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Complexes $\{Cp^*(Dppe)FeC\equiv CC_2R[Co_2L_2(CO)_4]\}^{n+}$ (R = H, $Si(CH_3)_3$; $n = 0, 1, 2$; $L_2 = (CO)_2$, Dppm): Synthesis, Redox Properties, and Electronic Characteristics

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Abstract—New neutral and cationic complexes containing the mononuclear organoiron Cp*(Dppe)Fe and cluster Co_2C_2 fragments have been synthesized. It was shown that the redox reactions substantially extend possibilities for the synthesis of the cationic complexes, and the transition metal derivatives with the unoccupied electron shell represent an interesting and promising direction of studies. It has been confirmed by spectroscopy in the near-IR range a substantial intramolecular electron interaction between the cobalt and iron atoms in the cationic complexes. The obtained estimates for the interaction energy suggest that these compounds can be perspective as molecular devices.

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INTRODUCTION

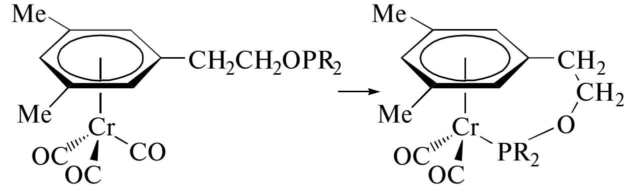
Along with widely used thermal and especially photochemical methods for the substitution of CO ligands in mono- and polynuclear carbonyl complexes of transition metals, the redox activation of the M-CO bond followed by the elimination of CO and the other ligands coordination has been developed. As a rule, this has been described for radical anions formed upon either the reduction of mononuclear [1, 2] or cluster complexes [3, 4], or the one-electron oxidation of the diamagnetic anionic clusters of Fe, Ru, or Os [5]. The 19*e*-species formed in the case of the mononuclear complexes easily lose CO to form the 17*e* complexes. The high lability of the paramagnetic species compared to the complexes with the closed electron shell is well known [6]. Then, a new ligand, for example, phosphine, phosphate, isonitrile, etc., comes to the formed coordination site, which is accompanied by the oxidation of the radical anion to the neutral 18*e* product. Similar processes are usually catalytic (with electron transfer catalysis) [7].

Unlike radical anions, no generation of radical cations was applied earlier for the activation of carbonyl complexes in substitution reactions. This is clear, because carbonyl ligands have the acceptor properties and, hence, impart the electron-deficient character to the central metal atoms in the most part of accessible carbonyl complexes, which additionally destabilizes the radical cations and results, as a rule, in their fast decomposition. We have previously studied the possibility of substituting the carbonyl ligands for the P(III) derivatives using mesitylenechromiumtricarbonyl and cyclopentadienyl manganese tricarbonyl [8, 9] under the electrochemical oxidation conditions. It was found that the preparative oxidation of these complexes at the Pt electrode in acetonitrile in the presence of Triethyl phosphite followed by reduction afforded a mixture of mono- and disubstituted chromium or manganese complexes with the overall yield about 26%. The disubstituted product predominates in the case of manganese.

$$LM(CO)_3 \xrightarrow{-e} [LM(CO)_3]^{+\cdot} \xrightarrow[2.\ +e]{1.\ P(OEt)_3,\ -CO} LM(CO)_2P(OEt)_3 + LM(CO)[P(OEt)_3]_2$$

$$L = 1,3,5\text{-}Me_3C_6H_3,\ M = Cr,\ C_5H_5M = Mn$$

Only the dicarbonyl derivatives (**IIa–IIc**) [8, 9] were isolated in 30–40% yields when the arenechromiumtricarbonyl complexes with the phosphite group in the ω position of the side chain (**Ia–Ic**) were used.



Ia–Ic **IIa–IIc**

R = OEt (a), OPh (b), F (c)

There are no published works on activation by oxidation with the purpose of substituting carbonyl ligands for clusters and mononuclear complexes. This is caused by their high oxidation potential and instability of the formed radical cations [10]. Therefore, we used a new approach to the activation and substitution of CO: the oxidation of the electroactive organometallic group linked to the cluster through the conducting chain rather than the cluster itself. We chose as an electroactive group the well known group Cp*Fe(Dppe) [11] bonded to the cluster of the Co_2C_2 type by the acetylenide bridge. These pseudotetrahedral clusters are studied fairly well [12]. Several examples for similar structures are also well known in which the Co_2C_2 fragment is linked by the conducting bridge to the same Co_2C_2 group [13, 14] or the mononuclear group $CpRu(PPh_3)_2$ [15]. In addition, several examples for compounds of this type with other metals were described [16]. These works are devoted to the synthesis and the study of the structures and intramolecular electron transfer processes. However, none of them attempted to study the redox activation of clusters for any chemical transformations.

