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Bimolecular Homolytic Displacement of Transition-Metal Complexes from Carbon[†]

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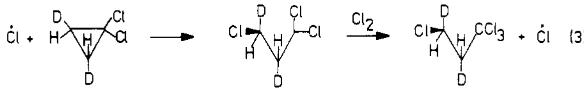
Seldom postulated, rarely discussed, frequently discarded as improbable, but potentially of immense interest in synthetic organic chemistry, is the homolytic displacement of a radical Y· from saturated carbon by another radical X·; the S_H2 reaction (eq 1). Why, with

$$\dot{X} + RCH_2Y \rightarrow RCH_2X + \dot{Y} \qquad (1)$$

the host of different radicals available, each having different character and reactivity, should this reaction so seldom have peen postulated? It is not that such a reaction is forbidden; a simple molecular orbital energy diagram of the transition state for the symmetrical displacement of Y· from RY by Y· shows that it is no more forbidden than the corresponding nucleophilic displacement of Y^- by Y^- or electrophilic displacement of Y^+ by Y^+, of which there are abundant examples. Indeed, since a radical may interact with a filled, a half-filled, or an empty orbital of the substrate, one might expect the homolytic displacement to be at least as common as its heterolytic counterparts! The answer to this question lies in the fact that other processes, namely, homolytic displacements at other centers, such as phosphorus, sulfur, halogen, hydrogen, and addition to unsaturated centers, are usually favored in the majority of the systems so far studied.[1] The few clear exceptions included,[2] in the gas phase, attack of a trifluoromethyl radical on a peripheral carbon of neopentane (eq 2)[3] and, in solution, attack of a chlorine atom on C-2 of 1,1-dichlorocyclopropane (eq 3).[4]

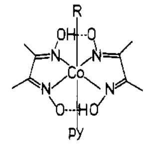
$$F_3\dot{C} + Me_4C \rightarrow F_3CMe + Me_3\dot{C} \qquad (2)$$



(3)

Under what circumstances would one expect to observe homolytic displacement at carbon? Since the enthalpy change for reaction 1 is simply the difference in enthalpies of dissociation of the two bonds, i.e., *D*(C–Y) - *D*(C–X), the bond formed must be at least as strong as the bond broken.[5] A first prerequisite is thus a substrate that is sufficiently stable to be isolated and characterized but with a weak bond between carbon and a suitable homofugal atom or group Y. However, this condition alone is insufficient, for there are two ends to any bond and, if the X–Y bond is also as strong as the C–Y bond of the substrate, attack is more likely to occur at Y than at the protected quadrivalent carbon, especially if Y is a univalent atom (H, Cl, etc) or has a relatively unprotected bi- or trivalent element directly attached to the carbon. Therefore, a second prerequisite is that the group Y is not susceptible to attack by X·, especially at the element bonded to carbon, for example, by ensuring that that element is sterically inaccessible.

One such substrate, with which this work is substantially concerned, is a d^6 low-spin organobis(dimethylglyoximato)(ligand)cobalt(III) complex (**1**).[6]



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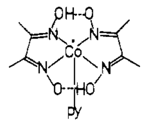

2

These complexes are usually easily prepared under mild conditions[7] such that many hundreds have now been isolated and characterized, having a wide range of different organic ligands (R). It is an essential feature of this work that the inorganic radical (**2**), formed on homolytic cleavage of the carbon–cobalt bond, is the d^7 bis(dimethylglyoximato)(ligand)cobalt(II) complex, which can also be readily synthesized *and isolated*, and may be maintained under anaerobic conditions in some solvents indefinitely, unlike the majority of conventional radicals, for it neither disproportionates under neutral conditions nor dimerizes to any significant extent.

As the strength of the carbon–cobalt bond is a key feature of these substrates, we examine first the tendency of the organocobaloximes to undergo unimolecular homolysis.

