[9,11,12] These comprise the saturated Fe_4 parent cluster **1**, its unsaturated counterparts **2**–**4**, the Fe/Ru mixed compounds **5** and **6**, and the Ru_4 parent **7**. An extensive series of substituted derivatives was included, consisting of the monoisonitrile Fe_4 compounds **8** and **9**, the phosphite iron and phosphite ruthenium compounds **10** and **14**, three phosphine iron derivatives (**11**–**13**), and five bis-substituted Fe_4 compounds, all of which contained at least one isonitrile ligand (**15**–**19**). Of the Fe_4 multiple clusters the two basic double clusters **20** and **21**, containing the *p*-phenylenebis(phosphite) and -bis(isonitrile) bridges, respectively, were chosen together with the phosphite-substituted double cluster **22** and the triple cluster **23**.

Table IV gives a complete listing of all compounds used for or obtained in this work. In order to distinguish the isolated cobaltocenium salts of the cluster anions from the ions alone, we used the suffixes **a** and **b** for the former and the charges for the latter; e.g., 7^- and 23^{2-} denote the ions whereas **7a** and **23b** denote the corresponding salts.

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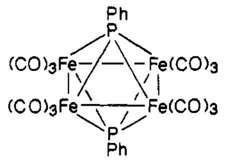
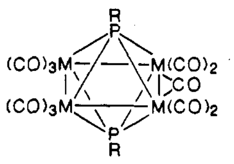
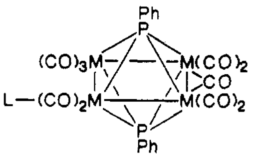


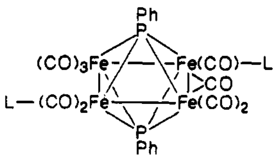
1



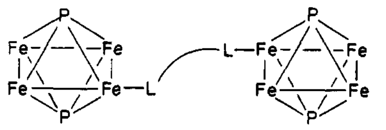
2-7: M = Fe, Ru



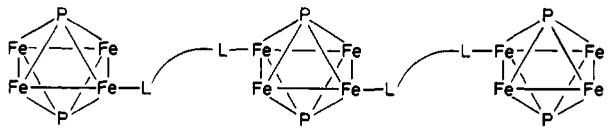
8-13: M = Fe
14: M = Ru, L = P(OMe)$_3$



15-19



20-22 (framework only)



23 (framework only)

Electrochemistry. The molecular orbital calculations for the M_4P_2 clusters[10] lead to the conclusion that their distinguishing feature is a MO of b_u symmetry situated in the energy gap between the bonding and antibonding levels. If this orbital is unoccupied the total electron count corresponds to seven skeletal electron pairs (SEP) which is the closo case in terms of Wade's rules but which also means two missing electrons in terms of the 18-electron rule. Conversely, with a filled b_u MO the clusters would fit the 18-electron rule for all four metal atoms but fail to correspond to the nido geometry expected for eight SEP systems. Of the existing M_4P_2 cluster compounds $Co_4(CO)_{10}(PPh)_2$, an eight SEP compound, has the metal atoms of highest electronegativity and thus the lowest lying b_u orbital, and it has not been possible to decarbonylate this system in order to reach the seven SEP situation.[7a] The same holds true for $Fe_2Co_2(CO)_{11}(PPh)_2$.[7a] The Fe_4 system, however, exists in both the saturated $Fe_4(CO)_{12}(PR)_2$ and the unsaturated $Fe_4(CO)_{11}(PR)_2$ forms.[8,11] With iron being less electronegative than cobalt, the b_u orbital is higher in energy, and the seven SEP (11 CO) and eight SEP (12 CO) compounds are now of comparable stability. For the Ru_4 case the b_u orbital is still higher in energy, and it is understandable that it cannot be filled: $Ru_4(CO)_{12}(PPh)_2$ with eight SEP does not exist, and the carbonylation of seven SEP $Ru_4(CO)_{11}(PPh)_2$ only leads to Ru–Ru bond breaking and formation of $Ru_4(CO)_{13}(PPh)_2$.[9]

It was therefore predictable that electrochemistry would provide an even simpler verification of the MO scheme in that the seven SEP clusters should be reducible and the eight SEP clusters oxidizable. While the corresponding measurements of the Co_4 and Fe_2Co_2 systems were plagued with reversibility problems,[7] the prediction was borne out to a large extent by the results for the Fe and Ru systems described herein.

The compounds selected for the electrochemical study were the Fe_4 parent clusters **1**, **3**, and **4**, the Ru_4 parent cluster **7**, the phosphite derivatives **10** and **14**, and the isonitrile derivative **9**. This selection provided the essential foundation for the inclusion and discussion of the bis(phosphite)- and bis(isonitrile)-bridged double clusters **20** and **21**. Full details of the measurement results are given in Table I. The potentials for the first reduction step that are pertinent to the following discussion are summarized in Table V.