EXPERIMENTAL

All procedures on the synthesis and isolation of the compounds were carried out in an argon atmosphere using absolute solvents. Complexes Cp*(Dppe)FeC≡CC≡CR [11] and $Co_2(CO)_6$Dppm [12] were synthesized using known procedures.

IR spectra in the range from 4000 to 400 cm^{-1} were measured on a Magna-R 750 FT-IR spectrometer (Nicolet) with a resolution of 2 cm^{-1} in CH_2Cl_2 solutions. Spectra in the near-IR range were recorded on a Vector 22N FT-IR spectrometer (Bruker) with a resolution of 2 cm^{-1}. The spectra were measured in situ using optical fiber sensors and were processed using the Grams Research PE 1000g program. NMR spectra were recorded on a Bruker-AMX-400 instrument (working frequency 400.13 MHz). Tetramethylsilane served as an internal standard for ^{1}H NMR, and the external standard for ^{31}P NMR was H_3PO_4 (85%). EPR spectra were recorded on a Varian E-12 spectrometer equipped with a dual resonator. The studied sample was placed in one compartment of the resonator, and the second compartment included a reference. Cyclic voltammograms were detected with a PI-50-1 potentiostat. The working electrode was glassy carbon ($S = 2$ mm^2), a platinum wire served as an auxiliary electrode, and a saturated calomel electrode was a reference. The measurements were carried out in CH_2Cl_2 solutions using 0.1 M Bu_4NBF_4 as a supporting electrolyte. The concentration of the studied compounds was 1×10^{-3} mol/L. The number of electrons involved in the reactions was estimated by a comparison of the currents of the observed peaks with the current of the one-electron oxidation/reduction ferrocene/ferrocenium at the same potentials.

Synthesis of [(pentamethylcyclopentadienyl)(bisdiphenylphosphinoethane)iron(II)] [(bisdiphenylphosphinomethane)tetracarbonyldicobalt](μ-η^1,η^2-butadiynyl) Cp*(Dppe)FeC≡CC_2H[$Co_2(CO)_4$(Dppm)] (IVa). Cp*(Dppe)Fe(C≡C)$_2$H (181 mg, 0.285 mmol) was added to a solution of $Co_2(CO)_6$(Dppm) (191 mg, 0.285 mmol) in benzene (16 mL), and the mixture was heated with stirring in a water bath (50–55°C) for 3 h. After the removal of the solvent in vacuo and extraction with Et_2O, the solution was filtered under argon through a Celite layer, Et_2O was evaporated to 5 mL, and hexane (5 mL) was added. The mixture was additionally concentrated and stored in a refrigerator. The precipitated black-green crystals were dried in vacuo in a water bath (50°C). The yield of compound **IVa** was 297 mg (84%).

For **IVa** (empirical formula)		
anal. calcd., %:	C, 66.15;	H, 4.99.
Found, %:	C, 67.00;	H, 5.48.

IR (CH_2Cl_2, ν, cm^{-1}): 2019, 1979, 1952, 1931 ν(CO). ^{1}H NMR (400 mHz, C_6D_6), δ, ppm: 1.69 (s, 15 M, CH_3), 2.10, 2.99 (both m, 2H, CH_2–CH_2), 2.84, 3.26 (both m, 1H, CH_2), 5.79 (t, 1H, CH, $J_{HP} =$ 8.8 Hz), 7.0–8.2 (m, 40H, Ph). ^{31}P NMR: 42.03 s, 99.82 s.

Synthesis of [(Pentamethylcyclopentadienyl)(bisdiphenylphosphinoethane)iron(II)] [(bisdiphenylphosphinomethane)tetracarbonyldicobalt](μ-η^1,η^2-trimethylsilylbutadiynyl) Cp*(Dppe)FeC≡CC_2SiMe_3 [$Co_2(CO)_4$(Dppm)] (IVb) was performed similarly to compound **IVa**. IR (CH_2Cl_2, ν, cm^{-1}): 2011, 1977, 1949, 1931 ν(CO).

Synthesis of Cp*(Dppe)FeC≡CC_2H[$Co_2(CO)_4$ (Dppm)]BF_4 ([IVa]$^{+\bullet}$). Cp_2FeBF_4 (4 mg, 0.016 mmol) was added to a solution of **IVa** (20 mg, 0.016 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred at room temperature for 30 min. The solvent was evaporated to 1 mL, an Et_2O layer was added above, and the mixture was kept at –20°C. The precipitated dark green powder was dried in vacuo. The yield of **[IVa]**$^{+\bullet}$ was 16 mg (75%).

IR (CH_2Cl_2, ν, cm^{-1}): 2024, 2000, 1976, 1957 ν(CO).

