76. S_N2 or Electron Transfer? A New Technique Discriminates the Mechanisms of Oxidative Addition of Alkyl Halides to Corrinato- and Porphyrinatocobalt(I)

by **De-Ling Zhou, Peristera Walder, Rolf Scheffold,** and **Lorenz Walder***

Institut für Organische Chemie, Universität Bern, Freiestrasse 3, CH-3012 Bern

(17.III.92)

A fast electrochemical technique for the discrimination of one- and two-electron mechanisms in the oxidative addition of alkylating agents (RX) to corrinato- and porphyrinatocobalt(I) ([Co^{I}L]) is described. It is based on single-scan voltammograms of [Co^{II}L] in the presence of RX and variable amounts of the radical trap acrylonitrile. In the first part of the voltammogram, [Co^{II}L] is reduced, and fast oxidative addition of RX to [Co^{I}L] is triggered. If the reaction proceeds *via* a two-electron mechanism, [R–Co^{III}L] is formed independently of acrylonitrile concentration, but if a transient free radical R˙ is involved, R˙ is competitively trapped by acrylonitrile and [Co^{II}L] to yield, at high enough acrylonitrile concentration, exclusively the olefin-inserted [R_{CN}–Co^{III}L]. [R_{CN}–Co^{III}L] is reducible in the intermediate potential range, [R–Co^{III}L] at the negative end of the single-scan voltammogram. Hence, from the appearance of the reduction waves due to [R_{CN}–Co^{III}L] and [R–Co^{III}L], the mechanism of oxidative addition of RX to [Co^{I}L] is easily deduced. The method is applied to the study of the mechanistic borderline of oxidative addition using a series of 15 RX and 4 [CoL]'s, *i.e.* cobalamin (Cbl), heptamethyl cobyrinate ('Cby'), (tetraphenylporphyrinato)cobalt ([Co(tpp)]), and (octaethylporphyrinato)cobalt ([Co(oep)]). All non-activated primary alkyl iodides and bromides exhibit, at room temperature, pure two-electron mechanisms with all [Co^{I}L]'s, except neopentyliodide with Cbl^{I} and 'Cby^{I}'. All secondary alkyl iodides involve free radicals with Cbl^{I} and 'Cby^{I}', but a pure two-electron mechanism or a mixed one-electron two-electron mechanism with [Co^{I}(tpp)] and [Co^{I}(oep)]. The mechanistic switch from a two-electron to a one-electron mechanism for increasingly sterically demanding RX's occurs earlier with the supernucleophilic Cbl^{I} and 'Cby^{I}' than with [Co^{I}(tpp)] and [Co^{I}(oep)].

1. Introduction. – A very general method for the preparation of alkylcob(III)alamins, organometallic derivatives of vitamin B_{12} model compounds, and of (alkyl)porphyrinatocobalts(III) is based on the 'supernucleophilicity' of the corresponding macrocyclic Co^{I} complexes towards organic electrophiles [1a–d]. Besides its synthetic importance, the reaction attracted much mechanistic interest over the past 25 years, especially with respect to the formation of R–Cbl^{III}'s[1]) [1a, b] and the alkyl vitamin B_{12} model compounds [1b], but much less in the case of R–'Cby^{III}'[1]) and (alkyl)porphyrinatocobalts(III) [1c]. It is tempting, and from an unbiased point of view justified, to assume a common mechanism for the simple substitution of a leaving group at an sp^3 C-atom by different [Co^{I}L]'s[1]) (*Eqn. 1*). Far from it – the literature reveals a whole range of partially incompat-

[1]) The following abbreviations are used: Cbl = cobalamin [1e]; for convenience, we use 'Cby' instead of $Cby(MeO)_7$ for heptamethyl cobyrinate (*cf.* Cby = cobyric acid [1e]), [Co(oep)] = (2,3,7,8,12,13,17,18-octaethylporphyrinato)cobalt [1f], [Co(tpp)] = (5,10,15,20-tetraphenylporphyrinato)cobalt [1f]; [CoL] = any of the Co complexes under investigation; mechanism abbreviations are explained in *Scheme 1*.

ible mechanisms that were invoked for this reaction [2–17][2]). Either oxidative addition is really located on a mechanistic borderline (eventually crucially depending on the structures of [Co^{I}L], RX, and experimental conditions) or false conclusions due to side or follow-up reactions are responsible for the current situation. A conservative description of the [Co^{I}L] reactivity, based on the available results, can still be formulated in terms of trends: at least two mechanisms (S_N2 and a (several?) mechanism(s) involving radicals) seem to be accesible and S_N2 tends to become more important in the order: iodide < bromide < chloride ≈ tosylates ≈ brosylates ≈ triflates and tertiary < secondary < primary alkyl halide.

$$[Co^{I}L] + R\text{-}X \rightarrow [R{-}Co^{III}L] + X^- \quad (1)$$

Further mechanistic studies should include: *i*) the unprejudiced *consideration of all mechanistic possibilities* known to be accessible to low-valent macrocyclic transition-metal complexes in the oxidative addition of RX [1d], *ii*) a discussion of the possible *follow-up and side reactions* that may blur the experimental result, *iii*) a discussion of the *discriminative power of the experimental technique* and its *susceptibility to false conclusions* due to parallel and follow-up reactions, and *iv*) the influence of *structural changes* of L in [Co^{I}L] and R and X in RX as well as *changes in the experimental conditions* on the mechanism.

In analogy with other low-valent macrocyclic transition-metal complexes, oxidative addition of RX to [Co^{I}L] may follow any reaction path shown in *Scheme 1* [1d]. The

Scheme 1. *Mechanistic Scope of Oxidative Addition*

Two-electron mechanisms:

a) S_N2[3])

b) *Anion(or benzimidazole)-assisted* S_N2 (= a.-a. S_N2)[4])

c) *Halonium-ion abstraction* (= h.-i. a.; *Eqn. 2* followed by *Eqn. 3*)[5])

$$[Co^{I}L] + R{-}X \longrightarrow [X{-}Co^{III}L] + R^- \quad (2)$$

$$[X{-}Co^{III}L] + R^- \longrightarrow [R{-}Co^{III}L] + X^- \quad (3)$$

---

[2]) For primary [2] [3] [4] [6] and/or secondary [5] alkyl tosylates [4] [5], brosylates [2] [6], and triflates [2] as well as for epoxides [5] [7] and chlorides [8b], S_N2 mechanisms were univocally claimed by various authors and for very different [Co^{I}L]'s. The reactivity of MeI with Cbl^{I} was early interpreted as S_N2-like [8b], but an i.s.e.t. mechanism[1]) was invoked for its reaction with 'Cby'[1] [9a] and a mixed o.s.e.t./S_N2 mechanism with [Co^{I}(tpp)] [9c]. The reaction of primary alkyl iodides with different [Co^{I}L]'s was interpreted as S_N2 [8] and e.t. [4]. Inconsistent conclusions were presented for primary [4] [8] [10] and secondary [4] [5] [8] [11–13] alkyl bromides, *i.e.* S_N2 reactivity [5] [8] [10] [11] and mechanisms involving free radicals [4] [12] [13], although some of these results were obtained with different [Co^{I}L]'s and under different experimental conditions. Secondary alkyl iodides – originally also classified as obeying an S_N2 mechanism [8] – were later found to involve radicals [4] [14] [15]. The S_N2 pathway was ruled out for the reaction of some bulky tertiary alkyl halides with [Co^{I}L]'s [13] [16].

[3]) An S_N2 mechanism with attack at the C-atom leading to retention of configuration was considered by *Ugi* [16] and *Jensen* [17].

[4]) Co^{I} does not coordinate benzimidazole or anions, but nucleophilicity may be enhanced by concomitant coordination of such a moiety to [Co^{I}L] on the way to the S_N2 transition state.

[5]) The h.-i.a. mechanism corresponds to an inner-sphere two-electron transfer. X^- must dissociate from [X–Co^{III}L], or [X–Co^{III}L] must rotate prior to Co–C bond formation. H-i.a. may be active in the case of stabilized anions (R^-).

One-electron mechanisms:

d) Outer- or *inner-sphere dissociative electron transfer* (= o.s.e.t. and i.s.e.t., resp.; *Eqn. 4* followed by *Eqn. 5*)[6])

$$[Co^{I}L] + R{-}X \xrightarrow{\text{o.s.e.t.}} [Co^{II}L] + X^{-} + R^{\cdot} \quad (4)$$
$$\xrightarrow{\text{i.s.e.t.}} [X{-}Co^{II}L] + R^{\cdot}$$

$$[Co^{II}L] + R^{\cdot} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [R{-}Co^{III}L] \quad (5)$$

e) Radical chain (= r.c. ([R–Co^{II}L]); o.s.e.t. involving a short-lived [R–Co^{II}L] as electorn donor and as chain carrier, *Eqns. 6* and *7*)[6])[7]).

$$[R{-}Co^{II}L] + R{-}X \longrightarrow [R{-}Co^{III}L] + R^{\cdot} + X^{-} \quad (6)$$

$$[Co^{I}L] + R^{\cdot} \underset{k_{-7}}{\rightleftharpoons} [R{-}Co^{II}L] \quad (7)$$

f) Atom abstraction (= a.a. ([Co^{II}L])) by a catalytic amount of [Co^{II}L] (*Eqn. 8*)[8]) followed by [X–Co^{III}L]/[Co^{I}L] + X^{-} comproportionation and *Eqn. 5*.