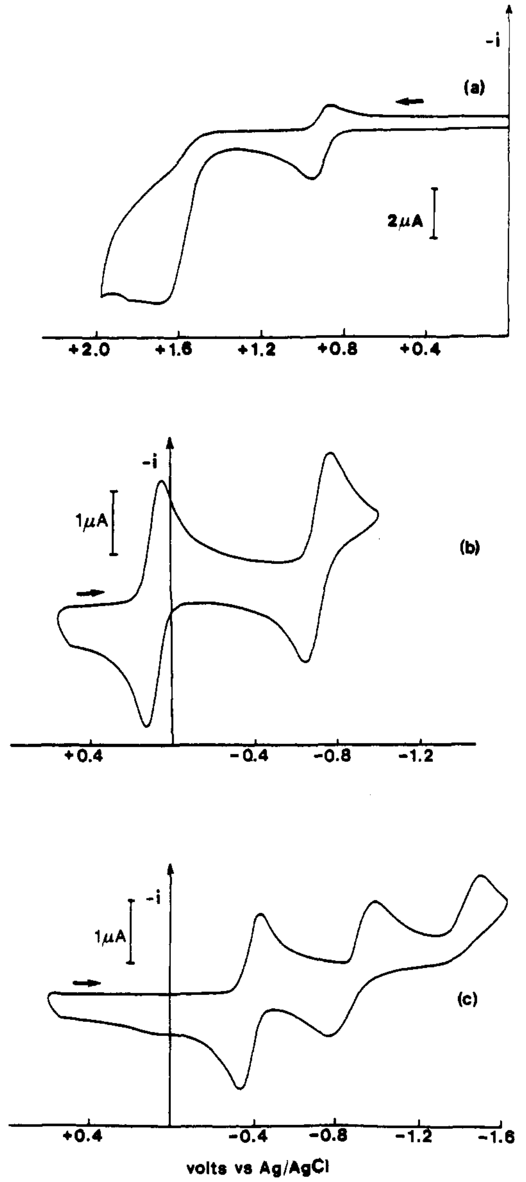


Figure 1. CV scans on Pt in benzonitrile of (a) **1**, (b) **4**, and (c) **7**: (a) and (b) at 293 K; (c) at 268 K. Scan rate = 200 mV s^{-1}.

1, the only saturated cluster investigated in this study, behaved according to expectation in that it could not be reduced without decomposition while the monocation was easily accessible. Further oxidation predicted by the MO scheme could not be performed, but instead irreversible multielectron transfer took place accompanied by decomposition. **3** and **4**, the unsaturated counterparts of **1**, showed exactly complementary behavior. Attempts at their oxidation were unsuccessful, but they easily accepted the anionic state. Furthermore, for both of them a second reductive step was observed, this time in complete accordance with the predictions from the MO scheme. The unsaturated Ru_4 parent cluster **7** behaved similarly to its iron counterparts in not allowing oxidation without decomposition. Its reductive behavior was bound to be different from that of **4** because of its different MO scheme and chemical behavior. At room temperature three one-electron reductions were possible within the solvent limit, the second of which was accompanied by partial chemical conversion as indicated by an additional oxidation wave

Table II. Preparative Details for the (Cobaltocenium)^+_n(cluster anion)$^{n-}$ Salts

	starting cluster in THF				$CoCp_2$ in THF			yield	
salt no.	no.	mg	mmol	mL	mg	mmol	mL	mg	%
2a	**2**	35	0.05	10	10.5	0.05	20	20	50
3a	**3**	80	0.11	20	21	0.11	30	68	69
4a	**4**	150	0.20	20	38	0.20	50	165	88
5a	**5**	10	0.013	10	2.5	0.013	10	5	40
6a	**6**	10	0.012	10	2.3	0.012	10	4	30
7a	**7**	65	0.07	20	13	0.07	20	45	58
8a	**8**	70	0.08	20	16.5	0.08	20	60	70
9a	**9**	150	0.18	50	34	0.18	30	151	82
10a	**10**	111	0.13	30	25	0.13	30	100	75
11a	**11**	55	0.07	20	13	0.07	20	45	65
12a	**12**	30	0.03	10	6.5	0.03	10	24	65
13a	**13**	60	0.06	20	11	0.06	20	50	70
15a	**15**	40	0.04	20	9	0.04	20	19	45
16a	**16**	50	0.05	40	10	0.05	20	34	57
17a	**17**	35	0.04	30	7	0.04	20	21	48
18a	**18**	70	0.07	40	14	0.07	20	66	78
19a	**19**	100	0.11	50	21	0.11	30	100	82
20a	**20**	80	0.05	50	4.7	0.025	20	64	68
20b	**20**	125	0.07	50	14	0.07	30	120	82
21a	**21**	140	0.09	50	8.5	0.045	40	105	66
21b	**21**	140	0.09	50	17.0	0.09	60	92	54
22a	**22**	76	0.04	50	4.3	0.02	20	40	54
23a	**23**	117	0.04	50	3.8	0.02	20	71	62
23b	**23**	94	0.03	50	6.7	0.03	20	73	81