Synthesis of Cp*(Dppe)FeC≡CC_2SiMe_3 [$Co_2(CO)_4$(Dppm)][BF_4]$_2$ ([IVb]$^{+\bullet}$) was performed similarly to **[IVa]**$^{+\bullet}$. IR (CH_2Cl_2, ν, cm^{-1}): 2020, 1997, 1972, 1956 ν(CO).

Synthesis of $Cp^*(Dppe)FeC\equiv CC_2H[Co_2(CO)_4(Dppm)][BF_4]_2$ ([IVa]$^{2+}$). An equivalent amount of Cp_2FeBF_4 was added to a solution of **[IVa]**$^{+\bullet}$ in CH_2Cl_2. The formation of the product was detected by the IR spectra in CH_2Cl_2, ν, cm^{-1}): 2084, 2056, 2035, 2014 ν(CO).

Synthesis of $Cp^*(Dppe)FeC\equiv CC_2SiMe_3[Co_2(CO)_4(Dppm)][BF_4]_2$ ([IVb]$^{2+}$) was performed similarly to **[IVa]**$^{2+}$. IR (CH_2Cl_2, ν, cm^{-1}): 2034, 2014, 1988, 1964 ν(CO).

Synthesis of IVa by the redox reaction. A solution of **$Cp^*(Dppe)FeC\equiv CC_2H[Co_2(CO)_6]$ (IIIa)** (370 mg, 0.42 mmol) and Cp_2FeBF_4 (110 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) was stirred for 30 min, Dppm (154 mg, 0.4 mmol) was added, and the resulting mixture was stirred for 4 h at 20°C. Then a solution of Cp_2Co (76 mg, 0.42 mmol) in CH_2Cl_2 (4 mL) was added to the reaction mixture within 1.5 h, and the mixture was stirred for 1 h more. The solvent was removed in vacuo, and the residue was extracted with hexane. The extract was filtered under argon through a Celite layer and left overnight in a refrigerator. The precipitated dark green crystals were dried in vacuo in a water bath (50°C). The yield of **IVa** was 396 mg (75%).

IR (CH_2Cl_2, ν, cm^{-1}): 2019, 1979, 1952 s, 1931 ν(CO). ^{31}P NMR (CD_2Cl_2): 42.03 s, 99.82 s.

Synthesis of IVb by the redox reaction was similar to that of compound **IVa** from **$Cp^*(Dppe)FeC\equiv CC_2SiMe_3[Co_2(CO)_6]$ (IIIb)** in a yield of 68%. IR (CH_2Cl_2, ν, cm^{-1}: 2012, 1977, 1949 s, 1931 ν(CO) NMR (C_6D_6): 0.51 (c., 9H, $SiMe_3$); 1.75 (s, 15H, Me); 2.30, 3.22 (both m, 2H each, CH_2CH_2); 2.80, 3.36 (both m, 1H each, CH_2); 6.79–8.09 (m, 40H, Ph). ^{31}P NMR (C_6D_6): 33.42 s, 100.03 s.

X-ray diffraction analysis of complex $[IVb]^{+\bullet}BF_4^- \cdot 2CH_2Cl_2 \cdot OEt_2$. The crystals ($C_{78}H_{84}BO_5F_4SiP_4Cl_4FeCo_2$ *M*, FW = 1655.74) are monoclinic, space group $P2_1/n$, at 110 K $a = 14.455(5)$ Å, $b = 24.739(5)$ Å, $c = 23.274(8)$ Å, $\beta = 107.822(14)°$, $V = 7924(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.388$ g/cm^3, $\mu(MoK_\alpha) = 8.83$ cm^{-1}. The intensities of 32422 reflections (12401 independent reflections, $R_{int} = 0.0789$) were measured on a Bruker SMART 1000 CCD diffractometer with a coordinate detector (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode, $2\theta_{max} = 48°$). An absorption correction was applied semiempirically according to the SADABS program [17]. The structure was solved by a direct method and refined by full-matrix least squares for F^2_{hkl} with anisotropic thermal parameters for all non-hydrogen atoms, except for the atoms of the disordered solvate ether molecule. All hydrogen atoms were placed in the geometrically calculated positions and included into the refinement by the "rider" model. The final R_1 factors were $R_1 = 0.0645$ (refinement by F_{hkl} for 5348 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1466$ (refinement by F^2_{hkl} for all independent reflections). All calculations were performed on a personal computer (SHELXTL) [18]. The full tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1010854; deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Complexes of the **IIIa** and **IIIb** type were synthesized as follows:

$$Cp^*(Dppe)FeC\equiv CC\equiv CR + Co_2(CO)_8 \rightarrow Cp^*(Dppe)FeC\equiv CC_2R[Co_2(CO)_6]$$

