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CURRENT STATE OF ORGANOCOBALT(IV) AND ORGANORHODIUM(IV) CHEMISTRY *

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Summary

Studies of labile oxidized forms of organocobalt and organorhodium complexes are reviewed. Conditions of their generation, structure and reactivity are considered. Position of the oxidized forms in coordination and organometallic chemistry is also discussed. The scope of the review includes the authors' recent results on the structure and reactivity of organocobalt(IV) chelates with Schiff base ligands.

I. Introduction

To elucidate the relation between the valency of an element and properties of its organic derivatives is obviously of key importance for organometallic chemistry and homogeneous catalysis. However, this problem is still far from being solved. Few metals have been shown to form σ-organic derivatives in several oxidation states, but even in these cases the effect of valency is mostly unclear because of the varying environment of the metal. Particularly little is known about σ-organic derivatives of metals in upper oxidation states. In this connection, certain advances in cobalt chemistry may be of interest. While σ-organocobalt complexes containing the metal in oxidation states from III to I had been known before 1970, a new type of highly oxidized species containing a Co–C bond was studied during the last decade. The ability of certain organocobalt(III) complexes to release an electron without rupture of the metal–carbon bond was suggested and partially substantiated by three research groups headed by Halpern, Johnson and Costa in 1972 [1–3]; these works were considered in the extensive review of organocobalt(III) chemistry [4] a year later. The existence of the oxidized forms in solution was finally proved by Halpern's group and by the authors of the present paper in 1974–1975 [5–7]. These complexes turned out to be rather unstable so that none of them has been isolated up to now. Nevertheless, the just-mentioned works [5–7] and subsequent studies allowed both suitable conditions for the generation of these labile species in solution to be found,

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* Dedicated to Prof. J. Halpern on the occasion of his 60th birthday.

and their electronic structure and reactivity to be elucidated. The present paper reviews these advances as well as a similar, but less extensive development in organorhodium chemistry.

TABLE 1

OXIDIZED FORMS OF ORGANOCOBALT COMPLEXES[a]

Complex	R ligand	Method of generation	Medium	Evidence for existence and stoichiometry	Properties studied	Refs
$RCo(dmgH)_2{}^+$	n- or sec-alkyl; p-$XC_6H_4CH_2$ (X = NO_2, CN, COOEt, Br, Cl, F, H, Me, t-Bu);	EO, CO	Ap, Ac	CV, Rg, T	ESR 1, s; EAS, FP, R	6,7,15, 17,18,20, 23,30, 51, 52
	p-XC_6H_4 (X = Br, Cl, F, H, Me, MeO)	EO, CO	Ac	CV	ESR 1, s	7,15,29, 30
$RCo(dpgH)_2{}^+$	n-alkyl	EO, CO	Ap, Ac	CV	ESR 1, s; FP, R	17,20,29, 30
$RCo(4\text{-}MeO\text{-}dpgH)_2{}^+$	n-alkyl	CO	Ac		ESR 1, s	29,30
$RCo(c\text{-}hgH)_2{}^+$	n-alkyl	EO	Ap	CV	FP, R	17
$RCo(acac_2en)^+$	n-alkyl	EO, CO	Ap, Ac	CV, CM	ESR s, FP,	3,16,17, 20,51
	Ph	EO	Ap	CV	FP, R	16
$RCo(sal_2en)^+$	n- or sec-alkyl	EO, CO	Ap, Ac	CV, Rg, CM, T	ESR s, FP, R	3,6,13, 16,17,19, 20,51,53
	p-$XC_6H_4CH_2$ (X = NO_2, H, Me)	EO	Ap	CV	FP	53
	Ph	EO	Ap	CV	FP	3,16,53
	Me, Ph	EI	G	MS	R	21
$RCo(sal_2pn)^+$	n-alkyl	CO	Aq		ESR s	17
$RCo[(5\text{-}Cl\text{-}sal)_2en]^+$	n-alkyl	EO, CO	Ap, Aq	CV	ESR s, FP, R	17
$RCo[(5\text{-}Br\text{-}sal)_2en]^+$						
$RCo[(7\text{-}Me\text{-}sal)_2en]^+$						3,17
$RCo(sal_2oph)^+$	n-alkyl	EO, CO	Ap, Aq	CV	ESR s, FP, R	3,17,20, 51
	p-$XC_6H_4CH_2$ (X = NO_2, H, Me)	EO	Ap	CV	FP	52
$RCo(sal_2c\text{-}hn)^+$	n-alkyl	EO	Ap	CV	FP	51
$RCo(7\text{-}Me\text{-}salen)(en)^{2+}$	n-alkyl	CO	Aq		ESR s	17
$RCo(Ph_4por)^+$	Et	EO	Ap	CV	FP, R	14
	EtOCO			CV, CM	EAS, FP, R	14
$R_2Co(Cp)PPh_3{}^+$	Me	EO	Ap	CV	R	11

[a] The following abbreviations are used: in column 3 (methods of generation): EO (electrooxidation of organocobalt(III) compound), CO (chemical oxidation), EI (electron impact); in column 4 (media): Ap (aprotic), Ac (acidified $MeOH/H_2O$), Aq (non-acidified $MeOH/H_2O$), G (gas phase); in column 5 (evidence for existence and stoichiometry): CV (CV criteria for the reversibility of charge transfer and for number of electrons involved), Rg (regeneration of initial organocobalt(III) compound after electrochemical or chemical oxidation–reduction cycle carried out at low temperatures), CM (potentiostatic coulometry at low temperatures), T (low-temperature titration of the initial organocobalt(III) compound with an oxidant), MS (mass-spectral data); in column 6 (properties and characteristics): ESR (ESR spectrum), 1 (in liquid solution), s (in frozen solution); EAS (electronic absorption spectrum); FP (potential of formation, i.e. that of the equilibrium $RCo^{III} \overset{-e}{\rightleftarrows} RCo^+$); R (reactivity)

Table 1 lists the oxidized forms of organocobalt complexes the existence of which has been properly established. It also contains sources of information on the structure and properties of these species. Literature is covered through October 1983.

A reader may wonder why the only type of stable organocobalt(IV) compounds known so far is not included in Table 1 and will not be considered in the main sections (II–IV) of this review. Series of tetrakis(1-norbornyl) and analogous homoleptic derivatives of certain transition elements including cobalt were synthesized by Bower et al. in early 1970s [8–9]; all of these compounds contain tertiary and hence strongly donating, strained bicyclic hydrocarbon ligands. That elegant work is widely regarded as a real break-through in σ-organometallic chemistry as well as a further verification of Wilkinson concept of this field [10]. Nevertheless, in terms of our approach, tetrakis(1-norbornyl)cobalt and its analogues should be kept outside the scope of this review, since they cannot be considered as oxidized forms of any known organocobalt compound and thus cannot be related to the latter.