Table III. Characterization of (Cobaltocenium)^+_n(cluster anion)$^{n-}$ Salts

				anal. calcd (found)		
no.	mp, °C	formula	mol wt	C	H	X
3a	131 dec	$C_{29}CoH_{28}Fe_4O_{11}P_2$	896.9	38.83 (38.59)	3.14 (3.36)	Fe 24.90 (24.71)
4a	147	$C_{33}CoH_{20}Fe_4O_{11}P_2$	936.8	42.31 (42.10)	2.15 (2.02)	Fe 23.84 (23.62)
7a	141	$C_{33}CoH_{20}O_{11}P_2Ru_4$	1117.7	35.46 (35.24)	1.80 (1.59)	
8a	166 dec	$C_{37}CoH_{29}Fe_4NO_{10}P_2$	991.9	44.80 (44.81)	2.95 (2.90)	Fe 22.52 (22.90)
9a	159 dec	$C_{40}CoH_{27}Fe_4NO_{10}P_2$	1025.9	46.83 (46.69)	2.65 (2.54)	N 1.36 (1.43)
10a	139	$C_{35}CoH_{29}Fe_4O_{13}P_3$	1032.8	40.70 (40.85)	2.83 (2.77)	Fe 21.63 (21.45)
11a	117 dec	$C_{35}CoH_{29}Fe_4O_{10}P_3$	984.8	42.68 (42.92)	2.97 (3.20)	Fe 22.68 (22.42)
12a	156	$C_{40}CoH_{31}Fe_4O_{10}P_3$	1046.9	45.89 (46.19)	2.98 (3.10)	Fe 21.33 (20.98)
13a	129 dec	$C_{50}CoH_{35}Fe_4O_{10}P_3$	1171.1	51.28 (51.17)	3.01 (3.50)	Fe 19.07 (19.40)
15a	124 dec	$C_{41}CoH_{38}Fe_4N_2O_9P_2$	1047.0	47.03 (46.91)	3.66 (4.06)	N 2.67 (2.33)
16a	120 dec	$C_{47}CoH_{34}Fe_4N_2O_9P_2$	1115.1	50.62 (50.54)	3.07 (3.73)	N 2.51 (2.27)
17a	134	$C_{39}CoH_{38}Fe_4NO_{12}P_3$	1087.9	43.05 (42.53)	3.52 (3.71)	N 1.28 (1.16)
18a	137	$C_{42}CoH_{36}Fe_4NO_{12}P_3$	1122.0	44.96 (44.63)	3.23 (3.43)	N 1.25 (1.27)
19a	140 dec	$C_{42}CoH_{36}Fe_4NO_9P_3$	1073.9	46.97 (46.89)	3.38 (3.69)	N 1.30 (0.99)
20a	173 dec	$C_{64}CoH_{46}Fe_8O_{24}P_6$	1890.7	40.66 (41.08)	2.45 (2.95)	Fe 23.63 (23.48)
21a	127 dec	$C_{62}CoH_{34}Fe_8N_2O_{20}P_4$	1756.5	42.39 (42.49)	1.96 (2.16)	N 1.59 (1.17)
22a	117 dec	$C_{64}CoH_{43}Fe_8N_2O_{22}P_5$	1852.6	41.69 (41.92)	2.34 (2.80)	N 1.51 (1.45)
23a	138 dec	$C_{95}CoH_{72}Fe_{12}O_{37}P_{10}$	2844.5	40.11 (39.34)	2.55 (2.84)	Fe 23.56 (23.21)
23b	171	$C_{105}Co_2H_{82}Fe_{12}O_{37}P_{10}$	3033.7	41.57 (41.56)	2.72 (2.24)	Fe 22.09 (22.40)

near 0 V on the reverse scan. This chemical conversion could be suppressed at 268 K. Thus the electrochemical and chemical behavior of the seven SEP cluster **7** can be fully correlated: the eight SEP situation is as unstable at room temperature for dianionic **7** as it is for its hypothetical CO addition product $Ru_4(CO)_{12}(PPh)_2$. As a consequence of this, **7** wants to take up more than two electrons, and it does so either by being reduced beyond the dianionic state or by adding two CO ligands. Altogether the voltammetry of the three parent compounds very clearly supports the MO picture outlined by Saillard et al.[10] Figure 1 shows the three pertinent cyclic voltammograms.

The relative potentials for the reduction of **4** (or **3**) and **7** are also as expected: the ruthenium compound **7** with the higher lying b_u orbital is more difficult to reduce than the iron compound **4** (cf. Table V). There is only a small difference between **3** and **4**, with the more electron-rich **3** having a slightly more negative $E_{1/2}$ for the first reduction. The effects on the potentials due to the terminal ligands RNC and $P(OMe)_3$, which are somewhat more electron rich than CO, are also as expected. They shift all potentials for reductions by about 0.2 V to more negative values. As shown by the data for the Fe_4–RNC system **9** in comparison to the Fe_4–$P(OMe)_3$ system **10**, this effect is a little smaller for the *p*-tolueneisonitrile ligand than for the trimethyl phosphite ligand. On the other hand, the differences in potentials between the $P(OMe)_3$-substituted Fe_4 and Ru_4 clusters **10** and **14**, respectively, are similar to those between the Fe_4 and Ru_4 parent compounds **4** and **7**, respectively. Since all three substituted clusters **9**, **10**, and **14** show two reversible or quasi-reversible reductions, the correlation with their parent compounds and the MO schemes is virtually complete.