Michael D. Johnson was born in Newcastle-under-Lyme, England. He studied at Southampton University for his B.Sc. degree and continued in graduate work there, receiving the Ph.D. under N. B. Chapman in 1957. After a year of postdoctoral work with E. S. Lewis at Rice University and a year as a chemist at Imperial Oil Ltd, Sarnia, Canada, Dr. Johnson moved to University College London, where he is now Reader in Chemistry. His research is concerned with the mechanisms of reactions of σ-bonded organotransition-metal compounds, with special interest in homolytic displacement reactions, particularly at carbon centers, their use in organic synthesis, and their role in the interaction of olefins with metal hydrides.

[†] This Account is dedicated to Professor Chapman on his retirement.

(1) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions", Wiley-Interscience, New York, 1971.

(2) The formation of cyclopropanes from iodopropyl radicals may also be considered to be a special case of the S_H2 displacement at a saturated carbon: R. F. Drury and L. Kaplan, *J. Am. Chem. Soc.*, **95**, 2217 (1973).

(3) R. A. Jackson, and M. Towson, *J. Chem. Soc., Perkin Trans. 2*, 1452 (1972).

(4) J. H. Incremona and C. J. Upton, *J. Am. Chem. Soc.*, **94**, 301 (1972).

(5) We may assume that for neutral reagents solvent effects will be minimal. However, in cases where reagents are charged, solvent effects, even on $\Delta H^{\ne}$, may be appreciable; cf. R. G. Coombes and M. D. Johnson, *J. Chem. Soc. A*, 177 (1966).

(6) Commonly known as cobaloximes; dmgH = monoanion of dimethylglyoxime.

(7) In a typical preparation, $CoCl_2{\cdot}6H_2O$ (1 mol) and dimethylglyoxime (2 mol) under nitrogen in methanol are treated with a ligand such as pyridine (1 mol) and with aqueous sodium hydroxide (2 mol). This gives an orange-brown suspension of 2, which may be isolated if required. On addition of more sodium hydroxide (1–2 mol), complex 2 disproportionates to give a blue-black suspension of the highly nucleophilic cobaloxime(I) ion. On addition of an organic halide or tosylate, the color changes to orange and the organocobaloxime (1) may be precipitated by pouring the mixture into an excess of water in the presence of air.

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Thermolysis of Organocobaloximes

The enthalpy change for reaction 4 has been determined from the variation of the equilibrium constant with temperature.[8] From the known or estimated values of the heats of formation of styrene, hydrogen, and the α-phenylethyl radical, the enthalpy change for reaction 5 has also been determined and hence the bond dissociation enthalpy for reaction 6 has been calculated, for several different ligands L.

$$\underset{\mathbf{3}}{\mathrm{PhCHMeCo(dmgH)_2L}} \rightleftarrows \mathrm{PhCH{=}CH_2 + 1/2H_2 + \dot{C}o(dmgH)_2L} \quad (4)$$

$$\mathrm{PhCH{=}CH_2 + 1/2H_2 \rightleftarrows Ph\dot{C}HMe} \quad (5)$$

$$\mathrm{PhCHMeCo(dmgH)_2L \rightleftarrows Ph\dot{C}HMe + \dot{C}o(dmgH)_2L} \quad (6)$$

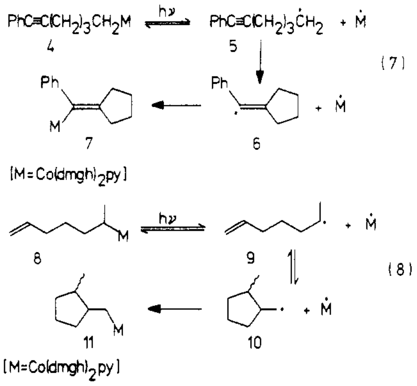
The results show that the carbon–cobalt bond-dissociation enthalpy of **3** increases from ca. 18 kcal $\mathrm{mol^{-1}}$ for L = 4-cyanopyridine to ca. 21 kcal $\mathrm{mol^{-1}}$ for L = 4-aminopyridine. Morevoer, as the activation enthalpy for reaction 4 is less than 2 kcal $\mathrm{mol^{-1}}$ greater than the calculated bond-dissociation enthalpy of **3**, it is probable that reaction 4 takes place through a rate-determining homolysis identical with that shown in eq 6, and that the reverse of reaction 6 is an encounter-controlled process with an activation enthalpy of the order of 2 kcal $\mathrm{mol^{-1}}$.[9]