$$[Co^{II}L] + R{-}X \longrightarrow [X{-}Co^{III}L] + R^{\cdot} \quad (8)$$

Scheme 2. *Possible Follow-up Reactions of [R–Co^{III}L]*

$$[R{-}Co^{III}L] \xrightarrow{k_{-5}} [Co^{II}L] + R^{\cdot} \quad (-5)$$

$$[R{-}Co^{III}L] + h\nu \xrightarrow{k_9} [Co^{II}L] + R^{\cdot} \quad (9)$$

$$[R{-}Co^{III}L] + [Co^{II}L]^{*} \xrightarrow{k_{10}} [Co^{II}L] + [R{-}Co^{III}L]^{*} \quad (10)$$

$$[R{-}Co^{III}L] + [Co^{I}L]^{*} \xrightarrow{k_{11}} [Co^{I}L] + [R{-}Co^{III}L]^{*} \quad (11)$$

$$[R{-}Co^{III}L] + R'^{\cdot} \xrightarrow{k_{12}} [R'{-}Co^{III}L] + R^{\cdot} \quad (12)$$

follow-up reactions to be considered (*Scheme 2*) are the photolysis of [R–Co^{III}L] (*Eqn. 9*)[9]) followed by *Eqn. 5*, the thermal homolysis and reformation of the Co–C bond

---

[6]) Rates of o.s.e.t. from electron donors to RX (k_{4a}) follow *Marcus* theory and are predictable [18]. k_5 Values reported for different R$^{\cdot}$ are $4 \cdot 10^8$ to $9 \cdot 10^8$ l/mol·s [19], *i.e.* $k_5 < k_{diff}$, and R$^{\cdot}$ generated in a solvent cage together with Co^{II} may escape. It's not clear if radicals which do not leave the solvent cage are detectable, even by a trap which is part of the solvent cage.

[7]) [R–Co^{III}L] reduction may involve the one-electron-reduced intermediate [R–Co^{II}L] exhibiting a lifetime depending on L and R. Co–C bond cleavage occurs in Me-Cbl^{II} with $k_{-7} = 1200$ s^{-1} at −30° [20], but [Me–Co^{II}(tpp)] is stable for severals [9c].

[8]) Rate constants of oxidative addition reported for [Co^{II}L] [21] are generally several orders of magnitude smaller than those for [Co^{I}L] [8].

[9]) k_9 depends on the light intensity, the absorption spectrum of [R–Co^{III}L] and Φ, see [22] and ref. cited there.

(*Eqn. 5* and its back-reaction)[10]), (multiple) alkyl transfer (*Eqns. 10* and *11*) as long as unalkylated [$Co^{II}L$] or [$Co^{I}L$] is present[11]), and finally S_H2 and S_H2' displacement reactions of [R–$Co^{III}L$] by an organic free radical in a chain process (*Eqn. 12*) [10] [25]. The importance of the follow-up reactions with respect to misinterpretation of the mechanism of oxidative addition is related to the corresponding rates and the time lag between oxidative addition and its mechanistic analysis. Photolysis (*Eqn. 9*) is easily suppressed in the absence of light[9]). Thermolysis (*Eqn. 5*, back-reaction) becomes important with time lags of *ca.* 30 min at room temperature in the case of sterically hindered (primary R)–Cbl^{III}'s, but with (*sec*-R)–Cbl^{III}'s, time lags as short as 1 min may lead to misinterpretations[10]). Alkyl-transfer reactions (*Eqns. 10* and *11*) were reported efficient in the case of Me-Cbl, however, with sterically more demanding residues, their importance decreases rapidly[11]). The S_H2 reaction (*Eqn. 12*) involves an organic radical as chain carrier that may be quenched with radical traps or reducing agents [10].

The discrimination of the mechanisms is generally based on experiments concerning *A*) the stereochemical course of the reaction at the Co-bound C-atom [2] [3] [5] [6] [11–14] [16a], *B*) the stereochemical course of the reaction at Co (α- or β-isomers of R–Cbl^{III} and R–'Cby'^{III}) [9a, b], *C*) comparative rates of oxidative addition [8] [9c], and *D*) trapping of radical intermediates [4] [10] [15]. The stereochemical argument *A* is reliable if, *e.g.*, using two enantiomeric RX's, inversion of configuration at the C-atom independent on the thermodynamic stability of [R–$Co^{III}L$]. Thus, any equilibrating reaction involving free $R^{\cdot}$ or R^{-} during or after oxidative addition is ruled out, and an S_N2 mechanism is highly probable. However, if in a two-step mechanism, molecular rotation and solvent-cage escape are slow as compared to Co–C bond formation, some stereochemical information of RX may (kinetically controlled) translate into [R–$Co^{III}L$]. If inversion of configuration is not observed or inversion occurs only to yield the thermodynamically more stable [R–$Co^{III}L$], any of the equilibrating reactions may be active. 'No inversion' may still be conclusive, if, in a differential analysis, a change of X in RX shifts the mechanism from 'inversion' to 'no inversion' under otherwise identical conditions. More recently, the argument *B* was invoked. With a kinetically controlled α/β-isomeric mixture, all equilibrating reactions are excluded[12]). However, it is not possible to discriminate the different mechanisms, because all Co–C bond-forming steps are kinetically controlled and exhibit so far unpredictable differences in the activation barriers. Both arguments *A* and *B* require time-consuming isolation methods and physicochemical measurements on [R–$Co^{III}L$]. They are inherently prone to include follow-up reactions and, thus, to underestimate the kinetically controlled reactions. Rate measurements (argument *C*) cut

---

[10]) k_{-5} is related to the bond-dissociation energy ($E_{b.d.}$) of the Co^{III}–C bond *via* $\Delta H^{\neq}_{-5}$. Selected values of $E_{b.d.}$ (kcal/mol) and $t_{1/2}$ ($= 0.69/k_{-5}$) for different R–Cbl's from literature are: Me-Cbl, $E_{b.d.} \approx 37$ [23a]; Ado-Cbl, $30.1 < E_{b.d.} < 34.5$, $t_{1/2}$ (90°) 950 min [23b]; neopentyl-Cbl, $E_{b.d.} \approx 23.4$, $t_{1/2}$ (25°) 75 min [23c]; benzyl-Cbl, $E_{b.d.} \approx 24.6$, $t_{1/2}$ (24°) 5 min [23c]; isopropyl-Cbl, $E_{b.d.} \approx 20.7$, $t_{1/2}$ (25°) 3 min [23c]. The corresponding base-off forms are 2–8 kcal/mol more stable.

[11]) Methylcob(III)inamide exchanges the Me group with Cbl^{II} within 1 h and with Cbl^{I} within 3 min [24a], absolute rates (k_{10}) for Me transfer involving sterically less demanding [CoL]'s and Cbl ([Me–$Co^{III}L$] and [Co^{II}**L**]*) are 1 to $5.6 \cdot 10^4$ l/mol·s [24b]. The rate constant for alkyl exchange between alkylcob(III)aloximes and cob(II)aloximes follows the order Me (44 l/mol·s) ≫ Et ≫ Pr ≈ Oct > i-Pr > i-Bu > *sec*-**Bu** ($2.6 \cdot 10^4$ l/mol·s) [24c]. The reaction exemplifies a key step in nucleophilic catalysis of nucleophilic substitutions [24d].

[12]) The diastereoisomeric α/β-ratio was found to be kinetically controlled [9a] in Me-'Cby' formation, but thermodynamic control was invoked for R–Cbl under different experimental conditions [9b].

off much better with respect to that source of false conclusions, *i.e.* only follow-up reactions with rates comparable to those of oxidative addition can interfere. The rate constants for oxidative addition of a set of RX with cob(I)alamin as compared to those of other nucleophiles with the same set of RX and with known mechanism were early used to discriminate S_N2 from electron transfer [8b], but later this method was questioned [26]. However, based on rate *vs.* driving-force correlations, it is generally possible to distinguish o.s.e.t. involving [$Co^{I}L$] from all other mechanisms[6]). There are no simple models that predict the kinetic advantage of S_N2 over i.s.e.t. Finally, kinetic methods should be well suited to check the importance of r.c. ([R–$Co^{II}L$]) and of a.-a. S_N2 by studying the influence of oxidizing agents or axial ligands, respectively, on the rate of oxidative addition. Trapping of radical intermediates (argument *D*) is inherently weaker than argument *A*–*C* because it includes another – though fast and predictable – reaction as a probe. If radicals are quantitatively trapped, any two-electron mechanism can be excluded, but one has to assume no radical-type follow-up reaction. The latter postulate can be checked; *e.g.*, if a change of X in RX shifts the mechanism from one- to two-electronic, then the radicals originate not from follow-up reactions. However, method *D* is less susceptible to follow-up reactions, *i.e.* reactions as described by *Eqns. 10* and *11* can not interfere, and the radical-chain reaction (*Eqn. 12*) is suppressed (if an odd-electron species is used as a trap). If no radicals are observed, one has to assume quantitative efficiency of the trap in order to exclude the one-electron mechanisms involving free radicals.

So far only *intramolecular* trapping was applied to the mechanistic analysis of oxidative addition of RX to [$Co^{I}L$], and this approach restricted the choice of RX considerably. Conventional workup and analysis of the products necessitated troublesome experimental techniques and produced long lag times between oxidative addition and analysis.

The purpose of this publication is two-fold. We report on an astonishingly simple *intermolecular* trapping technique useful for the mechanistic analysis of oxidative addition of RX to [$Co^{I}L$] (and, on the same principle, to other metal complexes; *Chapts. 2* and *3*). The whole experiment including the mechanistic analysis takes a few seconds. We then apply the method to a series of 15 alkyl halides RX and 4 [$Co^{I}L$]'s in order to study the mechanistic borderline, *i.e.* the influence of tiny differences in R, X, and L on the mechanism of oxidative addition (*Chapt. 5*). The mechanistic details presented in *Chapt. 4* are not necessarily required to understand the main points of this work.