The electrochemical behavior of the bis(phosphite)- and bis(isonitrile)-bridged Fe_4 double clusters **20** and **21**, respectively, should, to a first approximation, be related to that of the phosphite- and isonitrile-substituted clusters **10** and **9**, respectively. The potentials for the first reductions (cf. Table V) confirm this view. However, first a complete analogy would require two electrons to be transferred in each of the first and second reduction waves, thereby producing 4– ions, and second, an electronic interaction between the two half-molecules must lead to a splitting of the two-electron waves into one-electron waves with the peak separation being a measure of electron de-

Table IV. Listing of Compounds Studied[a]

1	$Fe_4(CO)_{12}(PPh)_2$
2, 2a	$Fe_4(CO)_{11}(PMe)_2$
3, 3a	$Fe_4(CO)_{11}(P\text{-}t\text{-}Bu)_2$
4, 4a	$Fe_4(CO)_{11}(PPh)_2$
5, 5a	$Fe_3Ru(CO)_{11}(PPh)_2$
6, 6a	$Fe_2Ru_2(CO)_{11}(PPh)_2$
7, 7a	$Ru_4(CO)_{11}(PPh)_2$
8, 8a	$Fe_4(CO)_{10}(PPh)_2CN\text{-}t\text{-}Bu$
9, 9a	$Fe_4(CO)_{10}(PPh)_2CN\text{-}p\text{-}Tol$
10, 10a	$Fe_4(CO)_{10}(PPh)_2P(OMe)_3$
11, 11a	$Fe_4(CO)_{10}(PPh)_2PMe_3$
12, 12a	$Fe_4(CO)_{10}(PPh)_2PMe_2Ph$
13, 13a	$Fe_4(CO)_{10}(PPh)_2PPh_3$
14	$Ru_4(CO)_{10}(PPh)_2P(OMe)_3$
15, 15a	$Fe_4(CO)_9(PPh)_2(CN\text{-}t\text{-}Bu)_2$
16, 16a	$Fe_4(CO)_9(PPh)_2(CN\text{-}p\text{-}Tol)_2$
17, 17a	$Fe_4(CO)_9(PPh)_2(CN\text{-}t\text{-}Bu)P(OMe)_3$
18, 18a	$Fe_4(CO)_9(PPh)_2(CN\text{-}p\text{-}Tol)P(OMe)_3$
19, 19a	$Fe_4(CO)_9(PPh)_2(CN\text{-}p\text{-}Tol)PMe_3$
20, 20a, 20b	$Fe_4(CO)_{10}(PPh)_2\text{-}L^1\text{-}Fe_4(CO)_{10}(PPh)_2$[b]
21, 21a, 21b	$Fe_4(CO)_{10}(PPh)_2\text{-}L^2\text{-}Fe_4(CO)_{10}(PPh)_2$[c]
22, 22a	$Fe_4(CO)_{10}(PPh)_2\text{-}L^1\text{-}Fe_4(CO)_9(PPh)_2P(OMe)_3$[b]
23, 23a, 23b	$Fe_4(CO)_{10}(PPh)_2\text{-}L^1\text{-}Fe_4(CO)_9(PPh)_2\text{-}L^1\text{-}Fe_4(CO)_{10}(PPh)_2$[b]

[a] The suffixes **a** and **b** indicate that cobaltocenium salts of the mono- and dianionic compounds have been obtained. [b] $L^1 = p\text{-}(MeO)_2P\text{-}C_6H_4\text{-}P(OMe)_2$. [c] $L^2 = p\text{-}CN\text{-}C_6H_4\text{-}NC$.

Table V. $E_{1/2}$ Values (V) for the First Reductive Step in the Cluster Voltammograms

compd	$E_{1/2}$	compd	$E_{1/2}$
3	−0.06	10	−0.17
4	+0.05	14	−0.65
7	−0.44	20	−0.20
9	−0.14	21	−0.05

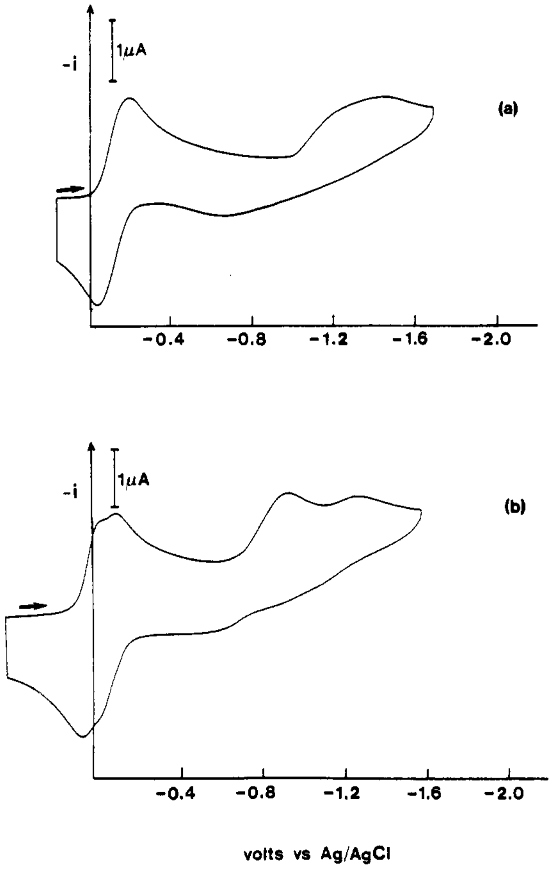


Figure 2. CV scans on Pt in benzonitrile of (a) **20** and (b) **21**. Scan rate = 200 mV s^{-1}.

localization over the entire redox system.[17] The voltammograms obtained for **20** and **21** (Figure 2) fulfill both these requirements. Controlled potential coulometry showed that the first reduction wave for **20** corresponds to the reversible transfer of roughly two electrons. The second reduction wave was irreversible in accordance with chemical experience which indicates that three or four negative charges are beyond the stability limit of organometallic molecules. Whereas no peak splitting occurred in the voltammograms of **20**, those of **21** clearly showed four separate one-electron reductions of which the first two were again reversible. This is in agreement with the fact that *p*-phenylenebis(isonitrile) is a better electronic conductor than the corresponding bis(phosphite), and therefore an intra-double-cluster electronic interaction is apparent in the cyclic votammograms of **21**, but not of **20**.