Symbolic formulae. Abbreviations used for polydentate ligands in review [4] are modified to display the nature of organic radicals (substituents) and their number as well as the number of carbonyl components (-ydenate residues) in Schiff base ligands. For example, Ph_4por and $acac_2en$ denote 5,10,15,20-tetraphenylporphyrinate(-2) and bis(acetylacetonate)ethylenediimine(-2) respectively. Also, to avoid confusion of the *o*-phenylenediimine residue with the *o*-phenanthroline molecule, the former is abbreviated to oph rather then to phen. Further, a general symbol chel is used for tetradentate or bis-bidentate chelating dianions. Finally, a ligand occupying the sixth position at cobalt ion (i.e. *trans* to a Co–C bond) is omitted anywhere it is unessential.

II. Generation of oxidized forms

A. Organocobalt complexes

Rather a wide range of organocobalt(III) complexes has been proved capable of reversible release of an electron. All of them but one * contain an equatorial (with respect to the Co–C bond) polydentate ligand with a more or less extensive π-electron system. Most of these ligands are either tetradentate or bis-bidentate chelating dianions derived from Schiff bases or α-dioximes respectively. The reversible electron transfer was also observed in two other cases. The first of them involves a tetradentate macrocyclic totally conjugated ligand, viz. a porphyrin dianion. The other complex contains two chelating ligands: a diamine and a tridentate Schiff base ligand [12].

To effect the electron transfer from organocobalt(III) complexes, either electro-oxidation [6] or the action of suitable oxidants [7], such as salts of cerium(IV) or cobalt(III), $IrCl_6^{2-}$, $[Fe(bpy)_3]^{3+}$, PbO_2 and Br_2, can be used. The resulting oxidized forms are so unstable, even in most favourable media (vide infra), that at ambient temperatures they can be detected only by fast-reaction techniques, e.g. by cyclic voltammetry (CV) and stop-flow methods [6,7]. At much lower temperatures (-30 to $-80\,^{\circ}C$) the lifetime of many complexes becomes as high as dozens of minutes and even several hours [6,7], so that a number of them could be effectively

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* A reversible one-electron oxidation of $Me_2Co(Cp)PPh_3$ was apparently observed by means of CV [11]. The oxidized species is very labile so that it could be detected only at low temperatures.

generated and adequately characterized by electronic and ESR spectra [7,13,14]. Moreover, several complexes, e.g. n-BuCo(sal$_2$en)$^+$ and EtOCOCo(Ph$_4$por)$^+$, were formed in almost quantitative yield by means of potentiostatic electrolysis of corresponding organocobalt(III) compounds in acetonitrile solution at ca. −40 °C [6,14].

Because of high electrophilic reactivity of the oxidized species (see Sect. IV, A), their generation is usually carried out in the absence of strong nucleophiles. Practically, it was performed in acidic aqueous solutions [7,15] or in suitable aprotic media [6]. The use of the CV technique allowed rates of decomposition of the Schiff base complexes in various aprotic solvents (CH_2Cl_2, $MeNO_2$, MeCN, $HCONMe_2$, Me_2SO, py) to be compared [16,17]. The comparison revealed two kinds of solvent effect [17]. On the one hand, a donor solvent occupying the sixth coordination position at the metal ion may reduce the positive charge of the latter and thus stabilize the oxidized form. Such an effect is apparent when dichloromethane or nitromethane solvent is replaced by acetonitrile. On the other hand, strongly donating solvents ($HCONMe_2$, Me_2SO, py) are evidently able to react with the oxidized forms as nucleophilic agents (see Sect. IV, A) thus causing or accelerating their decomposition. As Halpern et al. found [7,18] in the case of organocobaloximes, the same is true for the water solvent (in acidic media; at higher pH the life time of the oxidized forms must be greatly reduced by a fast reaction with hydroxide ion).

Thus, it becomes evident that acetonitrile is, ceteris paribus, the most suitable of solvents used for the generation of oxidized forms. In particular, it was shown [17,19] that MeCN solvent is not involved in the decomposition of the oxidized forms of alkylcobalt chelates with a Schiff base, RCo(sal$_2$en)$^+$. For this reason it was used in a comprehensive study [20] of reactivity of complexes under consideration (see Sect. IV).

Lastly, scarce gas-phase data should be mentioned. A slight volatility of the organocobalt(III) chelates of the RCo(sal$_2$en) series, with R = Me and Ph, allowed their mass-spectral study to be performed [21]. The peaks of the molecular ions were observed along with metastable ions which could be attributed to the Co(sal$_2$en)$^+$ ion. The presence of the latter peaks is indicative of the instability of the non-solvated molecular ions with respect to the homolytic splitting of the Co–C bonds (cf. Sect. IV, B).

B. Organorhodium complexes

Oxidized forms of n- and sec-alkylrhodium chelates with a Schiff base (RRh(sal$_2$en)$^+$) and dimethylglyoxime (RRh(dmgH)$_2{}^+$) were generated in a similar manner. As compared with the corresponding cobalt complexes, higher oxidation potentials are required for the formation of the organorhodium species (Fig. 1), and the latter are more labile than the former [6,22].

III. Structure of oxidized forms

A. Organocobalt complexes

1. Coordination of metal ion

Organometallic compounds of trivalent cobalt are known to be either six- or

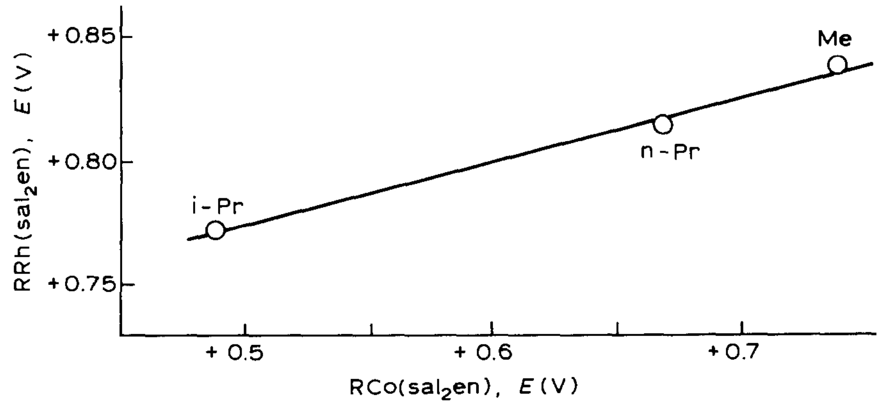

Fig. 1. Correlation of potentials of redox reactions $[RM^{III}(sal_2en)(py)] \overset{-e}{\rightleftarrows} [RM(sal_2en)(py)]^+$ for cobalt complexes, on the one hand, and those of rhodium, on the other. (CV data; 0.1 *M* solution of Et_4NBF_4 in MeCN as supporting electrolyte, 20 ° C; potential referred to a calomel electrode with 4 *M* aqueous LiCl).