IIIa: R = H;
IIIb: R = $SiMe_3$

It was found that the oxidation of compounds **IIIa** and **IIIb** by Cp_2FeBF_4 gave labile radical cation products **[IIIa]**$^{+\bullet}$, **[IIIb]**$^{+\bullet}$, formation of which was detected by the IR and EPR spectra (*g* = 2.26). The addition of Dppm to a solution of **[IIIa]**$^{+\bullet}$ or **[IIIb]**$^{+\bullet}$ results in the substitution of two carbonyl ligands already at room temperature and the formation of stable radical cation products **[IVa]**$^{+\bullet}$ or **[IVb]**$^{+\bullet}$ [19] isolated in the individual state. The X-ray diffraction analysis was carried out for **[IVb]**$^{+\bullet}$. All geometric parameters are similar to or insignificantly differ from those for similar complexes containing the Co_2C_2 [12] or Cp*(Dppe)Fe groups in the molecule [20, 21].

Radical cation complexes [**IVa** or **IVb**]$^{+\bullet}BF_4^-$ were reduced by Cp_2Co to neutral diamagnetic compounds **IVa** or **IVb**. The overall yield (**IIIa**, **IIIb** → **IVa, IVb**) was 70%. Complexes **IVa** and **IVb** were characterized using elemental analysis, IR spectra, and ^1H and ^{31}P NMR spectra. Although complexes **IVa** and **IVb** can be obtained from compounds **IIIa** and **IIIb** in one step, this transformation proceeds under more drastic conditions and is accompanied by the formation of the decomposition products and by a significant decrease in the yields.

Thus, we demonstrated the possibility of a new approach that can serve as a model for molecular devices operating according to the scheme: switching on (oxidation)–reaction–switching off (reduction):

$$\begin{tikzcd}
\mathbf{IIIa}, \mathbf{IIIb} \arrow[r, "-e"] \arrow[d, "80^\circ\mathrm{C}"', "\mathrm{Dppm}"] & \begin{array}{c}\mathrm{Cp^*(Dppe)FeC{\equiv}CC_2R[Co_2(CO)_6]^{+\bullet}}\\ \mathbf{[IIIa]}^{+\bullet}, \mathbf{[IIIb]}^{+\bullet}\end{array} \arrow[d, "20^\circ\mathrm{C}"', "\mathrm{Dppm}"] \\
\begin{array}{c}\mathrm{{\equiv}CC_2R[Co_2(CO)_4Dppm]}\\ \mathbf{IVa}, \mathbf{IVb}\end{array} & \begin{array}{c}\mathrm{Cp^*(Dppe)FeC{\equiv}CC_2R[Co_2(CO)_4Dppm]^{+\bullet}}\\ \mathbf{[IVa]}^{+\bullet}, \mathbf{[IVb]}^{+\bullet}\end{array} \arrow[l, "+e"']
\end{tikzcd}$$

Since the cyclovoltammograms (CV) of compounds **IVa** and **IVb** contain two reversible waves ($E_{1/2}$ = –0.28...–0.3 and +0.41...–0.46 V), we attempted to carry out an additional oxidation with the formation of the dication.

It turned out that the reaction with Cp_2FeBF_4 did not reach the end and afforded a mixture of mono- and dications, which gave a complicated view of the IR spectra. However, the spectrum of dication $\mathbf{[IVa]}^{+\bullet}$ was obtained after the spectrum of monocation $\mathbf{[IVa]}^{2+}$ was subtracted from the spectrum of the mixture. The IR spectra in the ν(CO) region for complexes **IVa**, $\mathbf{[IVa]}^{+\bullet}$, and $\mathbf{[IVa]}^{2+}$ are shown in Fig. 1.