The electrochemistry of the double cluster **21** thus provided the first indication of the possibility of mixed-valence phenomena in such systems. This was in fact the observation that triggered the subsequent chemical and spectroscopic investigations described in this paper, which can be related to analogous work on double clusters by Meyer[18a] and Robinson.[18b]

Preparative Redox Reactions. The electrochemical results suggested oxidation of **1** and reduction of all other clusters. All attempts at one-electron oxidation failed. The standard reagents $FeCp_2^+PF_6^-$, $Ag^+BF_4^-$, TCNQ, and I_2 either did not react with **1** and **4** or destroyed these clusters. An almost quantitative but undesired reaction took place between **4** and iodine that resulted in the extrusion of one iron atom and formation of the very stable clusters $Fe_3(CO)_9(PPh)_2$, reminiscent of the thermal- and CO-induced degradations of the Fe_4P_2 clusters.[8]

In contrast, the reductions proved to be extremely facile in accord with the fact that for instance the first reduction for the parent compound **4** is at a positive potential. Actually solutions of **4**, if not prepared with extreme care, always contained small amounts of its monoanion as evidenced by ESR spectroscopy. Of the two reductants tested, natrium naphthalenide and cobaltocene, the latter proved to be more convenient for obtaining pure salts and was used throughout. Of the compounds in Table IV those whose numbers are given with the suffixes **a** and **b** were obtained as cobaltocenium salts.

All four unsaturated parent clusters **2**–**7** were, according to IR control, quantitatively and quickly reduced to salts of their monoanions in THF. The low isolated yields of **2a**, **5a**, and **6a** were mainly due to the small amounts used for the reactions. For the same reason, **2a**, **5a**, and **6a** were also not subjected to elemental analysis and identified only by their IR and ESR spectra. The radical anion salts are remarkably stable. For instance solid **4a** can be handled for short times in air, and it melts at 147 °C without decomposition under argon. Neither cobaltocene nor natrium naphthalenide produced salts of any of the single-cluster dianions nor was there any spectroscopic evidence for their formation.

All six singly substituted Fe_4 clusters **8**–**13** were converted to their cobaltocenium salts **8a**–**13a** without problems. The $Ru_4P(OMe)_3$ cluster **14**, however, was not reduced by cobaltocene, in accord with the observation (see above) that the Ru_4 clusters **7** and **14** are reduced at about 0.5 V more negative potentials than their iron counterparts **4** and **10**. For the same reason bis(phosphine) and bis-

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[17] Cf. Morrison, W. H.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998 and Taube, H. *Angew. Chem.* **1984**, *96*, 315; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 329 as well as references cited in these papers.

[18] (a) Baumann, J. A.; Salmon, D. S.; Wilson, S. T.; Meyer, T. J. *Inorg. Chem.* **1979**, *18*, 2472. (b) Robinson, B. H., private communication.

Table VI. IR Data of the Radical Anion Salts (THF, cm^{-1})

no.	ν(NC)	ν(CO)						
2a		2038 w	1967 vs	1948 s	1921 m	1785 w		
3a		2030 w	1960 vs	1941 s	1914 m	1776 w		
4a		2038 w	1970 vs	1951 s	1924 m	1784 w		
5a		2035 w	1980 vs	1955 m	1935 w	1800 w		
6a		2038 w	1980 vs	1975 sh	1955 s	1935 m	1790 w	
7a		2042 w	1985 vs	1962 s	1941 m	1795 w		
8a	2109 m	2009 s	1958 vs	1936 s	1908 m	1770 sh	1745 s	
9a	2100 m	1999 m	1961 vs	1942 s	1915 m	1774 sh	1749 s	
10a		2006 m	1998 m	1956 vs	1950 sh	1916 s	1775 w	1749 w
11a		1999 m	1952 vs	1946 sh	1917 s	1775 w	1749 w	
12a		1998 m	1955 vs	1949 sh	1915 s	1775 w	1748 w	
13a		2000 m	1959 vs	1952 sh	1919 s	1771 w	1742 sh	
15a	2120 m	1976 sh	1972 m	1941 vs	1930 sh	1896 s	1734 w	
16a	2100 m	1995 m	1951 vs	1942 sh	1905 s	1740 w		
17a	2115 w	1976 m	1940 vs	1930 sh	1903 m	1730 w		
18a	2076 w	2005 w	1976 m	1948 vs	1910 sh	1735 w		
19a	2100 w	2004 m	1995 m	1959 vs	1940 sh	1910 m	1770 m	1745 w
20a		2050 w	2010 vs	1960 vs	1922 m	1809 w		
20b		2010 w	1960 vs	1921 m	1778 w			
21a	2124 w	2058 m	2023 vs	1970 vs	1925 sh	1805 w,b		
21b	2097 w	2092 w	2000 sh	1967 vs	1925 sh			
22a	2120 w	2030 m	1993 vs	1978 sh	1969 vs	1958 sh	1928 m	1800 w
23a		2060 w	2020 vs	1991 vs	1962 vs	1918 sh	1800 w	
23b		2030 w	2010 w	1988 m	1960 vs	1923 m	1785 w,b	