Studies of other organocobaloximes have been at best semiquantitative, but the order of thermal stability in solution, which reflects the stability of the carbon–cobalt bond, is *sec*-allyl < *sec*-benzyl < allyl < benzyl < *tert*-alkyl < *sec*-alkyl < *n*-alkyl. Thus the least stable complexes dissociate at or below ambient temperature and secondary alkyl complexes show some evidence of homolysis above 80 °C, whereas primary alkylcobaloximes show little decomposition below 100 °C.

Photolysis of Organocobaloximes

In the flash photolysis of a number of *n*-alkylcobalt(III) complexes, the threshold for homolytic cleavage is at relatively long wavelengths, consistent with bond dissociation energies of ca. 30 kcal $\mathrm{mol^{-1}}$.[10] Tungsten lamps and glass apparatus are therefore sufficient for preparative photolysis experiments. There is also direct evidence that the rates of recombination of organic radicals with a variety of closely related cobalt(II) complexes are not far short of the encounter rate.[10]

In the photolysis of methylcobaloxime in aqueous solution, the organic products are those expected from the formation of methyl radicals, and the quantum yield is markedly higher in the more acidic solutions because of the acid-catalyzed decomposition of the cobaloxime(II) fragment **2**, which effectively reduces the extent of the recombination reaction.[11] The homolysis of primary and secondary alkylcobaloximes under tungsten illumination and the efficiency with which the fragments can recombine have been illustrated by the observation of several rearrangements.[12] For example, the hexynylcobaloxime **4** rearranges very efficiently on irradiation in pyridine solution to the vinylic (cyclopentylidenebenzyl)cobaloxime **7**, and the hept-6-en-2-ylcobaloxime **8** rearranges somewhat less efficiently into the two isomers of [(2-methylcyclopentyl)methyl]cobaloxime **11**.[13] The intermediate radicals **5** and **9**, which are known to rearrange readily into the radicals **6** and **10**, respectively,[14] can be trapped by the addition of appropriate halogen atom donors.



Reaction of Organocobaloximes with Metal Radicals

Having established that the carbon–cobalt bond is significantly weak and that organic and inorganic radicals are formed on photolysis and thermolysis of the organocobaloximes, we may now consider how each of these radical fragments can react, either directly or indirectly, with the organocobaloxime substrate.

Since the cobaloxime(II) radical (**2** and its analogue **2a**[15]) may be prepared in quantity in known concentration in solution, it is a relatively straightforward matter to examine the rate of the near-symmetrical exchange reaction shown in eq 9, for which the strengths of the bonds broken and formed are essentially the same and for which any entropy change would be expected to be minimal.[16]

$$\underset{\mathbf{2}}{\mathrm{L(dmgH)_2\dot{C}o}} + \underset{\mathbf{12a}}{\mathrm{RCo(chgH)_2L}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\mathbf{12}}{\mathrm{L(dmgH)_2CoR}} + \underset{\mathbf{2a}}{\mathrm{\dot{C}o(chgH)_2L}} \quad (9)$$

Thus when **2** is mixed with the methylcobaloxime **12a** (R = Me, L = py) in methylene chloride or in methanol (both reagents ca. 0.01 mol $\mathrm{dm^{-3}}$) under anaerobic conditions at 0 °C, an equilibrium mixture containing **2**, **2a**, **12**, and **12a** is formed within 30 s.[17] The corresponding reaction between **2** and **12a** (R = Et, L = py)

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(8) T. Tsou, M. Loots, and J. Halpern, *J. Am. Chem. Soc.*, **104**, 623 (1982); see also H. B. Gjerde and J. H. Espenson, *Organometallics*, 1, 435 (1982).

(9) K. U. Ingold in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, 1973, Vol. 1, Chapter 2.