The IR spectrum of neutral complex **IVa** (Fig. 1a) in the range of stretching vibrations of CO groups contains four bands corresponding to the stretching vibrations of four CO groups of the cluster fragment. The band at 1979 cm^{-1} has a high-frequency shoulder that can belong to the ν(C≡C) stretching vibrations (they are fairly weak in the IR spectra and can be disguised by the intense bands ν(CO)). It is known that the formation of a positive charge in the molecule of carbonyl complexes of transition metals results in an increase in the values of ν(CO). The oxidation of complex **IVa** at the Fe atom results in the high-frequency shift (by 5—21 cm^{-1}) of all four bands of CO stretching vibrations in the IR spectra, and the ratio of band intensities remains unchanged (Fig. 1b). This indicates that the symmetry of the $Co_2(CO)_4$ fragment is retained and the IR spectrum corresponds to the positively charged metallocarbonyl fragment of the same structure. In addition, a band at 1903 cm^{-1}, which is absent from the spectrum of neutral complex **IVa**, appears in the IR spectrum of cation $\mathbf{[IVa]}^{+\bullet}$ (Fig. 1b), and the high-frequency shoulder at a band of 2000 cm^{-1} also disappears. It can be assumed that the band at 1903 cm^{-1} corresponds to the stretching vibration of the uncoordinated triple bond ν(C≡C), whereas in neutral compound **IVa** this band is hidden under the absorption bands corresponding to the ν(CO) vibrations. It is most likely that in the IR spectrum of dication $\mathbf{[IVa]}^{2+}$ the band at 1989 cm^{-1} corresponds to this vibration. The change in this frequency in complexes $Cp^*(Dppe)\ FeC{\equiv}CC{\equiv}CFe(CO)_2Cp^*$ [20] and $Cp^*(Dppe)\ FeC{\equiv}CC{\equiv}CFe(Dppe)Cp^*$ [21] is consistent with the registered change in the values of ν(C≡C), i.e., a decrease on going from the neutral to monocationic complexes and an increase in the case

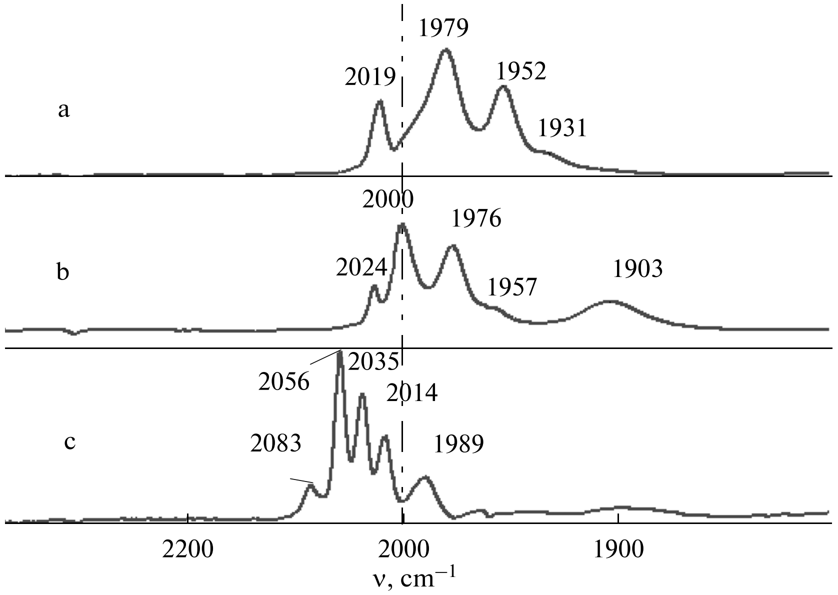


Fig. 1. IR spectra in the ν(CO) range of complexes (a) **IVa**, (b) $\mathbf{[IVa]}^{+\bullet}$, and (c) $\mathbf{[IVa]}^{2+}$ in CH_2Cl_2.