(phosphite)-substituted Fe$_4$ clusters were not reduced by cobaltocene. They seem to be just beyond the potential limit since the bis(isonitrile) compounds **15** and **16** as well as the mixed isonitrile–phosphine compounds **17**–**19** were all reduced to **15a**–**19a** in reasonable to good yields.

For the symmetrical double clusters **20** and **21** the question arose as to whether the almost identical potentials for their first and second reduction steps would render their monoanions stable or unstable with respect to disproportionation to the neutral and dianionic states. The results of the chemical reductions in THF were unambiguous in that the salts of the monoanions were formed in good yields and, according to IR evidence, did not disproportionate when redissolved. Likewise the unsymmetrical double cluster **22** and the triple cluster **23** were converted to the salts of their monoanions. All four salts **20a**–**23a** gave satisfactory elemental analyses, but occasional erratic results from their ESR and near-IR measurements (done abroad) did indicate a limited stability. Dianionic salts could be obtained from **20**, **21**, and **23** but not from **22**. Only **23b** gave reproducible spectra and elemental analyses. For this reason **20b** and **21b**, which seem to revert partially to **20a** and **21a** upon standing, are included only in the IR table and not discussed further here.

The cluster radical anion salts were easily identified by their IR spectra (Table VI). For the single clusters **2**–**19** the IR patterns of their ν(CO) bands are shifted by an average of 45 cm^{-1} to lower wavenumbers without changing much in appearance. Figure 3 exemplifies this for the case of the parent cluster **4**. The IR spectra of the double- and triple-cluster anions substantiated the stepwise one-electron reductions. Due to the fact that the neutral clusters (unsubstituted, substituted, and symmetrical double clusters) show just one prominent ν(CO) band[11] for each kind of Fe$_4$ unit the type of cluster units present in the multiple-cluster anions could be found and distinguished. Thus the monoanion of **20a** shows two strong ν(CO) bands close to those for neutral **10** (2017 cm^{-1}) and the anion of **10a** (1956 cm^{-1}). This indicates that the double-cluster monoanion **20$^-$** contains one reduced and one unreduced Fe$_4$ half-molecule, and moreover closer inspection of the IR spectrum shows that the solution contains neither neutral **20** nor dianionic **20b**. Similarly, as shown in Figure 4, the neutral triple cluster **23** has a ν(CO) pattern with strong bands in a 2:1 intensity ratio representing the two monosubstituted and the one disubstituted Fe$_4$ subunits. In the monoanionic state of **23** there are now three strong bands resulting from the neutral external Fe$_4$ unit (2020 cm^{-1}), the neutral internal Fe$_4$ unit (1991 cm^{-1}), and the reduced external Fe$_4$ unit (1962 cm^{-1}). The dianion of **23**, albeit less clearly, gives rise to the 2:1 pattern of one neutral disubstituted Fe$_4$ unit (1988 cm^{-1}) and two reduced monosubstituted Fe$_4$ units (1960 cm^{-1}).

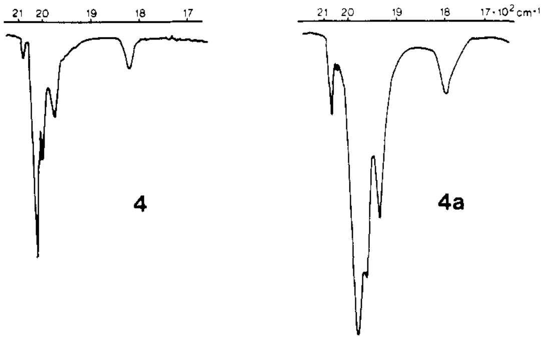

Figure 3. IR spectra of **4** and **4a** (in THF).

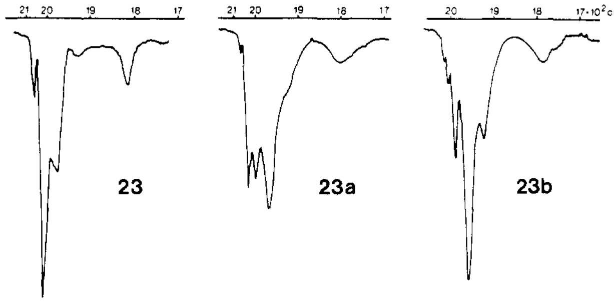

Figure 4. IR spectra of **23**, **23a**, and **23b** (in THF).