(10) J. F. Endicott and G. J. Ferraudi, *J. Am. Chem. Soc.*, **99**, 243 (1977); T. S. Roche and J. F. Endicott, *Inorg. Chem.*, **13**, 1515 (1974); H. Elroi and D. Meyerstein, *J. Am. Chem. Soc.*, **100**, 5540 (1980).

(11) B. T. Golding, T. J. Kemp, P. J. Sellars, and E. Nocchi, *J. Chem. Soc., Dalton Trans.*, 1266 (1977).

(12) P. J. Bougeard, C. J. Cooksey, M. D. Johnson, M. Lewin and F. Rajah, *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.

(13) The majority of attempts to rearrange organocobalt(III) complexes have failed because the products have been less stable than the reagents. In these cases, the reverse is true.

(14) A. L. J. Beckwith and K. U. Ingold, "Rearrangements in Ground and Excited States", P. DeMayo, Ed., Academic Press, New York, 1980, Vol. 1, Chapter 4.

(15) chgH = conjugate base of cyclohexanedione dioxime.

(16) This reaction has a kinetic form similar to that shown by bimolecular isotopic exchange reactions if it is assumed that the rate constants for the forward and reverse processes are identical.

(17) There is a second, slower, reaction in which scrambling of the equatorial ligands occurs, but this does not affect the conclusions drawn.[18]

Table I
Kinetics of Reaction of Alkylcobaloximes [$RCo(dmgH)_2py$] with Cobaloxime(II) [$Co(chgH)_2py$][a]

R′	T/°C	solvent	k_2/L mol^{-1} s^{-1}
Me	0	MeOH	4400
Et	0	MeOH	10
n-Pr	28	MeOH	12
n-Bu	28	MeOH	8
n-Oct	0	MeOH	0.64
n-Oct	0	CH_2Cl_2	0.034
n-Oct	28	CH_2Cl_2	1.0
$PhCH_2CH_2$	28	MeOH	3.6
PhCHDCHD	28	MeOH	3.7
i-Pr	28	MeOH	0.54
i-Bu	28	MeOH	0.026

[a] In this system, $k_2 = k_{-2}$.

is appreciably slower and the rate of approach to equilibrium decreases dramatically down the series Et > *n*-Pr > *n*-Bu > *i*-Bu > *i*-Pr > *sec*-Bu as shown in Table I.[18] This very large decrease in the rate of substitution is indicative of an attack of **2** at the α-carbon of the alkyl ligand with inversion of configuration, i.e, with a homolytic displacement of an inorganic radical by attack of another inorganic radical at saturated carbon.[19] This is confirmed by the observation that the rate constant for the interconversion of **12a** (R = *erythro*-PhCHDCHD, L = py) into **12a** (R = *threo*-PhCHDCHD, L = py) in the presence of **2a** is the same as that for the interconversion of **12** and **12a** (R = $PhCH_2CH_2$, L = py) in the presence of **2**.

Equilibrium constants and, in some cases rate constants, have also been determined for the transfer of methyl groups between various cobalt complexes containing significantly dissimilar equatorial ligands (e.g., eq 10 and 11, ref 24 and 25, respectively).[19-21] A

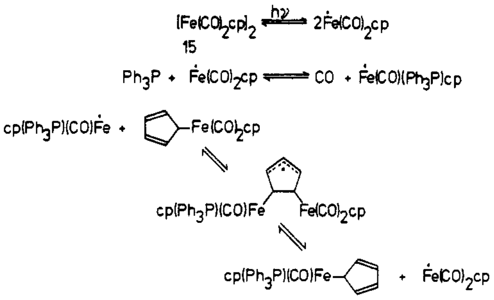
$$\mathrm{Co(Tfacacen) + PrCo(Acacen) \rightleftharpoons PrCo(Tfacacen) + Co(Acacen)} \quad (10)$$

$$\mathrm{Co(dmgH)_2aq + MeCo([14]aneN_4)^{2+} \rightleftharpoons MeCo(dmgH)_2aq + Co([14]aneN_4)^{2+}} \quad (11)$$

knowledge of the equilibrium constants allows further deductions to be made about the *relative* carbon–methyl bond-dissociation enthalpies for the several types of complex.