2. The Phenomenon: *In situ* Generation and Double-Trapping of Radicals Originating from Oxidative Addition in the Course of Single-Scan Voltammetry. – The single-scan voltammogram of hydroxocob(III)alamin ($OHCbl^{III}$) in dimethylformamide (DMF) is shown in *Fig. 1*. During equilibration of the electrode at −0.5 V for 10 s, Cbl^{II} is formed, and the only reduction wave observed during the potential scan from −0.5 to −1.6 V[13]) is attributed to the Cbl^{II}/Cbl^{I} redox couple (*Scheme 3*, *Eqn. 13*; dotted traces in *Fig. 1a* and *1b*). In the presence of an appropriate amount of PrI (RX) and as soon as Cbl^{I} is formed during the potential scan, complete oxidative addition takes place in a reaction layer close to the electrode yielding Pr–Cbl^{III} (*Eqn. 1*, *Scheme 3*). The organometallic species is also electroactive, but at a more negative potential (E_p(Pr–Cbl^{III}); *Eqn. 14*; broken trace in

[13]) All potentials are reported *vs.* SCE.

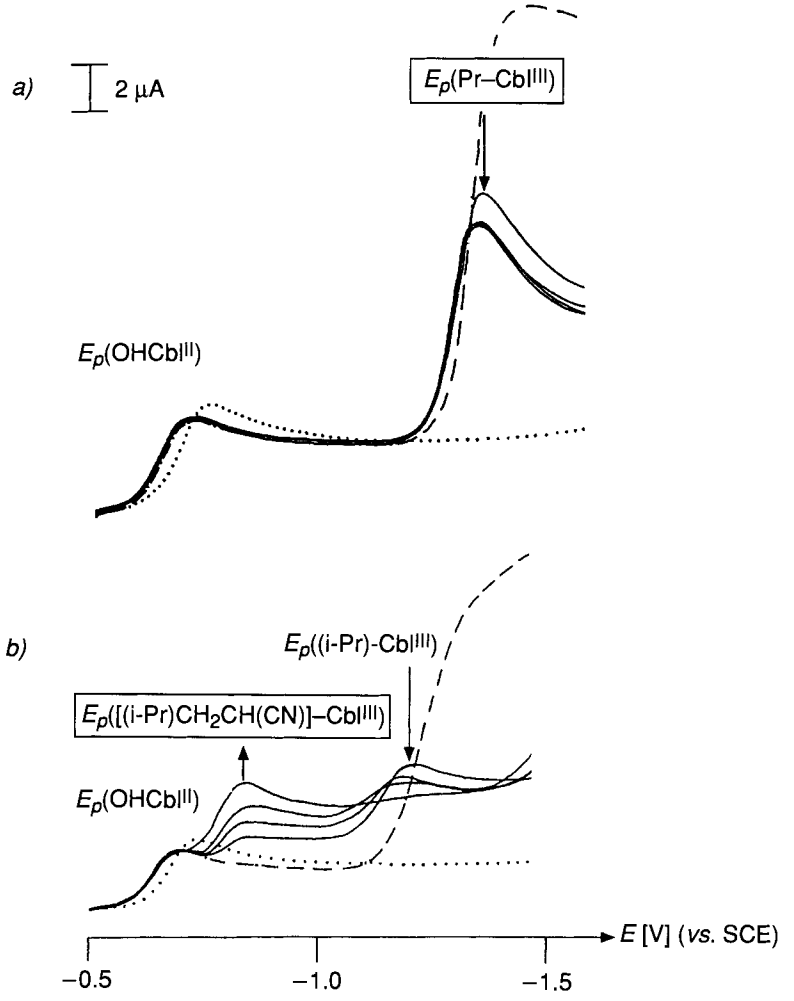
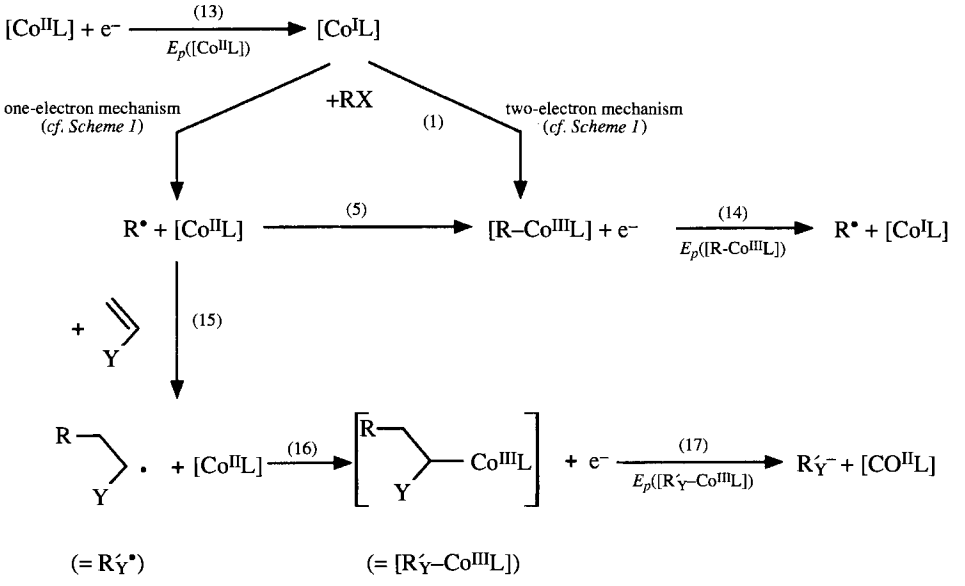


Fig. 1. *i-Pr Radicals involved in the oxidative addition of i-PrI to Cbl^{I}, as demonstrated by single-scan voltammetry.* OHCbl^{III} ($c \approx 0.7 \cdot 10^{-3}$ M; · · ·) in 0.1M (Bu_4N)ClO_4/DMF at $v = 100$ mV/s; *a*) OHCbl^{III} ($c \approx 0.7 \cdot 10^{-3}$ M)/PrI ($c = 15 \cdot 10^{-3}$ M; – – –) and OHCbl^{III} ($c \approx 0.7 \cdot 10^{-3}$ M)/PrI ($c = 15 \cdot 10^{-3}$ M)/acrylonitrile ($c = 7.5$, 30, 75, and $150 \cdot 10^{-3}$ M; —); *b*) OHCbl^{III} ($c \approx 0.7 \cdot 10^{-3}$ M)/i-PrI ($c = 120 \cdot 10^{-3}$ M; – – –) and OHCbl^{III} ($c \approx 0.7 \cdot 10^{-3}$ M)/i-PrI ($c = 120 \cdot 10^{-3}$ M)/acrylonitrile ($c = 3.8$, 7.6, 15, and $23 \cdot 10^{-3}$ M; ——).

Fig. 1a). Upon addition of increasing amounts of acrylonitrile, the reduction wave at E_p(Pr–Cbl^{III}) decreases, but otherwise no change is observed (solid traces in *Fig. 1a*; for an explanation of the current drop, *cf. Chapt. 4*). If i-PrI is used in stead of PrI, a similar wave develops at E_p((i-Pr)–Cbl^{III}) (broken trace in *Fig. 1b*). However, upon stepwise addition of acrylonitrile, it disappears completely, and a new wave develops simultaneously at E_p([(i-Pr)CH_2CH(CN)]–Cbl^{III}) = −0.87 V (solid traces in *Fig. 1b*). This reduction potential is typical for a (*sec*-R)–Cbl^{III} containing a nitrile group in α-position to the

Scheme 3. *Reaction Sequence During Single-Scan Voltammetry of [Co^{II}L] in Presence of RX and an Activated Olefin.* Y = Electron-withdrawing group.



Co-bound C-atom, *i.e.* for (1-cyano-3-methylbutyl)–Cbl[14]). An explanation is given in *Scheme 3*: PrI reacts according to a two-electron mechanism (probably S_N2) to yield Pr–Cbl, and acrylonitrile cannot interfer. i-PrI reacts *via* a one-electron mechanism involving the free radical i-Pr$^•$. If no acrylonitrile is present, i-Pr$^•$ combines with Cbl^{II} to yield (i-Pr)–Cbl^{III}. With increasing acrylonitrile concentration, i-Pr$^•$ is competitively trapped by the activated olefin[15]) to yield the 1-cyano-3-methylbutyl radical (*Eqn. 15*) which then combines in a subsequent step with Cbl^{II} (*Eqn. 16*) and shows up with its more positive reduction potential E_p(R'$_Y$–Cbl^{III}) (*Eqn. 17*).

---

[14]) a) The reduction potential of RCbl (E_p(R–Cbl^{III})) and R'Cby' (E_p(R–'Cby'^{III})) follows *Eqns. 18* and *19*, *i.e.* E_p becomes increasingly positive with rising acidity of the corresponding alkane RH [27]. Similar correlations are known for vitamin B_{12} model compounds [R–Co^{III}L] with L = $(DMG)_2$, (DO)(DOH), salen, and bae (*cf.* ref. cit. in [27a]), [R–Co^{III}(tpp)], and [R–Co^{III}(oep)] [27b]. For convenience, we use E_p ([R–Co^{III}L]) for a [R–Co^{III}L] with pK_a(RH) > 35 and E_p ([R'$_Y$–Co^{III}L]) for a [R'$_Y$–Co^{III}L] with pK_a(R'$_Y$H) < 35, where y = electron-withdrawing group at the Co- or H-bound C-atom, respectively.

$$E_p(\text{R–Cbl}^{III})\,[\text{V}] = -0.235\,[\text{V}] - 0.021\,[\text{V}]\cdot \text{p}K_a(\text{RH}) \quad (18)$$

$$E_p(\text{R–'Cby'}^{III})\,[\text{V}] = -0.223\,[\text{V}] - 0.020\,[\text{V}]\cdot \text{p}K_a(\text{RH}) \quad (19)$$

b) Other pK_aE_p correlations are known for [R–Fe(cp)$(CO)_2$] and [Hg–R] [28].