five-coordinate diamagnetic complexes with octahedral or square-pyramidal geometry (at metal ion) respectively (e.g. of the types [RCo(chel)L] and [RCo(chel)]) [4]. The coordination number of the metal in oxidized forms should be apparently not less than that in the initial cobalt(III) complexes. On the other hand, a planar polydentate ligand in organocobalt complexes often causes steric hindrance (see, for example, [23–25]) and in any case would render impossible an increase of coordination number up to more than six. Thus, octahedral coordination should be characteristic of oxidized forms in the presence of a Lewis base. This conclusion is supported by experimental data [16,17,20] concerning the effect of such bases (acting, evidently, as the sixth ligand) on the potentials of redox reactions, eq. 1, where chel

$$[RCo^{III}(chel)L] \overset{-e}{\rightleftarrows} [RCo(chel)L]^+ \tag{1}$$

stands for a ligand derived from a Schiff base or α-dioxime, and L = MeCN, Me_2SO or py.

2. *Electronic structure*

An electron transfer from diamagnetic organocobalt(III) compounds must result in the formation of paramagnetic species with one or several unpaired electrons. Whatever the spin state of the oxidized form, its structure can be presented in terms of several limiting formulae differing in location of an unpaired electron and/or in valency of the metal: (**1**) a complex with a common-type covalent Co–C bond and unusual oxidation state (+4) of the metal; (**2**) and (**3**) complexes of organic free radicals or carbenium ion with the metal in an usual oxidation state (+3 or +2); (**4**) an organocobalt(III) complex with polydentate ligand in the form of cation radical *. These structures are exemplified below for the case of tetradentate chelating dian-

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* Although some of these formulae may seem unlikely, they should not be rejected a priori, since the proposed structures refer to rather exotic and very labile complexes. Three of the four structures in question can at present be related to the ground states of some oxidized forms (**1** and **2**, vide infra), or to their reactivity (**2** and **3**, see Sect. IV) and thus probably contribute to their excited or transitional states.

ion:

$$\begin{array}{cccc} \mathrm{R{-}Co^{IV}(chel)^+} & \mathrm{R^{\bullet}Co^{III}(chel)^+} & \mathrm{R^+Co^{II}(chel)} & \mathrm{RCo^{III}(chel^+)} \\ \mathbf{(1)} & \mathbf{(2)} & \mathbf{(3)} & \mathbf{(4)} \end{array}$$

a. Organocobaltporphyrins

The structure of such complexes $(\mathrm{RCo(Ph_4por)^+}$, $\mathrm{R = Et}$ or EtOCO) was established by Dolphin et al. [14]. The potentials of formation (E_1) and oxidation (E_2)

$$\mathrm{RCo^{III}(Ph_4por)} \underset{E_1}{\overset{-e}{\rightleftarrows}} \mathrm{RCo(Ph_4por)^+} \qquad (2)$$

$$\mathrm{RCo(Ph_4por)^+} \underset{E_2}{\overset{-e}{\rightleftarrows}} \mathrm{RCo(Ph_4por)^{2+}} \qquad (3)$$

(eq. 2,3) of both the complexes and, in particular, the values of $(E_2 - E_1)$, as well as the electronic spectrum of the relatively more stable of the two species (with $\mathrm{R = EtOCO}$), were shown to be very close to the corresponding characteristics of the related "inorganic" complex $\mathrm{Co(Ph_4por)^{2+}}$. Since the latter is known to be a complex of trivalent cobalt with cation-radical porphyrin ligand [26], the authors ascribed a similar structure to the organocobalt complexes, i.e. that of $\mathrm{RCo^{III}(Ph_4por^+)}$.

b. Organocobalt chelates with α-dioximes and Schiff bases

The electronic spectra of oxidized forms in these cases can hardly be used for the elucidation of their structures because of low symmetry of the complexes and unreliable attribution of bands in the spectra of corresponding cobalt(III) compounds [4,27]; besides, the only spectra of oxidized forms registered so far, viz. those of the organo(aquo)cobaloxime series, $[\mathrm{RCo(dmgH_2)H_2O}]^+$, are poorly resolved [7,18]. Nevertheless, the electronic structure of oxidized forms of the organocobalt chelates in question has been established unambiguously due to the analysis of their ESR spectra as well as the study of electron transfer from organocobalt(III) chelates (eq. 1) and to them (eq. 4) by methods of electrochemical kinetics (CV, voltammetry at rotating disk electrode).

$$\mathrm{RCo^{III}(chel)} \overset{+e}{\rightleftarrows} \mathrm{RCo(chel)^-} \qquad (4)$$

First of all, it was shown [3,5–7] that oxidation of organocobalt(III) complexes (process 1) is electrochemically reversible, which indicates the electron transfer in both directions to be fast. This fact suggests that the oxidized form essentially retains the system of electronic levels of the initial complex and, consequently, its low-spin character. Further, Costa et al. showed [3,28] that the difference between the potentials of redox reactions 1 and 4 for a series of ethylcobalt chelates with Schiff bases was practically independent of the nature of the polydentate ligand. This result definitely indicates the similarity of the MO system both in the series of initial complexes and in the products of the two redox processes. Finally, the suggested low-spin ground state of oxidized forms is consistent with their well-resolved anisotropic ESR spectra (vide infra).

Now it becomes clear that limiting formula **3**, with divalent cobalt, should be rejected, since a transition from $\mathrm{RCo^{III}(chel)}$ to $\mathrm{R^+Co^{II}(chel)}$ would require a substantial reorganization of the MO system. The choice between the three remaining structures (**1**, **2** and **4**) is based on ESR data.