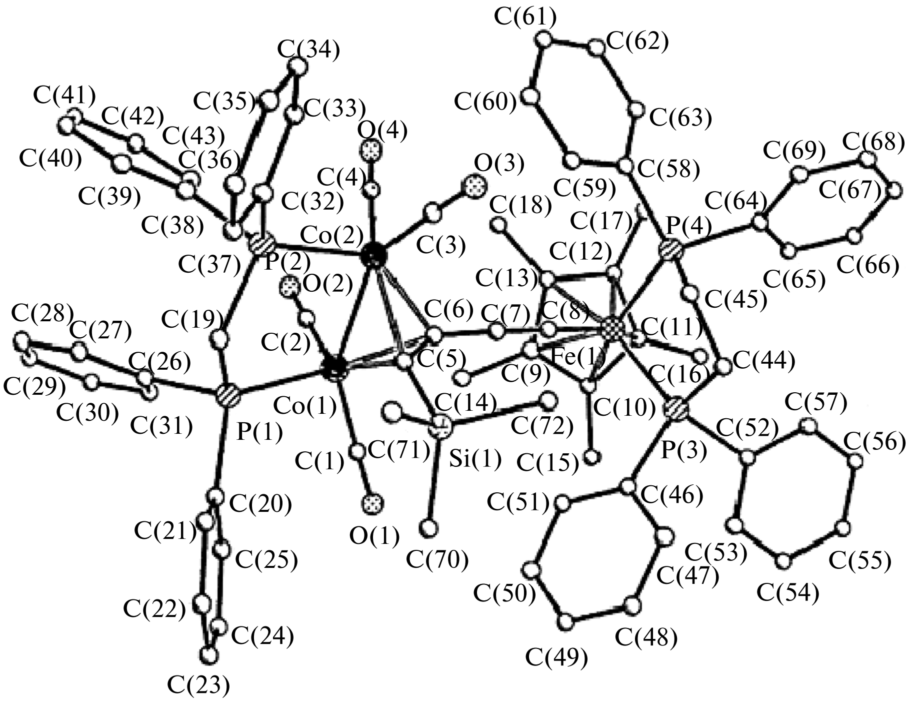


Fig. 2. Molecular structure of **[IVb]**$^{+\bullet}$. Selected bond lengths and bond angles: Co(1)–Co(2) 2.470(1); Co(1)–C(1) 1.782(9); Co(1)–C(2) 1.778(9); Co(1)–C(5) 1.976(6); Co(1)–C(6) 1.955(6); Co(2)–C(3) 1.756(8); Co(2)–C(4) 1.779(9); C(5)–C(6) 1.323(8); C(6)–C(7) 1.392(9); C(7)–C(8) 1.239(8); Fe(1)–C(8) 1.841(7); Fe(1)–P(4) 2.227(2) Å and O(1)C(1)Co(1) 177.4(7)°, O(2)C(2)Co(1) 178.0(8)°, O(3)C(3)Co(2) 177.1(8)°, O(4)C(4)Co(2) 177.7(9)°.

of the dicationic complexes. The X-ray diffraction data, according to which all carbonyl ligands are terminal (Fig. 2), serve as an additional argument for this assignment of the band at 1903 cm^{-1} in the spectrum of complex **[IVa]**$^{+\bullet}$ to the vibrations ν(C≡C) rather than to the vibration of the semibridging CO bond. Interestingly, the X-ray diffraction analysis gives the standard value of the triple bond length, whereas a fairly low value (1903 cm^{-1}) is ascribed to the stretching vibration of the triple bond in the IR spectrum of a solution of complex **[IVa]**$^{+\bullet}$. However, the X-ray diffraction and IR spectral data were analyzed for many compounds [22] and revealed no correlation between the bond lengths obtained from the X-ray diffraction data and the frequencies ν(C≡C).

The frequencies of the ν(CO) and ν(C≡C) stretching vibrations of the studied complexes are given in Table 1.

It is seen from Table 1 that the changes in the IR spectra in the regions of ν(CO) and ν(C≡C) of complexes **IVa** and **IVb** for the one-electron oxidation to the mono- and dication are similar. However, the values of stretching vibration frequencies of the CO groups differ for dications **[IVa]**$^{2+}$ and **[IVb]**$^{2+}$. In the spectrum of dication **[IVb]**$^{2+}$ the ν(CO) frequencies are higher by approximately 60 cm^{-1} than those in the spectrum of the corresponding monocation **[IVa]**$^{+\bullet}$, which is expected for the appearance of the positive charge at the metal atom of the cluster fragment. However, in the case of **[IVb]**$^{2+}$, the high-frequency shift is much lower for both ν(CO) and ν(C≡C), which can refer to the charge distribution between two cobalt atoms.

Since the synthesized cationic complexes contain metal centers in different oxidation states linked through the acetylene linkage, it was of interest to estimate the degree of intramolecular electron interaction between different metal atoms. Molecular spectroscopy in the near-IR range 14 000–4000 cm^{-1} is informative for this purpose.

The neutral complexes have no absorption bands in the near-IR range, whereas a broad intense band related to the intramolecular electron density transfer from one metal atom to another (so-called intervalent

Table 1. Frequencies of stretching vibrations ν(CO) and ν(C≡C) for complexes **IVa** and **IVb** and their mono- and dications in CH$_2$Cl$_2$

Complex	ν(CO)	ν(C≡C)
IVa	2019, 1979, 1952, 1931 sh	
[IVa]$^{+\bullet}$	2024, 2000, 1975, 1957 sh	1903
[IVa]$^{2+}$	2084, 2056, 2035, 2014	1989
IVb	2011, 1977, 1949, 1931	
[IVb]$^{+\bullet}$	2020, 1997, 1972, 1956	1982
[IVb]$^{2+}$	2034, 2014, 1988, 1964	1906

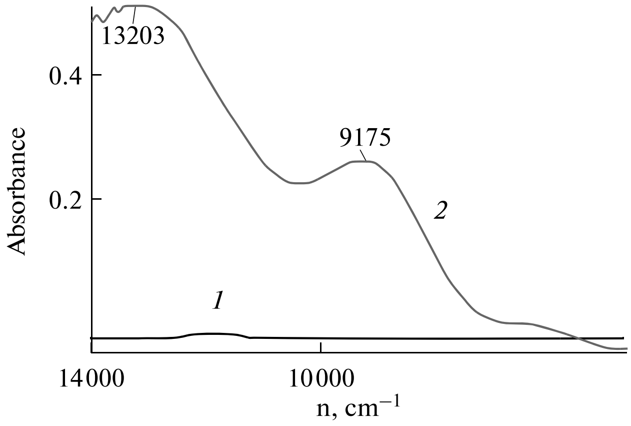


Fig. 3. Absorption spectra in the near-IR range of solutions of complex (*1*) **IVa** and (*2*) its monocation $[\mathbf{IVa}]^{+\bullet}$ in dichloromethane.

charge transfer band) through the bridging ligand (linkage) appears in the spectra of the complexes with a noticeable interaction between heteroligand metal centers.