[15]) Selected 2nd-order rate constants for the addition of different radicals to acrylonitrile are: k_{15}(heptyl) $= 6\cdot 10^5$, k_{15}(i-Pr) $= 4\cdot 10^6$, and k_{15}(MeCH(CN)) $= 1\cdot 10^2$ l/mol·s [29a], *i.e.* k_{15} is orders of magnitude smaller than k_5[6]). Yet, trapping is possible for nucleophilic R$^•$, because the steady-state concentration of Cbl^{II} (= [Cbl^{II}]$_{ss}$) is low ([Cbl^{II}]$_{ss}$ $\ll 0.7\cdot 10^{-3}$ M).

Further evidence for the fast formation of the proposed 'olefin-inserted' organocobalamin R'_Y–Cbl^{III} is obtained from trapping the generated i-Pr˙ during the oxidative addition of i-PrI to Cbl^{I} with other activated olefins differing in their electron-withdrawing groups y (*Fig. 2*). The reduction potential $E_p(R'_Y–Cbl^{III})$ shifts to more and more positive

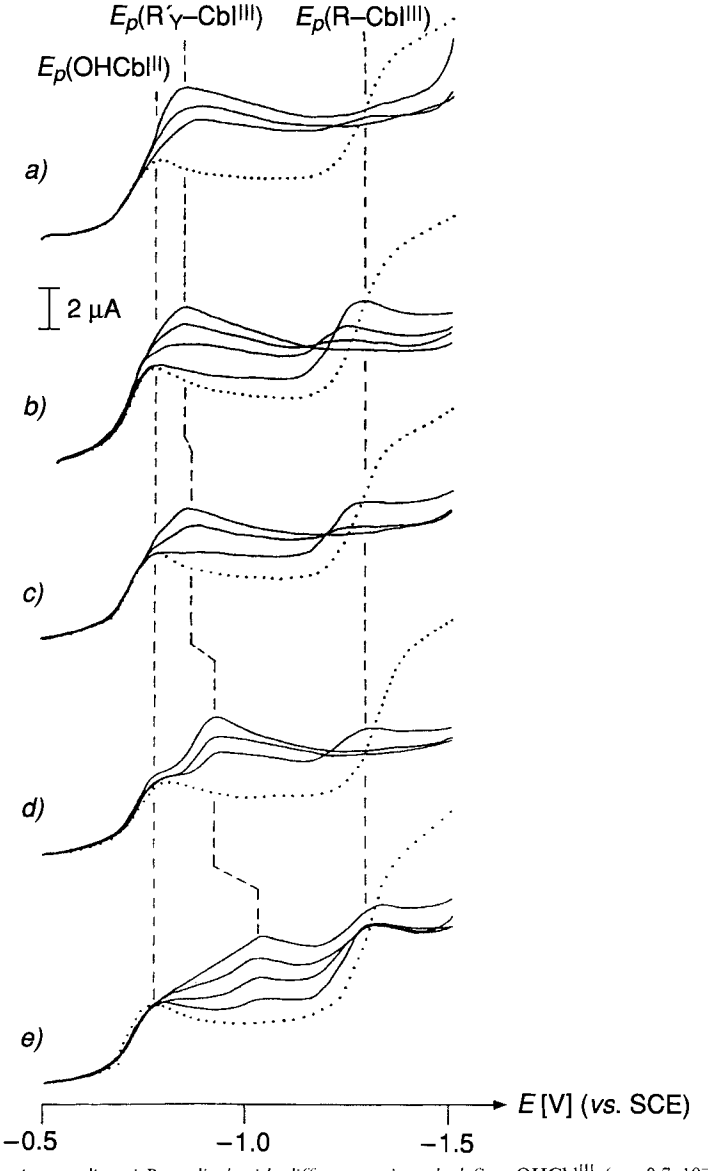


Fig. 2. *Trapping the intermediate i-Pr radical with different activated olefins.* $OHCbl^{III}$ ($c \approx 0.7 \cdot 10^{-3}$ M)/i-PrI ($c = 25 \cdot 10^{-3}$ M) in 0.1M $(Bu_4N)ClO_4$/DMF at $v = 50$ mV/s (···); *a*) acrolein ($c = 15$, 30, and $75 \cdot 10^{-3}$ M); *b*) 2-methylpent-1-en-3-one ($c = 7$, 26, 52, and $100 \cdot 10^{-3}$ M); *c*) = ethyl acrylate ($c = 9$, 37, and $92 \cdot 10^{-3}$ M); *d*) acrylonitrile ($c = 8$, 15, and $110 \cdot 10^{-3}$ M); *e*) acrylamide ($c = 35$, 98, 190, and $350 \cdot 10^{-3}$ M).

values as the electron-withdrawing group becomes stronger, as predictable from our earlier measurements[14]) [27]. Thermal homolysis or reductive cleavage of the Co–C bond in (i-Pr)–Cbl^{III} after oxidative addition, but during the experiment, is excluded, as the voltammogram of isolated (i-Pr)–Cbl in the presence of acrylonitrile does not show $E_p(R'_Y–Cbl^{III})$, *i.e.* isopropylcobalamin is stable under the conditions of single-scan voltammetry for potentials > $E_p(R'_Y–Cbl^{III})$. Furthermore, there is no reaction observed between the activated olefins and Cbl^I under our experimental conditions (*Fig. 3*).

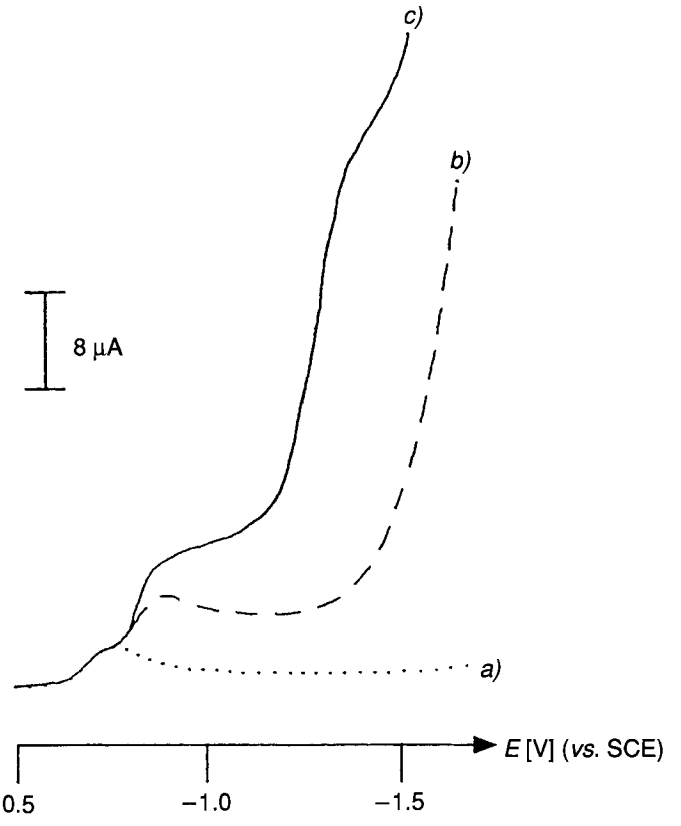


Fig. 3. *Inhibition and regeneration of electrocatalysis on the $R'_Y–Cbl^{III}$ reduction wave. a)* $OHCbl^{III}$ ($c \approx 0.7 \cdot 10^{-3}$ M)/acrylonitrile ($c = 230 \cdot 10^{-3}$ M; ···); *b)* $OHCbl^{III}$ ($c \approx 0.7 \cdot 10^{-3}$ M)/acryonitrile ($c = 230 \cdot 10^{-3}$ M)/i-PrI ($c = 200 \cdot 10^{-3}$ M; – – –; one-electron reduction of $R'_Y–Cbl^{III}$); *c)* $OHCbl^{III}$ ($c \approx 0.7 \cdot 10^{-3}$ M)/acrylonitrile ($c = 230 \cdot 10^{-3}$ M)/i-PrI ($c = 200 \cdot 10^{-3}$ M)/AcOH ($c = 9 \cdot 10^{-3}$ M; ——; a catalytic plateau current is observed). Direct reduction of i-PrI occurs at $E < -1.45$ V.

3. The Method: Evidence for a One-Electron Mechanism in Oxidative Addition from Single-Scan Voltammograms. – A very similar behavior as described in *Chapt. 2* for Cbl^I is observed for 'Cby'^{I}, [Co^I(tpp)], and [Co^I(oep)][14]). Generalization of the phenomenon

leads directly to a new method that can provide evidence for a mechanism involving free radicals in oxidative addition of RX to Cbl^I, 'Cby'^{I}, [Co^I(tpp)], and [Co^I(oep)]. The criterion is simply the appearance of E_p([R'_Y–$Co^{III}L$]) in a single-scan voltammogram of [$Co^{II}L$] in the presence of RX and an activated olefin. The method is related to the radical-trapping technique reported by *Puddephatt* and coworkers, who studied the reaction of alkyl halides with Pt^{II} complexes in the presence of acrylonitrile by conventional techniques [30]. In our approach, the formation of the reactive metal complex and the analysis of the product situation is achieved by two sequential electron transfers in the course of a single-scan voltammogram, *i.e.* within a few s. The advantages are obvious: *i*) the whole experiment including preparations takes only a few min, allowing the operator to check the influence of R and X in RX as well as L in [CoL] on the mechanism in reasonable time (*cf. Chapt. 4*), and *ii*) the danger of false conclusions (*cf. Chapt. 1*) are minimized because lag times as short as 1–3 s between oxidative addition and mechanistic analysis are involved.