(b1) Dioximate complexes. Halpern et al. [7,29,30] obtained well-resolved ESR spectra of oxidized dioximate complexes both in liquid and frozen solutions. The solid state spectra reveal a slight two-component anisotropy of g-factor (thus, in a long series of species studied by the authors, with R = primary or secondary alkyl, p-$XC_6H_4CH_2$ or Ph; chel = $(dmgH)_2$, $(dpgH)_2$ or $(4\text{-MeO-dpgH})_2$; L = H_2O, py or Ph_3P, the values of $g_\parallel$ and $g_\perp$ vary from 2.016 to 2.037 and from 2.022 to 2.031, respectively). All the spectra studied exhibit the characteristic HF patterns due to ^{59}Co nucleus, the coupling constants being consistently far smaller (a_{iso}, $A_\parallel$ and $A_\perp$ in the range $(11.7 \div 14.3) \times 10^{-4}$, $(24.8 \div 34.9) \times 10^{-4}$ and $(4.0 \div 5.4) \times 10^{-4}$ cm^{-1} respectively) than the values theoretically estimated for free cobalt ions [31]. For several complexes (e.g. Me- and $PhCo(dmgH)_2{}^+$), in CH_2Cl_2) superhyperfine (SHF) structure due to four equivalent ^{14}N nuclei was observed ($a_{iso}^{N} = 2.28 \times 10^{-4}$ cm^{-1}, $A_\perp^{N} = 2.86 \times 10^{-4}$ cm^{-1}). Experiments with $^{13}CH_3Co(dmgH)_2{}^+$ allowed the splitting from ^{13}C of the methyl ligand to be estimated: $a_{iso}^{13C} \sim 1 \times 10^{-4}$ cm^{-1}. No SHF structure from other atoms (such as H or D in methyl ligands, N or P in L = py or Ph_3P) was observed.

These data and, above all, the small couplings from ligand atoms enabled the authors to conclude that the unpaired electron is localized predominantly on the cobalt atom [29,30], the corresponding MO being formed mainly by the equatorial $3d$ orbital directed along the bisectrices of N–Co–N valent angles ($3d_{x^2-y^2}$ in the coordinate system adopted in ref. 30,31 as well as in the present paper). Further, the authors succeeded in accounting for the unusually small values of both a_{iso}^{Co} and ($A_\parallel^{Co} - A_\perp^{Co}$) due to the assumption that the MO is contributed by $4s$ (2÷6%) and $4p_z$ (~30%) orbitals. On the basis of these results and assuming the interaction of filled metal d-orbitals with antibonding π-orbitals of equatorial ligands in oxidized forms to be essentially similar to that in other bis-dioximate complexes of transition elements (see e.g. ref. 32), they constructed [30] the MO diagram for the complexes in question (Fig. 2).

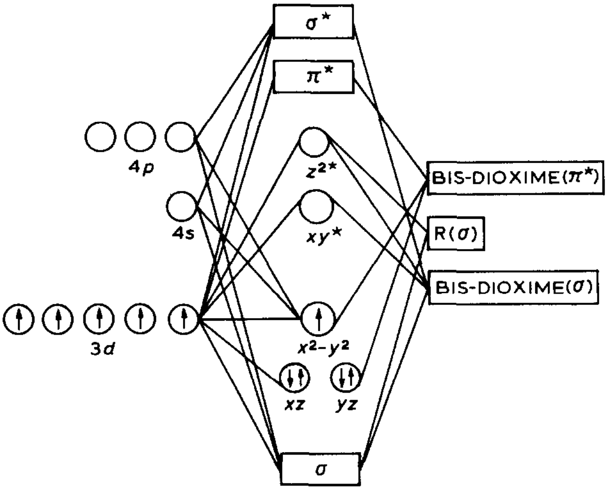

Fig. 2. MO diagram for organobis(dioximato)cobalt(+1). Reproduced from ref. 30 by courtesy of the American Chemical Society.

(b2) Schiff base complexes. In this case only solid state ESR spectra could be obtained [13,17]. Unlike the spectra of dioximate complexes, they reveal a pronounced three-component anisotropy, in accordance with lower symmetry of Schiff base complexes. HF structure was observed from ^{59}Co, with splittings being considerably larger than those for dioximates.

The ESR parameters of these complicated spectra could be obtained only by computer simulation. The computer synthesis was performed on assuming that principal axes of g- and A-tensors coincide and that the linewidths of all the lines within any single orientation are equal. ESR parameters obtained for a series of ethylcobalt complexes [13,17] are presented in Table 2. For all the complexes studied spin-orbital contributions to g-factors (especially to g_1) and to HF constants are too large to be accounted for by a free-radical structure. This fact as well as the absence of observable splitting from ligand atoms provides direct evidence for the localization of the unpaired electron on metal atom. The data presented in Table 2 also reveal that the values of g-factors depend notably on the nature of the chelating ligand. On the other hand, ESR spectra proved insensitive to the nature of the organyl ligand. Both the latter findings suggest that in the Schiff base complexes the unpaired electron is also localized in the equatorial plane. The choice between the alternative orbitals, $3d_{xy}$ and $3d_{x^2-y^2}$, could be done if the splitting constant on ^{14}N atoms of the equatorial ligand were known. Unfortunately, the upper estimate of this constant $(10 \div 15) \times 10^{-4}$ cm^{-1} obtained from linewidths does not afford such an opportunity.

The analysis of ESR parameters of Schiff base complexes in terms of crystal field theory showed [13] that the observed cobalt HF splittings could not be accounted for unless a considerable admixture of $4p_z$ orbital (~ 10%) to the MO of unpaired electron was assumed, just like in the case of dioximates.

Thus, the analysis of ESR spectra shows that in oxidized forms of organocobalt chelates with α-dioximes and Schiff bases the unpaired electron is localized at the orbitals of the metal. Consequently, only one of the three remaining limiting formulae, viz. **1** with cobalt(IV), may fit.

This conclusion is further supported by a correlation analysis of potentials of formation ($E_{1/2}$) of oxidized forms for the series of *para*-substituted benzylcobal-

TABLE 2

SOLID-STATE ESR PARAMETERS OF OXIDIZED FORMS OF ETHYLCOBALT CHELATES WITH SCHIFF BASES [a]

Complex	10^4A^{Co} (cm^{-1})			g		
	1	2	3	1	2	3
$\mathrm{EtCo(sal_2oph)^+}$	68.9	53.7	30.8	2.235	2.09	1.997
$\mathrm{EtCo(sal_2en)^+}$	74.6	~ 39	25.2	2.218	2.095	1.998
$\mathrm{EtCo[(5\text{-}Br\text{-}sal)_2en]^+}$	77.1	~ 57	29.0	2.216	2.05	2.004
$\mathrm{EtCo[(5\text{-}Cl\text{-}sal)_2en]^+}$	77.1	~ 57	29.0	2.216	2.05	2.004
$\mathrm{EtCo\,[(7\text{-}Me\text{-}sal)_2en]^+}$	71.2	~ 52	30.8	2.209	2.10	2.000
$\mathrm{EtCo(sal_2pn)^+}$	75.1	~ 41	33.1	2.204	2.07	2.003
$\mathrm{EtCo(acac_2en)^+}$	82.4	~ 27	24.3	2.180	2.08	2.001
$\mathrm{EtCo(7\text{-}Me\text{-}salen)(en)^{2+}}$	85.9	~ 27	87.8	2.165	2.08	2.021