The semiempirical formulas were proposed [23] for the estimation of the parameters of intervalent transfer bands.

The expected band half-width is calculated by the formula

$$\Delta\nu_{1/2\,\text{calcd}} = \sqrt{2310\nu_{\max}}$$

and is compared with the half-width of the band in the experimental spectrum. The more the narrowing of the observed band compared to the calculated one, the higher the degree of interaction between the metal atoms.

The energy of the electron interaction between the Mo and Fe atoms is estimated by the formula

$$V^2\,(\text{cm}^{-1}) = 4.2 \times 10^{-4}\nu_{\max}\varepsilon_{\max}\Delta\nu_{1/2}/d^2_{\text{MM}}.$$

The delocalization coefficient (α) takes the form

$$\alpha = \sqrt{4.2 \times 10^{-4}\varepsilon_{\max}\Delta\nu_{1/2}/\nu_{\max}d^2_{\text{MM}}},$$

where $\nu_{\max}$ is the maximum of the intervalent transfer band (cm^{-1}, $\varepsilon_{\max}$ is the molar absorption coefficient, $\Delta\nu_{1/2}$ is the band half-width, and d_{MM} is the distance between the metal atoms.

The classification was proposed [24], according to which molecular conductors are classified in line with the degree of interaction between the metal centers determined by the delocalization coefficient α. The substances without this interaction ($\alpha \approx 0$) belong to first-class conductors, i.e., insulators. The substances with a substantial interaction ($0.707 > \alpha > 0$), where the charge separation between the metal atoms of different valence is retained, are second-class conductors. A substantial property of the second-class conductors is solvatochromism of intervalent transfer bands. Finally, the substances with a high degree of interaction between the metal centers ($\alpha > 0.707$) and without charge separation between the metal atoms are ascribed to molecular third-class conductors.

No bands are observed in the near-IR spectral range (14000–5000 cm^{-1}) of solutions of the initial neutral complexes **IVa** and **IVb** (Fig. 1c).

Two broad intense intervalent transfer bands appear in the spectrum of a solution of monocation $[\mathbf{IVa}]^{+\bullet}$ at 13200 and 9175 cm^{-1} (Fig. 3, curve *1*). The expansion of the spectral curve to the Gaussian components made it possible to obtain the spectral charac-

Table 2. Parameters of the intramolecular charge transfer bands in monocationic complexes $[\mathbf{IVa}]^{+\bullet}$ and $[\mathbf{IVb}]^{+\bullet}$

Complex	ν, cm^{-1}	ν, nm	ε, mol^{-1} cm^{-1}	$\Delta\nu^{\text{obs}}_{1/2}$, cm^{-1}	$\Delta\nu^{\text{calcd}}_{1/2}$, cm^{-1}	$\Delta\nu^{\text{obs}}_{1/2}/\Delta\nu^{\text{calcd}}_{1/2}$	V, eV	α
$[\mathbf{IVa}]^{+\bullet}$ in CH_2Cl_2	13220 9175	756 1089	733 600	2312 1873	5526 4603	0.418 0.407	0.085 0.058	0.052 0.051
$[\mathbf{IVa}]^{+\bullet}$ in acetone	12710 9050	787 1105	588 488	2050 1822	5418 4572	0.378 0.398	0.07 0.051	0.045 0.045
$[\mathbf{IVa}]^{2+}$ in CH_2Cl_2	9890							
$[\mathbf{IVa}]^{2+}$ in acetone	9880							
$[\mathbf{IVb}]^{+\bullet}$ in CH_2Cl_2	12800 8750	790 1150	1052 1175	1863 1877	5438 4496	0.342 0.417	0.09 0.079	0.057 0.073
$[\mathbf{IVb}]^{+\bullet}$ in acetone	12700 8700	787 1150	827 950	1964 1931	5416 4483	0.362 0.431	0.082 0.072	0.052 0.066
$[\mathbf{IVb}]^{2+}$ in CH_2Cl_2	9400							
$[\mathbf{IVb}]^{2+}$ in acetone								

teristics of the bands (Table 2). The appearance of an intense absorption in the near-IR range of the spectra of the heterovalent complexes (which is absent from the spectra of the initial neutral complexes) is an indicator of the intramolecular electron interaction between the neutral and oxidized metal atoms (metal-to-metal charge transfer, intervalent transfer bands). Several intervalent transfer bands are rather frequently observed and are caused by several factors, for example, by the possibility of the electron transfer from several occupied molecular orbitals including *d* electrons and the possibility of level splitting due to the spin-orbital interaction. The intense bands disappear from the spectrum of a solution of dication **[IVa]**$^{2+}$ in CH_2Cl_2 and a weak broad absorption is observed at the bias of the intense metal-to-ligand charge transfer band in the visible range.