There are some important restrictions to be considered: *1*) [$M^{(n-1)+}L$], [R–$M^{n+}L$], and [R'_Y–$M^{n+}L$] should all be electroactive, and the following order should hold: E_p([$M^{(n-1)+}L$]) > E_p([R'_Y–$M^{n+}L$]) > E_p([R–$M^{n+}L$]) ≫ E_p(RX), E_p(activated olefin). *2*) Reduction of the unreactive precursor metal complex [$M^{(n-1)+}L$] at E_p ([$M^{(n-1)+}L$]) must lead to the reactive intermediate $M^{(n-2)+}$ exhibiting a minimal reactivity $k_1 > 1$ l/mol·s for [RX] < 0.5M and for scan rats > 0.05 V/s. *3*) The reactivity of [$M^{(n-1)+}L$] towards RX and activated olefin as well as of [$M^{n+}L$] towards the activated olefin should be negligible. *4*) Trapping of the intermediate radical R˙ by the activated olefin should be competitive with [$M^{(n-1)+}L$],R˙ bond formation. This is generally fulfilled for a nucleophilic, but possibly not for an electrophilic R˙, even at high concentration of activated olefin[15]). *5*) The rate of homolytic decomposition of [R–$M^{n+}L$] (k_{-5}) should be small as compared to the reciprocal time required for the single-scan voltammogram. Notably, in *1*)–*5*), the metal ion has not been specified. Indeed, we are convinced that the technique will prove very helpful with other metal complexes[14b]).

4. Details Concerning Reactions in *Scheme 3*. – 4.1. *The Break-Down of Electrocatalysis.* The single-scan voltammograms of Cbl^{III} in *Figs. 1* and *2* show a catalytic plateau rather than a peak current in the presence of i-PrI, but in the absence of the radical trap. Actually, an electrocatalytic situation exists for electrode potentials < E_p((i-Pr)–Cbl^{III}) because of the reaction sequence *Eqn. 14* → *Eqn. 1* → *Eqn. 14*, *etc.* The rate-determining step in this sequence is the oxidative addition (*Eqn. 1*) because a linear correlation between the plateau current and [i-PrI]$^{1/2}$ is found[16]). In the presence of a sufficient amount of the radical trap, the plateau current drops to a one-electron wave at E_p([(i-Pr)CH_2CH(Y)]–Cbl^{III}). Obviously, a new slow step forestalls efficient catalysis. As trapping of i-Pr˙ is complete, it follows that k_{15}·[activ. olefin] > k_5·[Cbl^{II}], *i.e.* the trapping reaction (*Eqn. 15*) cannot be rate determining. Furthermore, the rate of Co–C bond formation between R'_Y˙ and Cbl^{II} is probably not much slower than that of any other C-centered radical with Cbl^{II}, *i.e.* close to diffusion-controlled [19]. The only remaining reaction that can slow down electrocatalysis is thus the reduction of R'_Y–Cbl^{III}. According to *Eqns. 14* and *17*, the reduction of R–Cbl^{III} leads to the radical R˙, but the reduction of R'_Y–Cbl^{III} to the anion R'^-_Y [27]. In order to rationalize the break-down of catalysis, we assume a two-step mechanism for the reduction of R'_Y–Cbl^{III} (*Eqn. 21* followed by *Eqn. 22*). Notably, heterolysis of $R'^-_Y \cdots Cbl^{II}$ only occurs in presence of protons. Indeed, we could show that electrocatalysis on the R'_Y–Cbl^{III} reduction wave is re-established, if a small amount of AcOH is present (*Fig. 3*).

---

[16]) The catalytic plateau current (i_∞) in single-scan voltammetry is described by *Eqn. 20* [31]

$$i_\infty = n \cdot F \cdot A \cdot [[CoL]] \cdot (D \cdot k_1 \cdot [RX])^{1/2} \qquad (20)$$

$$[R'_Y\text{–}Co^{III}L] + e^- \longrightarrow [R'_Y{}^- \cdots Co^{II}L] \quad (21)$$

$$[R'_Y{}^- \cdots Co^{II}L] + H^+ \longrightarrow R'_YH + [Co^{II}L] \quad (22)$$

A similar inhibition by acrylonitrile and proton-induced regeneration of the RX reduction catalysis occurs on the E_p(R–Cbl^{III}) wave in the case of a two-electron mechanism (*Fig. 1a*). At this potential, radicals (R$^{\cdot}$) are also generated *via* reduction of R–Cbl^{III} (*Eqn. 14*). Again double-trapping occurs, and the same set of arguments with minor modifications can be used to explain the phenomenon[17]).

4.2. *The Isopropyl Radical Develops Free-Radical Reactivity. Fig. 2* shows, that with decreasing electron-withdrawing ability of the electron-withdrawing group y, increasing concentrations of the activated olefin are needed to trap i-Pr$^{\cdot}$ efficiently. It is possible to interpret these results as a 'dynamic titration', and thus to find the *Hammett* reactivity parameter ρ for the intermediate radical. This figure can be compared to the ρ value of a free *sec*-alkyl radical attacking an analogous series of activated olefins, and hence it may support or exclude the existence of a freely diffusing i-Pr$^{\cdot}$ involved in oxidative addition. A kinetic analysis of *Scheme 3* leads to *Eqn. 23*, where C_2 is an unknown constant, but independent of the type of olefin used (*cf. Exper. Part*). It says that the representation of the reciprocal peak current $1/i_p$(R$'_Y$–Cbl^{III}) *vs.* 1/[activ. olefin] is linear with a slope C_2/k_{15}. Thus, relative k_{15} values are available from such representation using different activated olefins (*Fig. 4*). Plots of relative k_{15} values *vs. Hammett*'s σ_p^- of the olefinic compounds [32] yield the reactivity parameter $\rho = 2.9$, *i.e.* close to $\rho = 3.4$ which was reported for the free cyclohexyl radical [29]. The i-Pr$^{\cdot}$ involved in the oxidative addition of i-PrI to Cbl^{I} is,

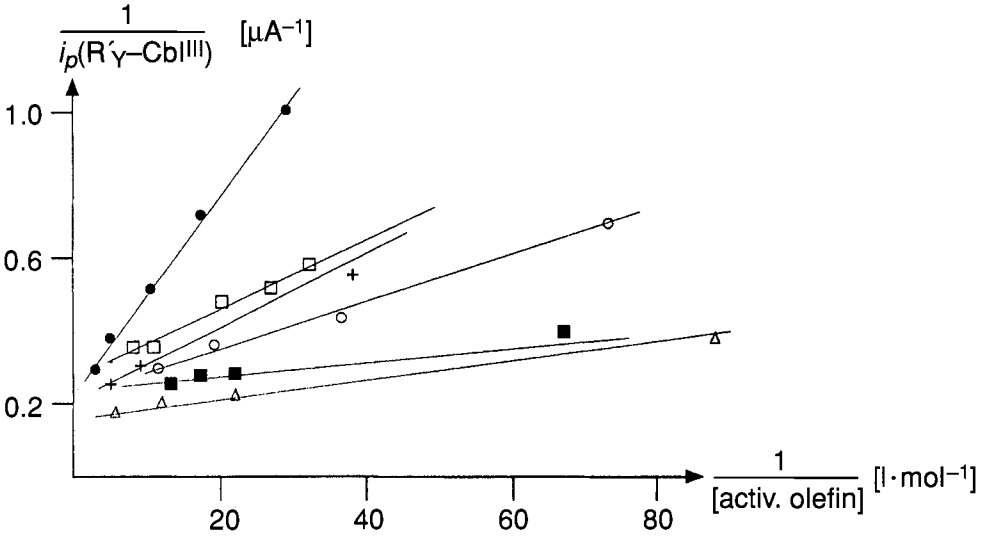


Fig. 4. *Evaluation of relative trapping rates* (rel. k_{15}). i_p (R$'_Y$–Cbl^{III}) values are from experiments as shown in *Fig. 2*; the slopes of $1/i_p$ (R$'_Y$–Cbl^{III}) *vs.* 1/[activ. olefin] yield relative trapping rates (rel. k_{15}; *cf. Eqn. 23* and *Exper. Part*); the straight lines are calculated by linear regression including values at higher [activ. olefin] (not shown in the plot); legends: ● acrylamide, + 2-methylpent-1-en-3-one, □ methyl vinyl ketone, ○ ethyl acrylate, ■ acrolein, △ acrylonitrile.