[a] −196 °C, 0.1 M in $\mathrm{HClO_4}$ or non-acidified solutions in $\mathrm{MeOH/H_2O}$, 4/1 (v/v).

oximes (potentials of equilibria (1), R $= p\text{-}XC_6H_4CH_2$, chel = $(dmgH)_2$). The values of $E_{1/2}$ were measured by CV, the most reliable data being obtained in acetonitrile solution [20] *. These values were shown [17] to correlate fairly well with the Hammett constants σ_p° which allow only for the inductive effect of substituents (Fig. 3). The value of $\rho = +1.80$ calculated thereby is rather typical of a covalent-bonded benzyl group. Evidently, this result is in full accord with structure **1** of oxidized organocobalt complex. On the other hand, formulae **2** and **3** correspond to electron transfer from an orbital of the organyl ligand. As a result, the substituents would have influenced $E_{1/2}$ more effectively so that a substantially higher value of ρ should be expected. Further, a considerable contribution of conjugation effects could be suggested here, and hence a correlation between $E_{1/2}$ and σ_p^+ might result. In fact, however, the correlation of $E_{1/2}$ with σ_p^+ ($r = 0.9782$) is much worse than with σ_p° ($r = 0.9976$).

B. Organorhodium complexes

The information on the structure of oxidized forms of organorhodium chelates was obtained from the analysis of their ESR spectra [22]. As can be seen from Table 3, the values of *g*-factors and HF couplings on ligand atoms (^{14}N in $(dmgH)_2$) for $RRh(chel)^+$ are close to those for corresponding cobalt complexes, which suggests

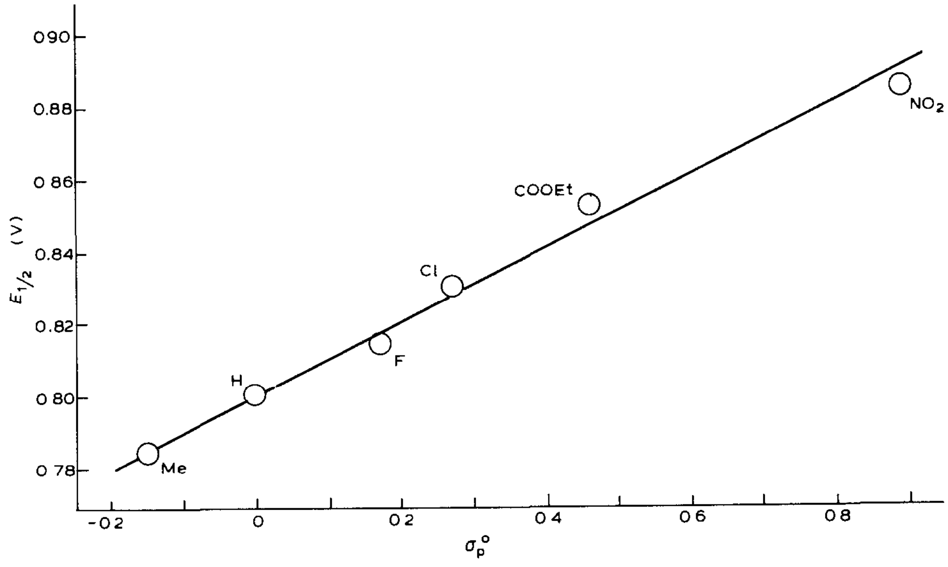

Fig. 3. Correlation of oxidation potentials of *p*-substituted benzylcobaloximes, $p\text{-}XC_6H_4CH_2Co(dmgH)_2$, with the σ_p° Hammett constants of the X substituents. (CV data; 0.1 *M* solution of Et_4NBF_4 in MeCN as supporting electrolyte, 20 ° C; potential referred to a calomel electrode with 4 *M* aqueous LiCl).

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* The values of $E_{1/2}$ obtained in aqueous solutions at pH = 0 [12,15] apparently refer not to the electron transfer proper, but rather to a composite equilibrium involving both that process and the reversible protonation of organocobalt(III) complex. To a lesser extent this applies to the measurements at pH = 2 [12]. A fair correlation between $E_{1/2}$ and σ_p° yielding $\rho = +1.2$ was obtained in the latter case, which is in qualitative agreement with the result presented below in the main text.

TABLE 3

COMPARISON OF ESR PARAMETERS FOR OXIDIZED FORMS OF ETHYLCOBALT AND ETHYLRHODIUM CHELATES EtM(chel)$^+$ [a]

(a) chel = (dmgH)$_2$, liquid (a^M, a^N, g_{iso}) and frozen ($g_{\parallel}$, $g_{\perp}$) solutions

M	$10^4 a^M$ (cm^{-1})	$10^4 a^N$ (cm^{-1})	g_{iso}	$g_{\parallel}$	$g_{\perp}$	Refs
Co	13.6 ±0.5	2.28±0.05	2.0292±0.0003	2.031±0.002	2.028±0.002	30
Rh	2.31±0.03	2.31±0.03	2.015 ±0.002	$\langle g \rangle = 2.015$		22

(b) chel = sal$_2$en, frozen solutions

M	$10^4 A^M$ (cm^{-1})			g			Refs
	1	2	3	1	2	3	
Co	74.6	~ 39	25.2	2.218	2.095	1.998	13,17
Rh	–	–	–	2.157	2.021	1.937	22

[a] Reproduced (with minor corrections) from ref. 22.

that their electronic structures are similar. At the same time, the HF coupling on metal atom in EtRh(dmgH)$_2$$^+$ is far less than that for the cobalt complex. This fact can be accounted for by the difference in magnetic properties of ^{59}Co and ^{103}Rh nuclei [22], which provides a further evidence for the close similarity between the electronic structures of the cobalt and rhodium complexes. It may be thus concluded that oxidized forms of organorhodium chelates with Schiff bases and α-dioximes, just like the corresponding cobalt species, are low-spin complexes of tetravalent metal, the unpaired electron being localized at one of the equatorial d-orbitals ($4d_{x^2-y^2}$ or $4d_{xy}$).

IV. Reactivity of organocobalt(IV) complexes

Table 4 summarizes information on reactions of species under consideration.

A. Nucleophilic substitution at metal-bonded carbon atom and related reactions

1. General

The most characteristic reactions of organocobalt(IV) complexes are likely to be those of nucleophilic substitution at carbon bound to the metal [6]:

$$\mathrm{RCo^{IV}(chel)^+ + Nu \rightarrow RNu^+ + Co^{II}(chel)} \qquad (5)$$

This conclusion is primarily based on the reactivity of both dioximate and Schiff base complexes towards pyridine [20]. In many cases (see Table 4) the nucleophilic substitution (eq. 5), Nu = py, proceeds smoothly and very rapidly in acetonitrile at 0–20 °C.