For the monoanionic double and triple clusters the IR spectra always show separate bands for neutral and reduced Fe$_4$ cluster subunits. This means that on the IR time scale no exchange of charge occurs between the two subunits linked by the bidentate ligands. Accordingly, just as indicated by the voltammetric measurements, an in-

Table VII. ESR Data for Cluster Radical Ions[a]

compd	solv	multiplet[b]	a, G
1^{+c}	DME	T	33.0
2a	THF	T	33.0
3a	THF	T	30.0
4a	THF	T	33.4
5a	THF	T	26.0
6a	THF	T	28.2
7a	THF	T	ca. 30
8a	THF	T	33.0
9a	THF	T	32.7
10a	THF	TD	33.0/14.2
11a	THF	TD	32.5/7.7
12a	THF	TD	33.0/7.5
13a	THF	TD	32.5/7.1
20a	CH_2Cl_2	TD	32.0/11.0
21a	THF	T	31.2
22a	THF	T	32.5
23b	THF	TD	31.5/7.7

[a] Obtained at room temperature; isotropic hyperfine splittings due to coupling with the phosphorus nuclei. [b] Abbreviations: T, triplet; TD, triplet of doublets. [c] During electrolysis in the ESR cell.

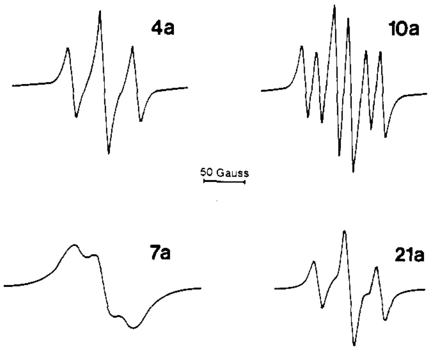

Figure 5. ESR spectra of **4a**, **7a**, **10a**, and **21a** (in THF).

tensive electronic interaction between the two half-molecules of the double-cluster radical anions was ruled out, and further spectroscopic measurements were necessary to quantify the nature of the mixed-valence interaction.

ESR Measurements. For trinuclear clusters of the M_3E tetrahedrane-type ESR spectroscopy of the paramagnetic species had shown that the unpaired electron resides in an orbital (i.e. the SOMO) which results predominantly from the atomic orbitals of the three metal atoms[2,3] in accord with EHMO calculations.[19] An illustrative example for this was provided by paramagnetic $Co_3(CO)_9PPh$ and the radical anion of $FeCo_2(CO)_9PPh$ whose ESR spectra showed spin–spin coupling with the cobalt nuclei but not with the phosphorus atom.[20] In contrast to this the EHMO calculations for the M_4E_2 systems[10] indicated that the LUMO of unsaturated $Fe_4(CO)_{11}(PPh)_2$ as well as the HOMO of saturated $Fe_4(CO)_{12}(PPh)_2$ should be comprised of significant metal *and* phosphorus AO contributions. The ESR data obtained here and summarized in Table VII provided experimental proof for this.

The cluster anion salts were used as such for the ESR measurements. The ESR data for **3a** and **4a** could be reproduced by electrolysis of **3** and **4** in DME solution in a combined ESR–electrochemistry cell.[16] The ESR data for $\mathbf{1}^+$, which could not be isolated as a salt, were only obtained by electrolysis of **1** in the ESR spectrometer.

All cluster ions subjected to ESR measurement provided simple spectra that allow straightforward interpretation. The g values for all anions are 2.044 ± 0.001 whereas that for $\mathbf{1}^+$, the only cation, is 2.036. These values are somewhat greater than the free electron value of 2.0023 expected for such purely covalent species but not unusual for iron-centered organometallic radicals.[21] The symmetrical nature of the ions is obvious from the triplet signals due to hyperfine coupling with the equivalent μ_4-bridging phosphorus atoms. The magnitude of this coupling with isotropic a values around 30 Gauss is quite high, compared with its absence in $Co_3(CO)_9PPh$ or the 12–18 G values in $Fe_3(CO)_8L(\mu_3\text{-}PPh)_2$ compounds.[22] A high degree of μ_4-phosphorus AO contribution to the SOMO is thereby indicated whereas the lack of iron nuclei capable of exhibiting hyperfine coupling does not allow a quantification of the iron AO contributions. However, the almost identical appearance of the ESR spectra observed for the two isoelectronic species $\mathbf{1}^+$ and $\mathbf{4}^-$ lends further support to the correctness of the EHMO model[10] even on a quantitative basis.

Variations of the parent cluster **4** lead to the expected variations of the ESR spectra. With increasing ruthenium content, e.g. in **5**, **6**, and **7**, line broadening becomes very noticeable until for $\mathbf{7}^-$ the triplet fine structure is almost lost. This can be related to the presence of two ruthenium isotopes with a nuclear spin of $^5/_2$ which contribute to the hyperfine structure as well as to the relaxation mechanism. The introduction of terminal phosphorus ligands gives rise to additional line splittings, again of noticeable size. Each line of the triplets is split into a clean doublet, the splitting by the phosphite-type ligands (cf. **10a**, **20a**) being significantly larger than by the phosphine-type ligands (cf. **11a**, **12a**, **13a**). The isonitrile ligands do not show up in the ESR spectra (cf. **8a**, **9a**). Neither do they affect the μ_4-phosphorus couplings nor the line widths (defined as the peak-to-peak separations) which for all the single M_4 cluster anions are 6.8 ± 0.7 G. Figure 5 shows representative examples of the ESR spectra.