---

[17]) In contrast, the catalytic wave i_p([(i-Pr)–Co^{III}(tpp)]) apparently increases upon addition of acrylonitrile (*Fig. 5b*). This is probably due to the high stability of [(i-Pr)–Co^{II}(tpp)][7]), and *Eqn. 14* rather than *Eqn. 1* is rate-determining in the absence of acrylonitrile, whereas [{(i-Pr)CH$_2$CH(CN)}–Co^{II}(tpp)] is less stable and oxidative addition is rate-determining [27b] in presence of the trap.

therefore, a freely diffusing radical. To the best of our knowledge, this is the first measurement of the reactivity parameter of a radical generated in the course of oxidative addition.

$$\frac{1}{i_p(R'_Y\text{–}Cbl^{III})} = C_1 + \frac{C_2}{k_{15}} \cdot \frac{1}{[\text{activ. olefin}]} \tag{23}$$

5. Applications: The Mechanistic Borderline of Oxidative Addition to Cbl^I, 'Cby'^{I}, [Co^I(oep)], and [Co^I(tpp)]. – The method described in *Chapt. 3* for the detection of one-electron mechanisms in oxidative addition was applied to a series of 15 RX and the 4[Co^{I}L]'s using acrylonitrile as the common trap. The results are reported in *Figs. 5* and *6*

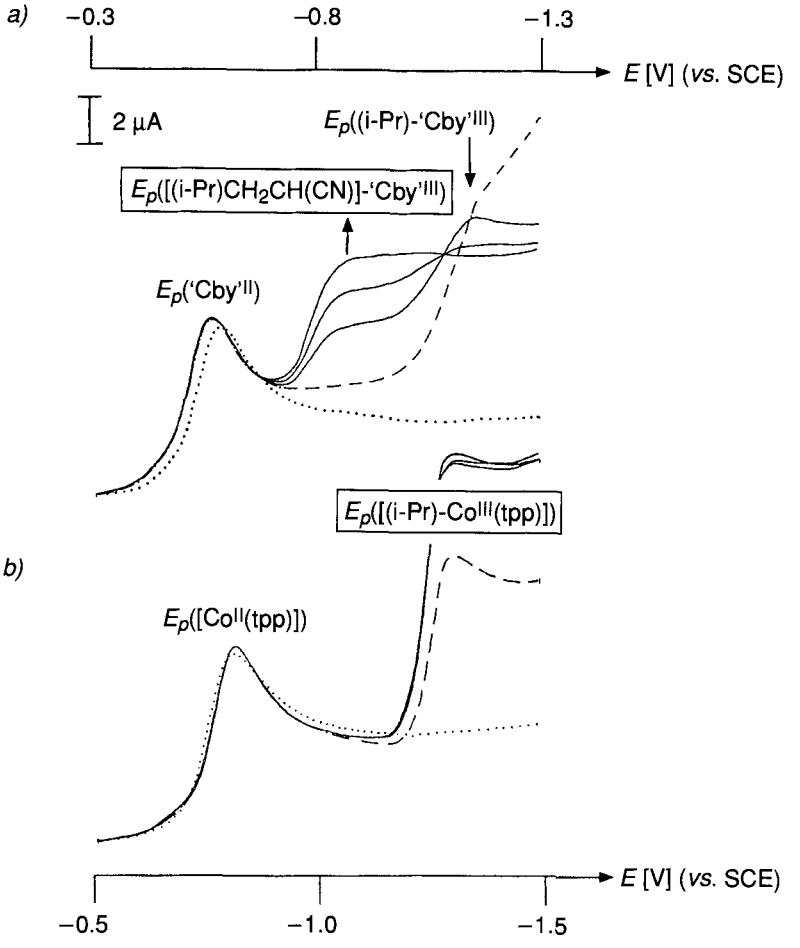


Fig. 5. a) *'Cby'^{I}* vs. b) *[Co^I(tpp)] in the oxidative addition of i-PrI displaying a one-electron mechanism, and* S_N2, *respectively.* [R'_Y–Co^{III}L] is observed for 'Cby' but not for [Co(tpp)]; *a*) 'Cby'^{II} ($c \approx 0.7 \cdot 10^{-3}$ M) alone (· · ·), in the presence of i-PrI ($c = 80 \cdot 10^{-3}$ M; – – –), and in the presence of i-PrI ($c = 80 \cdot 10^{-3}$ M)/acrylonitrile (c = 7.6, 30.4, and $243 \cdot 10^{-3}$ M; ——); *b*) [Co^{II}(tpp)] ($c \approx 0.7 \cdot 10^{-3}$ M) alone (· · ·), in the presence of i-PrI ($c = 40 \cdot 10^{-3}$ M; – – –), and in the presence of i-PrI ($c = 40 \cdot 10^{-3}$ M)/acrylonitrile (c = 15, 30, and $243 \cdot 10^{-3}$ M; ——).

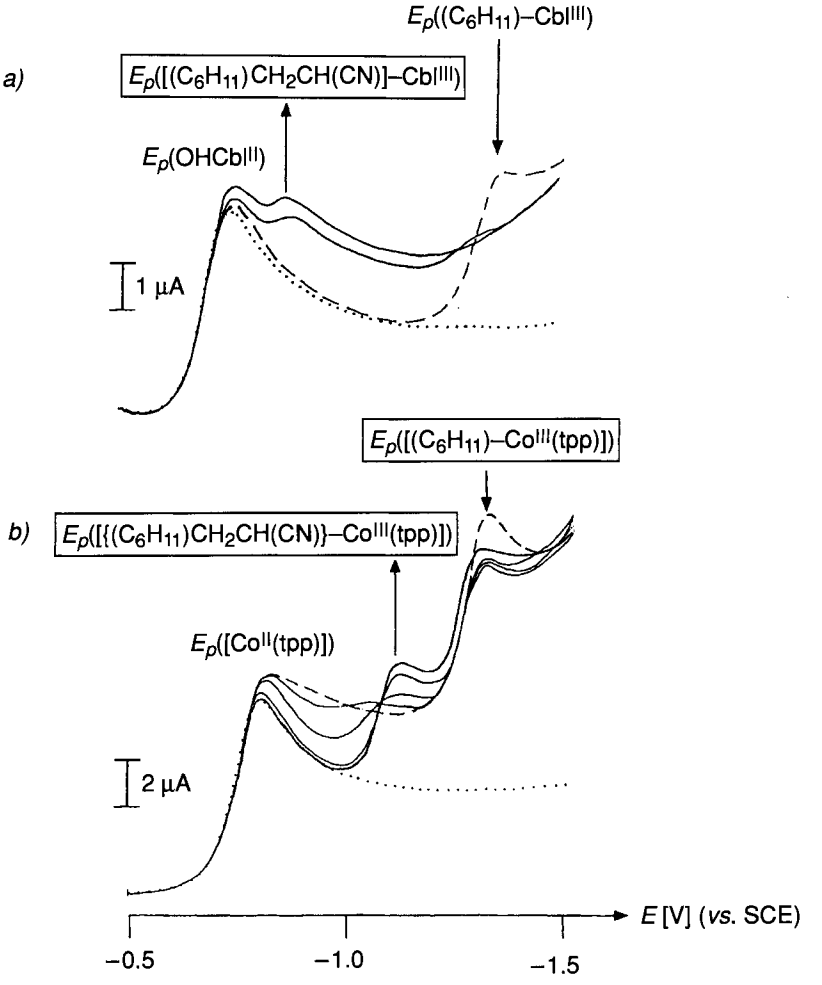


Fig. 6. a) Cbl^I vs. b) *[Co^I(tpp)] in the oxidative addition of cyclohexyl iodide displaying a one-electron mechanism and a mixed mechanism, respectively.* [R_Y–$Co^{III}L$] is observed for both [Co^IL]'s, but [R–Co^{III}(tpp)] does not disappear at high [acrylonitrile]. *a*) $OHCbl^{III}$ ($c \approx 0.7 \cdot 10^{-3}$ M) alone (···), in the presence of cyclohexyl iodide ($c = 124 \cdot 10^{-3}$ M; – – –), and in the presence of cyclohexyl iodide ($c = 124 \cdot 10^{-3}$ M)/acrylonitrile ($c = 8$ and $61 \cdot 10^{-3}$ M; ——); *b*) [Co^{II}(tpp)] ($c \approx 0.7 \cdot 10^{-3}$ M) alone (···), in the presence of cyclohexyl iodide ($c = 250 \cdot 10^{-3}$ M; – – –), and in the presence of cyclohexyl iodide ($c = 250 \cdot 10^{-3}$ M)/acrylonitrile ($c = 30$, 240, 970, and $1940 \cdot 10^{-3}$ M; ——).

and in *Table 1*. No radicals could be detected on reaction of MeI and of all non-activated primary alkyl iodides and bromides with the four metal complexes, indicating a common two-electron mechanism, except for the sterically most hindered neopentyl iodide (*t*-$BuCH_2I$) in its reaction with 'Cby'^{I} and Cbl^I. Indeed, negative evidence in the case of primary alkyl halides is conclusive, as the photolysis of Me–Cbl^{III} in the presence of even lower concentration of acrylonitrile yields the olefin-inserted organometallics [27a]. The measurement of the corresponding chlorides is not possible as the rate of oxidative addition is too low. The β-activated 3-bromopropiononitrile shows partial electron

Table 1. *Positive (+) and Negative (–) Evidence for a One-Electron Mechanism at Room Temperature in the Oxidative Addition of $R^1R^2R^3C-X$ to Cbl^I, 'Cby^I', $[Co^I(tpp)]$, and $[Co^I(oep)]$*[a])

R^1	R^2	R^3	X	Cbl^I	'Cby^I'	$[Co^I(tpp)]$	$[Co^I(oep)]$
H	H	H	I	–	–	–	–
Et	H	H	I	–	–	–	–
Et	H	H	Br	–	–	–	–
Pr	H	H	I	–	–	–	–
Pr	H	H	Br	–	–	–	–
t-Bu	H	H	I	+/–	+/–	–	–
NC-CH_2	H	H	Br	+/–	+/–	–	–
Ph	H	H	Cl	–[b])	–[b])	–[b])	–[b])
CH_2=CH	H	H	Cl	–[b])	–[b])	–[b])	–[b])
Me	Me	H	I	+	+	–	–
Me	Me	H	Br	[c])	[c])	–	–[c])
Et	Me	H	I	+	+	–	+/–
Et	Me	H	Br	[c])	[c])	–[c])	[c])
	$-(CH_2)_5-$	H	I	+	+	+/–	+/–
	$-(CH_2)_5-$	H	Br	[c])	[c])	[c])	[c])

[a]) All trapping with acrylonitrile in 0.1 M $(Bu_4N)ClO_4$/DMF, other exper. conditions, see *Exper. Part.* –: no $[R'_Y-Co^{III}L]$ but only $[R-Co^{III}L]$ observed, even at high [acrylonitrile], *i.e.* negative evidence for an electron-transfer mechanism. +: $[R'_Y-Co^{III}L]$ but no $[R-Co^{III}L]$ observed at high enough [acrylonitrile] *i.e.* positive evidence for an electron-transfer mechanism. +/–: $[R'_Y-Co^{III}L]$ and $[R-Co^{III}L]$ observed at high [acrylonitrile] at a ratio independent of [acrylonitrile], *i.e.* mixed mechanism.