Such a high electrophilic reactivity is certainly uncommon to organometallic compounds. In particular, no substitution occurs when corresponding cobalt(III) complexes are treated with pyridine even at much higher temperatures [33].

2. Dioximate complexes

A variety of these complexes (see Table 4) reacts with pyridine in MeCN via an

S_N2 mechanism [20], which is indicated by the second order kinetics

$$-d[RCo^+]/dt = k_{II}[RCo^+][py] \tag{6}$$

as well as by the dependence of the rate constant on the electronic influences of the ligands R and chel. Thus, the k_{II} values for a series of p-substituted benzylcobalt complexes, $p\text{-}XC_6H_4CH_2Co(dmgH)_2^+$, yield a good correlation ($r = 0.9925$) with the Hammett substituent constants σ_p° corresponding to $\rho = +1.33$ which seems quite reasonable for a reaction of that type.

The same mechanism evidently operates substitution reactions of certain organocobaloximes in acidic aqueous media, viz. those of the benzylcobalt(IV) complex with water [18] and of a sec-alkylcobalt(IV) complex with chloride ion. A stereochemical study of the latter reaction [34] showed that it occurs with inversion of configuration at the carbon atom, which is quite consistent with the S_N2 mechanism. It should be pointed out that the substitution is largely accompanied by the elimination of olefin:

$$RCo(dmgH)_2^+ + H^+ \rightarrow R_{-H} + Co^{2+} + 2dmgH_2 \tag{7}$$

The decomposition of primary alkylcobalt complexes reveals a more complicated pattern [7,18]. Its kinetics, while being first order in the concentration of the complex at room temperature, approaches second order (eq. 8) at lower (ca. −20 °C)

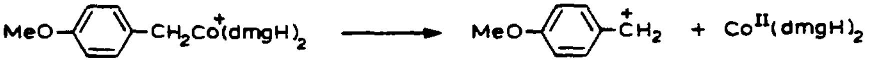
$$-d[RCo^+]/dt = k[RCo^+]^2 \tag{8}$$

temperatures. This fact combined with other kinetic data, in particular with slowing down the low-temperature reaction by the corresponding cobalt(III) complex added, suggests that the decomposition proceeds through an organocobalt intermediate which is even more highly oxidized and thus more active:

$$2RCo^{IV}(dmgH)_2^+ \rightleftarrows RCo(dmgH)_2^{2+} + RCo^{III}(dmgH)_2 \tag{9}$$

Such redox disproportionation reactions and mechanisms are widespread in the chemistry of radical ions and paramagnetic complexes (see e.g. [4,35,36]).

To complete this section, the hypothetic $p\text{-}MeOC_6H_4CH_2Co(dmgH)_2^+$ complex should be mentioned. It could not be detected after the oxidation of the corresponding cobalt(III) compound [7,20], the failure was explained [20] as being due to the mesomeric effect of the methoxy group which must stabilize the benzylcarbenium ion rather than the benzylcobalt complex. Hence the latter should be particularly unstable with respect to heterolytic cleavage of the metal–carbon bond, i.e. to a reaction of the S_N1 type:



(10)

3. Schiff base complexes

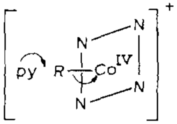
Although most alkylcobalt(IV) chelates of this type (see Table 4) react with pyridine in MeCN according to the same stoichiometric equation (eq. 5) as corresponding dioximates, their kinetic behaviour is quite different. Namely, in the case of Schiff base complexes the rate law is of overall first order, i.e. zero order in reagent [20]:

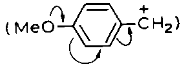
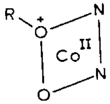
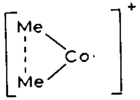
$$-d[RCo^+]/dt = k_I[RCo^+] \tag{11}$$

(Continued on p. 276)

TABLE 4

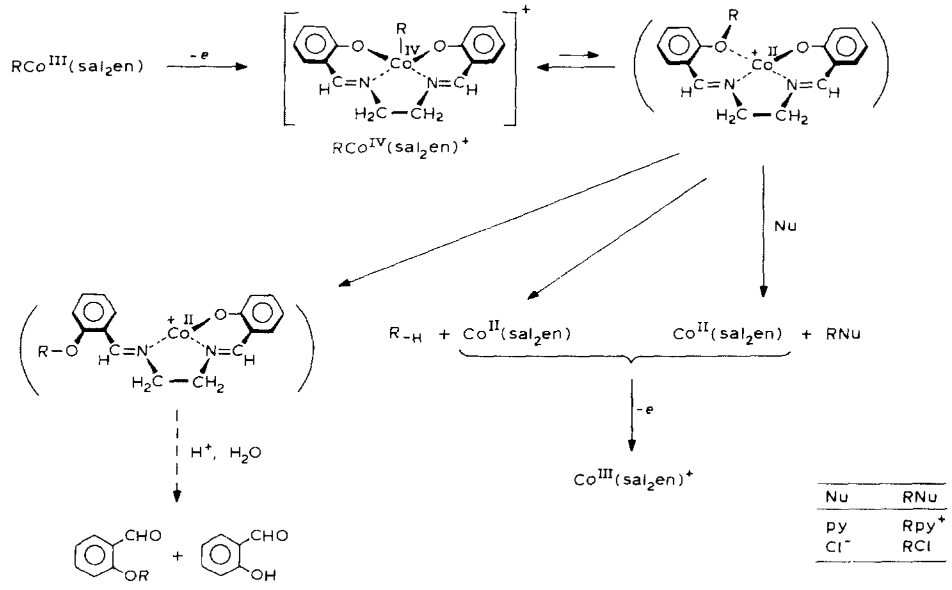
REACTIONS OF ORGANOCOBALT(IV) COMPLEXES

Complex	Reagent	Conditions	Organic products detected	Rate law and suggested mechanism	Transition state or active intermediate	Refs
$RCo(dmgH)_2^+$ $RCo(c\text{-}hgH)_2^+$ $RCo(dpgH)_2^+$ R = n- and sec-alkyl, $p\text{-}XC_6H_4CH_2$ ($X = NO_2$, COOEt, Cl, F, H, Me)	py	MeCN, 20 °C	Rpy^+	1st order in both compl. and reag.; S_N2		17 20
$RCo(dmgH)_2^+$ R = n- and sec-alkyl	Cl^-	MeCN, 20 °C; $MeOH/H_2O$, pH 0, −50 °C	RCl R_{-H}	S_N2		17,34
$RCo(dmgH)_2^+$ $R = PhCH_2$	H_2O (solv.)	$MeOH/H_2O$, pH 0–2, −20 to 20 °C	ROH	1st order in compl.; S_N2		7,18
$RCo(dmgH)_2^+$ R = n-alkyl, CH_2CH_2Ph	–	$MeOH/H_2O$, pH 0–2, −20 °C	R_{-H}	2nd order in compl.: redox disproport. as the 1st step	$RCo(dmgH)_2^{2+}$	18
$RCo(dmgH)_2^+$ R = sec-alkyl	–	$MeOH/H_2O$, pH 0–2, −20 °C	R_{-H}	1st ord. in compl.		7,18