A similar pattern is observed in the near-wavelength spectra upon the oxidation of complex **IVb** (Fig. 4).

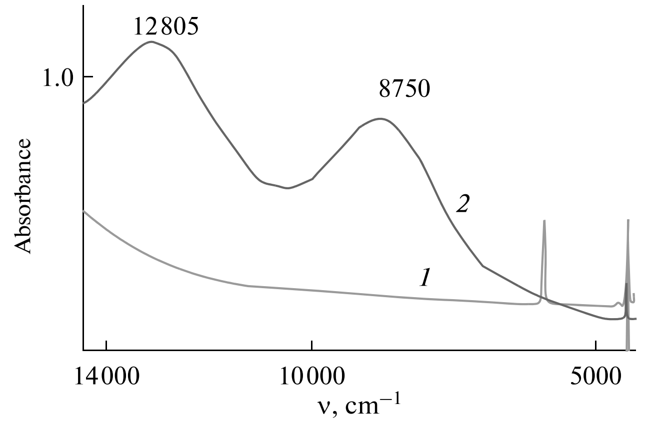


Fig. 4. Absorption spectra in the near-IR range of solutions of complex (*1*) **IVb** and (*2*) its monocation **[IVb]**$^{+\bullet}$ in dichloromethane.

The intervalent transfer bands are solvatochromic, but the dependence of the absorption frequency on the solvent nature is weak and differs for **[IVa]**$^{+\bullet}$ and **[IVb]**$^{+\bullet}$: for **[IVa]**$^{+\bullet}$, the hypsochromic shift of the most intense band on going from CH_2Cl_2 to acetone is 500 cm^{-1}; for **[IVb]**$^{+\bullet}$, it is 100 cm^{-1}; and for a less intense high-frequency band it is 50 and 97 cm^{-1} for **[IVa]**$^{+\bullet}$ and **[IVb]**$^{+\bullet}$, respectively.

The oxidation by the second equivalent of ferrocenium tetrafluoroborate results in the disappearance of the intense absorption, but broad weak bands, with maxima not coinciding with the bands of the monocations, still remain in the spectra of the dications. This absorption in the dicationic complexes is caused, most likely, by the fact that the second positive charge is distributed, as shown by the IR spectra of the dications in the medium range, between two cobalt atoms and the possibility of the intramolecular electron transfer from the iron atom to the cluster fragment.

The parameters of the intramolecular charge transfer were calculated using the Hush methodology [24]. For this purpose, the contours of the experimental bands were expanded into the Gaussian components and the values of frequencies and optical density for the most intense components were used. The distances between the interacting metal atoms taken from the X-ray diffraction data for **[IVa]**$^{+\bullet}$ as a distance from the iron atom to the carbon vertex of the cluster M_2C_2 is 4.47 Å. The obtained experimental parameters of the spectra in the near-IR area for solutions in dichloromethane and acetone and the calculated parameters of intramolecular electron communication are given in Table 2. It should be mentioned that the calculated values are only estimates because they are based on the semiempirical formulas, but the appearance of the band in the near-IR range upon the one-electron oxidation of the neutral complexes proves the existence of the intramolecular charge transfer and the obtained values of the interaction energy (V) and delocalization coefficient (α) make it possible to estimate the degree of intramolecular electron density transfer.

The data presented in Table 2 show a significant intramolecular electron interaction between the metal centers in different oxidation states in molecules of complexes **[IVa]**$^{+\bullet}$ and **[IVb]**$^{+\bullet}$. Solvatochromism observed for the bands in the near-IR range and the values obtained for the electron transfer energy and interaction parameter α make it possible to assign complexes **[IVa]**$^{+\bullet}$ and **[IVb]**$^{+\bullet}$ to second-class conductors according to the classification proposed by Robin and Day [23], i.e., there is a significant electron interaction between the metal atoms in the molecule; however, the charge separation is retained.

It is noteworthy that the electron interaction parameters for complex **[IVb]**$^{+\bullet}$ are higher than those for complex **[IVa]**$^{+\bullet}$.

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