[b]) The corresponding radical may not be enough nucleophilic to be trapped by acrylonitrile.

[c]) A catalytic wave on the $[Co^{II}L]/[Co^IL]$ wave covers the result.

transfer, but again only with the two corrinoid Co^I complexes (evidence for a mixed mechanism is described below). No acrylonitrile insertion observed with allyl and benzyl chloride (*Table 1*) is not conclusive, as the corresponding radicals may be too slow in their reactions with acrylonitrile. The influence of L on the mechanism shows up most dramatically with the *sec*-alkyl iodides. As shown in *Fig. 5*, 'Cby^I' reacts at room temperature in DMF with i-PrI *via* a transient free i-Pr˙ like Cbl^I (*cf. Fig. 1*), whereas $[Co^I(tpp)]$ follows a two-electron mechanism (probably S_N2). A similar result was obtained with *sec*-BuI (*Table 1*)[18]).

The oxidative addition of cyclohexyl iodide to Cbl^I as compared to $[Co^I(tpp)]$ is most instructive (*Fig. 6*): A clean one-electron mechanism is active (probably o.s.e.t. or i.s.e.t. (*cf. Scheme 1*)) in the reaction with Cbl^I as $i_p((C_6H_{11})-Cbl^{III})$ disappears completely at [acrylonitrile] = $61 \cdot 10^{-3}$ M, but with $[Co^I(tpp)]$ the $[\{(C_6H_{11})CH_2CH(CN)\}-Co^{III}(tpp)]$ wave develops only to a certain extent, and $i_p([(C_6H_{11})-Co^{III}(tpp)])$ does not disappear completely. At high enough [acrylonitrile], the ratio $i_p([\{(C_6H_{11})CH_2CH(CN)\}-Co^{III}(tpp)])/i_p([(C_6H_{11})-Co^{III}(tpp)])$ becomes independent of the trapping-agent concentration. This behavior is interpreted as a mixed mechanism, or rather two competing mechanisms – one showing radicals, the other not. As indicated in *Table 1*, several substrate/$[Co^{II}L]$ combinations exhibit mixed mechanisms, *i.e.* the method is well suited to visualize the mechanistic borderline situation. Preliminary results

[18]) The *sec*-alkyl bromides exhibit a catalytic current of unknown origin on the $[Co^{II}L]/[Co^IL]$ wave which covers the organometallic potential region.

indicate that $i_p([R'_Y{-}Co^{III}L])$, *i.e.* the portion following an electron-transfer mechanism, becomes increasingly important when the temperature is raised. Assuming no increasing interference of thermolysis (*Eqn. – 5, Scheme 2*), the observation is interpreted as a more negative entropy of activation for the sterically more restricted S_N2 transition state ($\Delta S^{\neq}_{SN2}$), combined with a smaller enhalpy of activation ($\Delta H^{\neq}_{SN2}$) due to stabilizing C,CoL interactions as compared to the corresponding activation parameters for electron transfer ($\Delta S^{\neq}_{e.t.}$ and $\Delta H^{\neq}_{e.t.}$), *i.e.* $\Delta S^{\neq}_{SN2} < \Delta S^{\neq}_{e.t.}$ and $\Delta H^{\neq}_{SN2} < \Delta H^{\neq}_{e.t.}$. Such a situation leads necessarily no crossing of the $\ln k$ *vs.* $1/T$ lines in an *Arrhenius* plot, *i.e.* to a temperature-dependent change in the dominant-mechanism results that happens to be located near room temperature [33]. The main conclusion of the present study is surprising: The mechanistic switch from a two-electron (probably S_N2) to a one-electron mechanism (probably dissociative electron transfer) for increasingly sterically demanding RX's occurs earlier with the supernucleophilic Cbl^I and 'Cby^I' than with $[Co^I(tpp)]$ and $[Co^I(oep)]$.

Further studies in our laboratories will take advantage of the new method for the mechanistic discrimination and the mixed-mechanism situation discovered for several RX/[CoL] combinations. The fundamental question is: Which are the parameters that determine the preference for a one-electron or two-electron mechanism? We believe, at least four are important: *1*) steric hindrance in the transition state, *2*) Co–C bond-dissociation energies, *3*) reduction potentials $E^o([Co^{II}L]/[Co^IL])$ and $E^o(RX/R^{\cdot} + X^-)$, and *4*) electron delocalization in the HOMO of $[Co^IL]$.

The authors thank the *Swiss National Foundation* for financial support.

Experimental Part

1. *Chemicals.* Vitamin B_{12b} (hydroxocob(III)alamin hydrochloride, $OHCbl^{III}\cdot HCl$; pyrogen-free *Fr. Ph. Bp.* 10.7% loss on drying; < 2% $CNCbl^{III}$) was purchased from *Roussel Uclaf*; heptamethyl perchloratocob(II)yrinate (ClO_4'Cby'^{II}) was prepared following the method of *Werthemann* [34]; (5,10,15,20-tetraphenylporphyrinato)cobalt(II) ($[Co^{II}(tpp)]$) and (2,3,7,8,12,13,17,18-octaethylporphyrinato)cobalt(II) ($[Co^{II}(oep)]$) were purchased from *Aldrich* and used directly without further purification. Alkyl halides and activated olefins: allyl chloride, benzyl chloride, acrylonitrile, methyl vinyl ketone (all *Fluka, puriss.*); MeI, PrBr, i-PrBr, PrI, i-PrI, 3-bromopropiononitrile, BuBr, *sec*-BuBr, BuI, *sec*-BuI, cyclohexyl bromide, cyclohexyl iodide, benzyl bromide, ethyl acrylate (all *Fluka, purum*); neopentyl iodide, acrolein (both *Fluka, pract.*); all alkyl halides and olefins were distilled through a *Vigreux* column under normal or reduced pressure before use (neopentyl iodide and 3-bromopropiononitrile were treated with $Na_2S_2O_3\cdot 5H_2O$ prior to distillation). AcOH, acrylamide, $(Bu_4N)BF_4$ (all *Fluka, puriss.*) were used as received. Ethyl isopropenyl ketone [35] and isopropylcobalamin [36] were synthesized according to known procedures. $(Bu_4N)ClO_4$ (*Fluka, purum*) was twice recrystallized from AcOEt and dried *in vacuo*. *N,N*-Dimethylformamide (DMF; *Fluka, puriss.* and *Siegfried, purum*) was dried over 4 Å molecular sieves and then distilled under reduced pressure prior to use.

2. *Electrochemistry.* 2.1. *General.* All measurements were performed in *Metrohm* cells under Ar at r.t. (21 ± 2°). The working electrode was a *Metrohm* (*6.0.804.010*) glassy carbon electrode with an active area of 0.07 cm^2. A KCl-sat. (aq.) calomel electrode (SCE) from *Metrohm* (*6.0724.100*), separated from the soln. by a salt bridge containing the same solvent/electrolyte as the soln., was used as reference system. The counter electrode was a Pt-wire placed directly in the soln. The electrochemical equipment was composed of an *EG & G P.A.R.* model *173* potentiostat/*175* function generator both from *Princeton Applied Research*. The voltammograms were plotted with a *Philips-PM-8041-X/Y* recorder. The scan rate was 50 or 100 mV/s.

2.2. *Measurements.* The measurements were carried out under dimmed-light conditions. The concentration of [CoL] was $0.7\cdot 10^{-3}$ M, except for $[Co^{II}(oep)]$ ($c = 0.3\cdot 10^{-3}$ M) because of its low solubility. Either 0.1 M $(Bu_4N)ClO_4$/

DMF or 0.1M $(Bu_4N)BF_4$/DMF was used as electrolyte/solvent system. No influence of the anion was observed. With Cbl^{III}, the electrode was equilibrated *ca.* 10 s at −0.5 V before the potential scan was started to assure a soln. of Cbl^{II} at the electrode. Appropriate amounts of the O_2-free RX were added in order to obtain slightly larger $i_p([R{-}Co^{III}L])$'s as compared with $i_p([Co^{II}L)$'s. O_2-Free acrylonitrile was added stepwise, and after each addition, a single-scan voltammogram was recorded until the voltammogram became independent on acrylonitrile addition. This happened generally at [acrylonitrile] ≪ 0.5M.

2.3. *Determination of the Reactivity Parameter ρ of the Isopropyl Radical Involved in the Oxidative Addition of Isopropyl Iodide to Cbl*^{I}. The first voltammogram was recorded in the absence of the olefin. The followings at different [activ. olefin]. All $i_p(R'_Y{-}Cbl^{III})$'s were measured from the same base line, *i.e.* the current at $E_p(R'_Y{-}Cbl^{III})$ in the absence of the olefin. The C_2/k_{15} value was obtained from linear regression analysis of the data pairs $(1/i_p(R'_Y{-}Cbl^{III})$ and 1/[activ. olefin]) for each olefin (*Fig. 4*; see *Table 2*). The relative k_{15} value for acrylamide was arbitrarily set = 1, and the other relative k_{15} values were calculated on this basis (*Table 2*). Linear regression analysis of log(rel. k_{15}) *vs.* σ_p^- (both sets of values are included in *Table 2*) yielded $p = 2.91$ with a correlation coefficient $r = 0.955$.