p-$MeOC_6H_4CH_2Co(dmgH)_2{}^+$		MeCN; MeOH/H_2O, pH 0–2		S_N1 (?)		7,17,20
$RCo(sal_2en)^+$, $RCo[(5\text{-}Cl\text{-}sal)_2en]^+$, $RCo(sal_2oph)^+$ R = n- and sec-alkyl (≠ Me)	py	MeCN, 20 °C	Rpy^+	1st order in compl., zero order in reag.; S_Ni		17,20
$RCo(sal_2en)^+$ R = n- and sec-alkyl (≠ Me)	Cl^-	MeCN, 20 °C	RCl, R_{-H}, o-ROC_6H_4CHO	S_Ni		17,20
The same as above	–	MeCN, 20 °C	R_{-H}, o-ROC_6H_4CHO	S_Ni		17,20
$MeCo(sal_2en)^+$	–	MeCN, 20 °C	o-$MeOC_6H_4CHO$ CH_4	S_Ni Homolyt. decomp.	As above R	17,20
$RCo(acac_2en)^+$ R = n-alkyl R = Ph	–	MeCN, 20 °C	RH, R_{-H} R_2	Homolyt. decomp.	R	16,17,20
$[MeCo(Cp)PPh_3]^+$	–	CH_2Cl_2 or MeCN, 20 °C	C_2H_6	Inner-sphere coupling of alkyl ligands		11

This fact as well as other kinetic data [20] is formally consistent with either "unimolecular" mechanism of nucleophilic substitution, S_N1 or S_Ni (the latter involves initial transfer of the organic group R from the metal to an adjacent donor atom of the chelating ligand).

To make a final decision between these alternatives, products and stoichiometry of decomposition of $RCo(sal_2en)^+$ complexes were related with reagents used. For doing this, we studied the potentiostatic electrooxidation of corresponding cobalt(III) complexes (R = Et, n- and i-Pr, n-Bu) in solutions containing pyridine, or chloride ion, or in the absence of reagents [17][*]. In the last case organic products include the corresponding olefin R_{-H} and, after the hydrolysis of anolyte, equal amounts of salicylic aldehyde and the *o*-alkoxybenzaldehyde *o*-ROC_6H_4CHO. It is evident that the latter results from alkylation of the chelating ligand. On the other hand, in the presence of pyridine the *N*-alkylpyridinium salt emerges as the only organic product (vide supra). Finally, the electrolysis in the presence of chloride ion can be regarded as an intermediate case: both the alkyl chloride RCl and the same products as found in the absence of reagents are obtained in comparable yields. Hence, in this system the "spontaneous" decomposition of the alkylcobalt(IV) chelate effectively competes with the nucleophilic substitution. Then it becomes evident that the latter complex reacts with chloride ion far more slowly than with pyridine. Such a strong dependence of the substitution rate on the nature of nucleophile is inconsistent with the S_N1 mechanism. There is further evidence against the S_N1 mechanism: no substitution product with isomerized alkyl group was found even in the case of the slow reaction with chloride ion.



Nu	RNu
py	Rpy^+
Cl^-	RCl

SCHEME 1. Electrooxidation of alkylcobalt(III) chelate with a Schiff base, $(salH)_2en$, in the presence of nucleophiles (Nu) or in their absence.

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[*] The electrolyses were carried out at a plateau potential applied to a platinum anode, with 0.1 *M* solution of $NaBF_4$ in MeCN as supporting electrolyte, at 20 °C.

Scheme 1 [17] provides explanation of the above results. According to it, all the reactions under consideration have the first step in common. Namely, the alkyl ligand is transferred in the form of a positively charged group from cobalt to oxygen within the coordination sphere. Thus, a S_Ni reaction occurs, and a labile cobalt(II) complex including a tercovalent oxygen atom is formed thereby. Unless a suitable nucleophile species is available, this intermediate converts into stable products through two parallel routes, viz. either eliminating olefin or via splitting of the bond between the alkylated oxygen atom and the metal. In the presence of pyridine, the transfer of alkyl group from cobalt(IV) to oxygen is followed by a fast substitution. In the case of chloride, a weaker nucleophile, the substitution is accompanied by the spontaneous transformations of the intermediate.

B. Homolytic splitting

In several cases the decomposition of organocobalt(IV) chelates in solution was found to involve the homolytic splitting of the metal–carbon bond [16,20] (see Table 4):

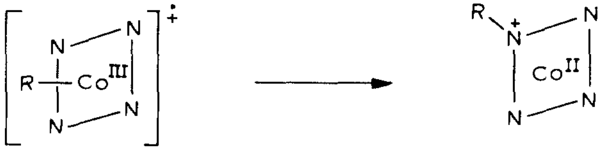
$$\mathrm{RCo^{IV}(chel)^+} \rightarrow (\mathrm{R^\cdot}) + \mathrm{Co^{III}(chel)^+} \tag{12}$$

Such routes were indicated by detection of hydrocarbon products corresponding to disproportionation and coupling of the free radicals, $R^\cdot$, [16,20] as well as by certain features of anode processes used to generate the complexes [20]. The phenylcobalt complexes give biphenyl in quantitative yield, which indicates the homolytic decomposition to be the only route [16]. In other cases it may be accompanied by the nucleophilic substitution and the related reactions (see Sect. IV, A). It was shown [20] that the homolytic decomposition is favoured by high ionization potential of the free radical, $R^\cdot$, and strong donor power of the other (than R) ligands, both chel and L. In particular, oxidized forms of *trans*-dialkylcobalt complexes are quite unstable with respect to the homolysis of a Co–C bond (see Sect. V), probably owing to strong donation from the other alkyl ligand.

Concluding this section, it is appropriate to remind that in the gas phase the non-solvated five-coordinate ions $[\mathrm{RCo(sal_2en)}]^+$ with R = Me and Ph (see Sect II, A) undergo very fast homolytic splitting.