The ESR spectra of the double- and triple-cluster anions are, at first glance, replicas of their single-cluster analogues: **20a** appears like **10a** and **21a** like **9a**. There is no visible coupling due to the additional μ_4-bridging or terminal (i.e. connecting) phosphorus atoms. However, in both cases the ESR line widths (15.0 G for **20a**, 10.0 G for **21a**) are approximately twice those for the corresponding single clusters (6.4 G for **10a**, 6.0 G for **9a**). This may represent either the unresolved long-range coupling or the beginning of line broadening due to charge exchange between the two Fe_4 units of the double clusters. If the latter is the case, the ESR spectra give an indication of the time scale of the charge exchange and thereby the degree of mixed-valence interaction:[23] this effect seems to be noticeable at the time resolution of ESR spectroscopy (10^{-9} s) whereas at the time resolution of IR spectroscopy (10^{-13} s) it cannot be detected.

In the cases of the monophosphite-substituted double-cluster salt **22a** and the triple-cluster salt **23b** there exist alternative locations for the unpaired electrons due to the nonequivalence of the available Fe_4 units. In both cases the ESR spectra verify the expected charge location. For **22a** no line splitting due to coupling with the $P(OMe)_3$ ligand is visible, indicating that the less electron-rich unsubstituted Fe_4 unit is reduced. For **23b** the two negative charges reside on the outer, less substituted, Fe_4 units as

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(19) Fisel, R.; Hoffmann, R. cited in Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1981**, *20*, 2540.

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(22) Ohst, H. H.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 2066.

(23) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

Table VIII. Near-IR Data[a]

	λ_{max} (ϵ)	
compd	in CH_2Cl_2	in THF
4	900 (770)	950 (810)
4a	850 (480)	850 (440)
	1325 (450)	1325 (460)
20	900 (1250)	910 (1190)
20a	900 (630)	850 (575)
	1250 (305)	1250 (395)
21	950 (485)	950 (360)
21a	900 (65)	850 (235)
	1300 (55)	1300 (170)

[a] λ_{max} in nm; ϵ in L/(mol cm).

evidenced by the ESR double triplet resembling those of **10a** and **20a**. In contrast to the symmetrical double-cluster monoanions no significant ESR line broadening occurs for **22a** and **23b** (line widths = ca. 8 G) which lends support to the time scale of charge exchange proposed above.

Electronic Spectra. Among the various criteria for mixed valence in ligand-bridged complexes the occurrence of an intervalence charge-transfer band in the electronic spectra is of great importance.[17,23,24] This band of low intensity is usually found in the near-IR region, and, due to the polar nature of the absorbing species, its position is solvent-dependent. In order to further substantiate the mixed-valence nature of the double-cluster anions their electronic spectra were recorded together with those of the relevant neutral or anionic parent compounds in CH_2Cl_2 and THF solutions.

The common feature of all recorded UV–vis spectra is a strong absorption below 300 nm, the tail of which extends across the whole visible range without any significant band structure. In this range the only difference between the neutral and anionic compounds is the higher absorption by the latter which seems to rise with increasing ligand substitution and specifically with double-cluster formation. The molar extinctions ϵ [L/(mol cm)] at 500 nm exemplify this. Their values for **4**/**4a** (1300/1200), **9**/**9a** (920/1660), **16**/**16a** (1200/3000), and **21**/**21a** (420/5400) show the orders of magnitude for a sequence of compounds with isonitrile ligands.

In the near-IR range beyond 700 nm there are weak bands for the neutral as well as for the anionic compounds that show characteristic variations (Table VIII). One band around 800 nm occurs in all recorded cases. In addition the anionic species show a band around 1300 nm. For the double cluster anions **20**$^-$ and **21**$^-$ this may be the expected intervalence charge-transfer band. However, the fact that this band also occurs for the single cluster anion **4**$^-$ limits its use in the discussion of mixed valence. A further weakness of the near-IR data with respect to intervalence charge transfer is the very limited solvent dependence of the band positions.

Thus the interpretation of the electronic spectra remains ambiguous. And, although of the four methods applied to study the mixed-valence nature of the double clusters (CV, IR, ESR, near-IR) three provide some evidence for electronic interaction between the two Fe_4 units, in no case could a definite conclusion be reached. We propose, therefore, that the double cluster salts **20a** and **21a** be at best classified as weak class II systems according to the mixed-valence terminology of Robin and Day.[24]

Conclusions

The availability of MO schemes for M_4E_2 clusters and of a large number of M_4P_2 compounds with M = Fe and Ru has enabled a detailed study of the redox and spectroscopic properties of these systems to be made. Voltammetric measurements, preparative redox chemistry, and ESR spectroscopy have verified the simple conclusions of the MO calculations with respect to saturation/unsaturation, orbital composition, and chemical interconversions. It was shown that stable cluster anion salts are easily accessible. The double clusters consisting of two Fe_4P_2 units linked by a bridging ligand could be reduced to stable monoanions that are mixed-valence systems. The electrochemical and spectroscopic (IR, ESR, near-IR) investigation of these systems did not give an unequivocal answer to the question whether electronic interaction occurs between the two Fe_4 units. In order to generate strong electronic interaction, it seems necessary to link the two Fe_4 units by a shorter or more electronically conducting bridge. The detailed study of physical properties of the ionic and mixed-valence compounds has to await the availability of larger single crystals.

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