Table 2. *Relative Trapping Efficiency* (rel. k_{15}) *of Different Activated Olefins Used for the Determination of the Reactivity Parameter ρ of the Transient Isopropyl Radical*

Activated olefin	C_2/k_{15}	rel. k_{15}	log(rel. k_{15})	σ_p^{-a})
acrylamide	$29 \cdot 10^{-3}$	1	0	0.62
methyl vinyl ketone	$9.4 \cdot 10^{-3}$	3.0	0.48	0.82
ethyl acrylate	$6.5 \cdot 10^{-3}$	4.4	0.64	0.74
acrylonitrile	$2.4 \cdot 10^{-3}$	12	1.1	0.99
acrolein	$1.8 \cdot 10^{-3}$	16	1.2	1.04

[a]) From [30].

2.4. *Derivation of* Eqn. 23. The kinetic evaluation is based on the reactions in *Scheme 3*. The experiments were performed under pseudo-first-order conditions with respect to the concentration of the activated olefine ([activ. olefin]). A steady-state concentration is assumed to hold for Cbl^{II} ($[Cbl^{II}]_{ss}$) during single-scan voltammetry, at least for $E < E_p(Cbl^{II})$ in a reaction layer. If the rate constant for Co–C bond formation between $R'_Y{}^{\cdot}$ and $Cbl^{II}(k_{16})$ is not influenced by y, $[Cbl^{II}]_{ss}$ is the same for different activated olefins. As R˙ is a common intermediate in the two competing irreversible reactions of *Eqns. 5* and *15*, the product distribution reflects the corresponding rate relationship (*Eqn. 24*). The concentrations of the two organometallic products add up to the concentration of the initially applied $OH{-}Cbl^{III}$ concentration $[OH{-}Cbl^{III}]_0$ (*Eqn. 25*). Combination of *Eqns. 24* and *25* yields *Eqn. 26*. As the peak current in cyclic voltammetry is linearly related to the concentration of the corresponding electroactive species and assuming identical diffusion coefficients for different $R'_Y{-}Cbl^{III}$'s, *Eqn. 26* can be transformed into *Eqn. 23* [37].

$$\frac{[R{-}Cbl^{III}]}{[R'_Y{-}Cbl^{III}]} = \frac{k_5 \cdot [Cbl^{II}]_{ss}}{k_{15} \cdot [\text{activ. olefin}]} \tag{24}$$

$$[R{-}Cbl^{III}] + [R'_Y{-}Cbl^{III}] = [OH{-}Cbl^{III}]_0 \tag{25}$$

$$\frac{1}{[R'_Y{-}Cbl^{III}]} = \frac{1}{[OH{-}Cbl^{III}]_0} + \frac{k_5 \cdot [Cbl^{II}]_{ss}}{[OH{-}Cbl^{III}]_0 \cdot k_{15}} \cdot \frac{1}{[\text{activ. olefin}]} \tag{26}$$

REFERENCES

[1] Reviews: a) D. Dolphin, Ed., 'B_{12}', J. Wiley, New York, 1982, Vols. 1 and 2; b) P. J. Toscano, L. G. Marzilli, *Prog. Inorg. Chem.* **1984,** *31,* 105; c) R. Guilard, C. Lecomte, K. M. Kadish, *Structure Bonding* **1987,** *64,* 205; d) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, CA, 1987; e) IUPAC/IUB, *Pure Appl. Chem.* **1976,** *48,* 495; f) IUPAC/IUB, *ibid.* **1987,** *59,* 779.

[2] a) P. L. Bock, G. M. Whitesides, *J. Am. Chem. Soc.* **1974,** *96,* 2826; b) M. Perree-Fauvet, A. Gaudemer, *J. Organomet. Chem.* **1976,** *120,* 439.

[3] M. Fountoulakis, J. Rétey, W. E. Hull, B. Zagalak, in 'Vitamin B_{12}', 'Proceedings of the 3rd European Symposium on Vitamin B_{12} and Intrinsic Factor', Zürich, 1979, Eds. B. Zagalak and W. Friedrich, W. de Gruyter, Berlin, 1979, p. 169.

[4] M. Okabe, M. Tada, *Bull. Chem. Soc. Jpn.* **1982,** *55,* 1498.

[5] F. R. Jensen, V. Madan, D. H. Buchanan, *J. Am. Chem. Soc.* **1970,** *92,* 1414.

[6] H. L. Fritz, J. H. Espenson, D. A. Williams, G. A. Molander, *J. Am. Chem. Soc.* **1974,** *96,* 2378.

[7] H. Su, L. Walder, Z. da Zang, R. Scheffold, *Helv. Chim. Acta* **1988,** *71,* 1073.

[8] a) G. N. Schrauzer, E. Deutsch, R. J. Windgassen, *J. Am. Chem. Soc.* **1968,** *90,* 2441; b) G. N. Schrauzer, E. Deutsch, *ibid.* **1969,** *91,* 3341; c) D. Datta, G. T. Sharma, *Inorg. Chem.* **1987,** *26,* 329.

[9] a) B. Kräutler, C. Caderas, *Helv. Chim. Acta* **1984,** *67,* 1891; b) K. L. Brown, X. Zou, *Inorg. Chem.* **1991,** *30,* 4185; c) G. B. Maiya, B. C. Han, K. M. Kadish, *Langmuir* **1989,** *5,* 645.

[10] E. G. Samsel, J. K. Kochi, *J. Am. Chem. Soc.* **1986,** *108,* 4790.

[11] D. Dodd, M. D. Johnson, *J. Chem. Soc., Chem. Commun.* **1971,** 571.

[12] M. Okabe, M. Tada, *Chem. Lett.* **1980,** 831.

[13] a) J. Schäffler, B. Deppisch, J. Rétey, *Chem. Ber.* **1982,** *115,* 2229; b) J. Schäffler, J. Rétey, *Angew. Chem.* **1978,** *90,* 906.

[14] L. Walder, G. Rytz, K. Meier, R. Scheffold, *Helv. Chim. Acta* **1978,** *61,* 3013.

[15] R. Breslow, P. L. Khanna, *J. Am. Chem. Soc.* **1976,** *98,* 1297.

[16] H. Eckert, D. Lenoir, I. Ugi, *J. Organomet. Chem.* **1977,** *141,* C23; b) P. Gillespie, I. Ugi, *Angew. Chem.* **1971,** *83,* 493.

[17] F. R. Hensen, D.-H. Buchanan, *J. Chem. Soc., Chem. Commun.* **1973,** 153.

[18] J.-M. Savéant, *Adv. Phys. Org. Chem.* **1990,** *26,* 1.

[19] A. Bakac, J.-H. Espenson, *Inorg. Chem.* **1989,** *28,* 4319.

[20] D. Lexa, J.-M. Savéant, *J. Am. Chem. Soc.* **1978,** *100,* 3220.

[21] H.-U. Blaser, J. Halpern, *J. Am. Chem. Soc.* **1980,** *102,* 1684.

[22] L. Walder, R. Orlinsky, *Organometallics* **1987,** *6,* 1606.

[23] a) B. D. Martin, R. G. Finke, *J. Am. Chem. Soc.* **1990,** *112,* 2419; b) B. P. Hay, R. G. Finke, *Polyhedron* **1978,** *7,* 1469; c) G. N. Schrauzer, J. H. Grate, *J. Am. Chem. Soc.* **1981,** *103,* 541.

[24] a) B. Kräutler, *Helv. Chim. Acta* **1987,** *70,* 1268; b) J. F. Endicott, K. P. Balakrishnan, C.-L. Wong, *J. Am. Chem. Soc.* **1980,** *102,* 5519; c) D. Dodd, M. D. Johnson, B. L. Lockman, *ibid.* **1977,** *99,* 3664; d) B. A. McCortney, B. M. Jacobson, M. Vreeke, E. S. Lewis, *ibid.* **1990,** *112,* 3554.

[25] B. D. Gupta, S. Roy, *J. Chem. Soc., Perkin Trans. 2* **1988,** 1377.

[26] R. G. Pearson, P. E. Figdore, *J. Am. Chem. Soc.* **1980,** *102,* 1541.

[27] a) D.-L. Zhou, O. Tinembart, R. Scheffold, L. Walder, *Helv. Chim. Acta* **1990,** *73,* 2225; b) D.-L. Zhou, L. Walder, unpublished results.

[28] L. Walder, in 'Organic Electrochemistry', Eds. H. Lund and M. M. Baizer, M. Dekker, New York, 1991.

[29] a) B. Giese, *Angew. Chem.* **1983,** *95,* 771; b) B. Giese, G. Kretzschmar, *Chem. Ber.* **1983,** *116,* 3267.

[30] a) P. K. Monaghan, R. J. Puddephatt, *Organometallics* **1983,** *2,* 1698; b) R. H. Hill, R. J. Puddephatt, *J. Am. Chem. Soc.* **1985,** *107,* 1218.

[31] J.-M. Savéant, E. Vianello, *Electrochim. Acta* **1963,** *8,* 905.

[32] O. Exner, in 'Correlation Analysis in Chemistry', Eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978.

[33] D. Lexa, J.-M. Savéant, K.-B. Su, D.-L. Wang, *J. Am. Chem. Soc.* **1988,** *110,* 7617.

[34] L. Werthemann, Dissertation, No. 4097, ETH-Zürich, 1968.

[35] P. Walder-Stamouli, Dissertation, Universität Bern, 1986.

[36] J. H. Grate, G. N. Schrauzer, *J. Am. Chem. Soc.* **1979,** *101,* 4601.

[37] A. J. Bard, L. R. Faulkner, 'Electrochemical Methods', J. Wiley & Sons, Inc., New York, 1980.