V. Position of oxidized forms of organocobalt(IV) complexes in coordination chemistry

Until recently the range of compounds of tetravalent cobalt was apparently restricted to a few complexes with the most hard anions as F^- and O^{2-} [37]. Therefore the oxidation state +4 was generally considered to be rather untypical of the metal. The situation has considerably changed since. The synthesis of tetrakis(1-norbornyl)cobalt and its analogues (see Sect. I, A) presents a clear-cut example of that development. Second, the studies reviewed above provided conclusive evidence for the existence of organocobalt(IV) chelates with Schiff bases and α-dioximes. Further, Marov et al. [38] while studying the low-temperature oxidation of "inorganic" cobalt complexes with α-dioximes registered ESR signals which could be attributed to low-spin paramagnetic species. Analysis of the spectra as well as the stoichiometry of the oxidation suggested the formation of cobalt(IV) complexes such as $[Co^{IV}(dmgH)_2Cl_2]$. On the other hand, Mok and Endicott [39] investigated electrooxidation of alkylcobalt(III) cation complexes with either a saturated or partially conjugated macrocyclic ligand, viz. $MeCo([14]aneN_4)^{2+}$ and $MeCo(Me_4[14]tetraeneN_4)^{2+}$ and found it to be irreversible. Hence, in this case the splitting of the Co–C bond is practically synchronous with the electron transfer so that oxidized forms do not exist at all or at least are extremely labile. A similar electrochemical behaviour was observed by Kochi and his coworkers in the case of *trans*-dialkylcobalt(III) complexes with partially conjugated equatorial ligands, $Me_2Co(dpnH)$ and $Me_2Co(Me_4[14]tetraene)^+$. Nevertheless, the kinetic study of the anode processes suggested intermediate formation of oxidized forms of the dialkylcobalt complexes followed by fast homolytic splitting of a Co–C bond. On the other hand, the oxidized form of a *cis*-dialkylcobalt complex, $Me_2Co(Cp)PPh_3$, proved very unstable with respect to coupling of the σ-bonded organic groups in the coordination sphere of the metal [11]. Lastly, as already stated (see Sect. III, A2a) Dolphin et al. showed that the electron transfer from organocobalt(III) complexes including a macrocyclic ligand with totally delocalized π-electron system, viz. $RCo(Ph_4por)$, results in the formation of the π-cation-radical species, $RCo^{III}(Ph_4por^+)$. Despite sharp differences between their electronic structure and that of organocobalt(IV) chelates with Schiff bases, there is a certain similarity in reactivities of the two types of complexes. Namely, an innersphere transfer of the R group occurs in the porphyrine complexes [14] (eq. 13) just as in the Schiff base chelates (see Sect. IV, A3).



(13)

The above sketchy survey is sufficient to show that chemistry of tetravalent cobalt is no longer restricted to complexes of the most hard ligands. The existence of organocobalt(IV) compounds, both tetrakis(1-norbornyl)cobalt and its analogues, and organocobalt(IV) chelates, indicates that strong donating power of the carbanion ligand is essential for the stabilization of the higher oxidation state of the metal. The effect of a σ-bonded organyl group on the oxidation of cobalt(III) complexes is apparent in the case of Schiff base chelates. According to CV data, the oxidation of an "inorganic" complex that does not contain strongly donating axial ligands, viz. $Co^{III}(sal_2en)^+$, requires much higher potentials than that of $RCo^{III}(sal_2en)$ and is totally irreversible [6]. On the other hand, the stabilizing influence of a σ-bonded alkyl group on the oxidized form of cobaloxime (in $RCo(dmgH)_2{}^+$) may be, in practical terms, compared with that of two axial chloride ions (in $[Co(dmgH)_2Cl_2]$ [38]). It is also apparent that the stabilization of the upper oxidation state of the metal is favoured by a π-donating equatorial ligand capable both of reducing a positive charge on the metal and partially accepting the unpaired electron density.

On this view, one can explain why the oxidized form of an organocobalt complex with a saturated cyclic tetramine, viz. $[MeCo([14]aneN_4)H_2O]^{2+}$ fails to exist. (An extra unfavourable factor may be the high positive charge (+2) of the complex). On the other hand, if an organocobalt complex includes a macrocyclic ligand with an extensive closed π-electron system, the release of an electron from a π-orbital of the ligand may become preferable so that the oxidation would result in the formation of cation radical species. Thus, the oxidation of organocobalt porphyrinates $RCo^{III}(Ph_4por)$, is essentially similar to that of the corresponding inorganic complex, $Co^{III}(Ph_4por)^+$ and related complexes of other transition metals [41]. The resulting π-cation radicals, with delocalized charge and spin, are known to be relatively stable [41]*.

It may be relevant to compare properties of isoelectronic compounds of cobalt(IV) and iron(III). Unlike cationic cobalt complexes, $RCo^{IV}(sal_2en)^+$, the neutral iron complexes $RFe^{III}(sal_2en)$ do not exhibit electrophilic reactivity [43]. Further, in contrast to the low-spin cobalt complexes, the iron compounds are of high spin type. This structural feature contributes to rather high homolytic lability of the Fe–C bond.

The investigations of organocobalt(IV) complexes proved essential for the elucidation of mechanisms of oxidative cleavages of Co^{III}–C bonds. In particular, recent detailed studies of stoichiometry, kinetics and stereochemistry of reactions of organocobalt chelates with halogens and interhalide compounds [44,45] indicated that most of these processes involve cobalt(IV) intermediates.

The intermediate formation of oxidized forms of organocobalt complexes in the course of oxidative cleavage of Co–C bonds may reveal a general trend in organic chemistry of transition metals [46].

At present the most challenging problem in the organocobalt(IV) chemistry may be that concerning the existence of oxidized forms of organocobalamins and their potential involvement in enzymatic and/or environmental processes. Attempts to generate and to detect oxidized forms of organocobalamins by analogy with their models have been unsuccessful so far [13,47]. Recently Fanchiang started systematic kinetic studies of reactions of alkylcobalamins with oxidizing agents [48–50] such as tetrahaloaurates. So far this work has not provided straightforward evidence for the existence of the oxidized forms in question. Nevertheless, it allowed the author to suggest the transient formation of a substrate to oxidant adduct followed by electron transfer in the intermediate complex and fast decay of the oxidized form of organocobalamin.

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* In this connection it may be appropriate to reconsider the interesting results obtaned by Fleischer and Lavalee [42] when studying porphyrin complexes of rhodium as early as in 1964. After having refluxed a benzene solution of Ph_4porH_2 and $[Rh(CO)_2Cl]_2$ in the air, they isolated a stable product and claimed it to be an organorhodium(IV) cation complex, $[PhRh^{IV}(Ph_4por)]Cl$, on the ground of X-ray analysis. In the light of the above consideration, it seems more plausible to suggest an alternative, cation-radical structure of this product, viz. that of the salt $[PhRh(Ph_4por^{+})]Cl$.

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