The bimolecular homolytic displacement of **2** from methyl- and from isobutylaquocobaloxime by the d^4 chromium(II) cation radical in aqueous acidic solution (eq 12) has rate constants of 23 and 6.1 × 10^{-5} L mol^{-1} s^{-1}, respectively, at 25 °C,[22] and a bimolecular homolytic displacement of the closely related, biologically important cobalamin(II) radical from methyl- and from ethylcobalamin by diamagnetic tin(II) halides (eq 13) has also been proposed, provided an oxidant is present to remove the radical products as formed.[23] The formation of a pair of radicals from two diamagnetic precursors is an allowed process, being the reverse of the abstraction of an atom or group from one radical by another (eq 14), but it is likely to be highly endothermic and the pair of radicals must be formed as a singlet state.

Scheme I



$$\mathrm{Cr(H_2O)_5{}^{2+} + RCo(dmgH)_2aq \rightarrow RCr(H_2O)_5{}^{2+} + 2} \quad (12)$$

$$\mathrm{SnCl_2 + Rcobalamin(III) \rightleftharpoons R\dot{S}nCl_2 + cobalamin(II)} \quad (13)$$

$$\mathrm{A\dot{B} + \dot{C} \rightleftharpoons A + BC} \quad (14)$$

Before discussing further the problem of attack of conventional radicals at the α-carbon of the organic ligand, it is pertinent to discuss some closely related displacements of cobalt(II) through attack of a metal radical at other sites on the organic ligand. With allylcobaloximes (**13**), the attack of **2** may take place at the α- and at the γ-carbon of the allyl ligand, but it is the latter process, an S_H2' displacement (eq 15), that

$$\mathrm{2 + \underset{\mathbf{13}}{CH_2{=}CHCH_2Co(dmgH)_2py} \rightleftharpoons \underset{\mathbf{14}}{py(dmgH)_2CoCH_2\dot{C}HCH_2Co(dmgH)_2py} \rightleftharpoons py(dmgH)_2CoCH_2CH{=}CH_2 + 2} \quad (15)$$

is most readily detected through its influence on the proton and ^{13}C NMR spectra of the allylcobaloxime.[26] When complex **13** is pure and its solution in $CDCl_3$ is fresh, the proton NMR spectrum is that expected for a nonlabile (η^1-allyl)cobaloxime. After a short while at ambient temperature the spectrum changes; the two sets of methylene proton resonances begin to coalesce, the methine proton resonance approaches a quintet, and the pyridine α-proton resonances broaden appreciably. On addition of a *trace* of bromotrichloromethane, the sharp spectrum of the (η^1-allyl)cobaloxime is restored for several minutes, after which it again begins to broaden. The cycle can be repeated, but in due course decomposition products begin to dominate the spectrum.

This behavior can be explained if the changes are caused by the formation of traces of the cobaloxime(II) complex **2**, which induce the rapid S_H2' exchange shown in eq 15 and which can be removed by bromotri-

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(18) D. Dodd, M. D. Johnson and B. L. Lockman, *J. Am. Chem. Soc.*, **99**, 3664 (1977).

(19) It is an interesting reflection on the different views of organic and inorganic chemists that the former are likely to think of them as S_H2 displacement reactions, the latter as one-electron inner-sphere redox reactions, cf. J. F. Endicott, C. L. Wong, J. M. Ciskowski, and K. P. Balakrishnan, *J. Am. Chem. Soc.*, **102**, 2100 (1980).

(20) J. F. Endicott, K. P. Balakrishnan, and C. L. Wong, *J. Am. Chem. Soc.*, **102**, 5519 (1980).

(21) A. Van den Bergen and B. O. West, *J. Organomet. Chem.*, **64**, 125 (1974).

(22) J. H. Espenson and T. D. Sellars, *J. Am. Chem. Soc.*, **96**, 94 (1974).

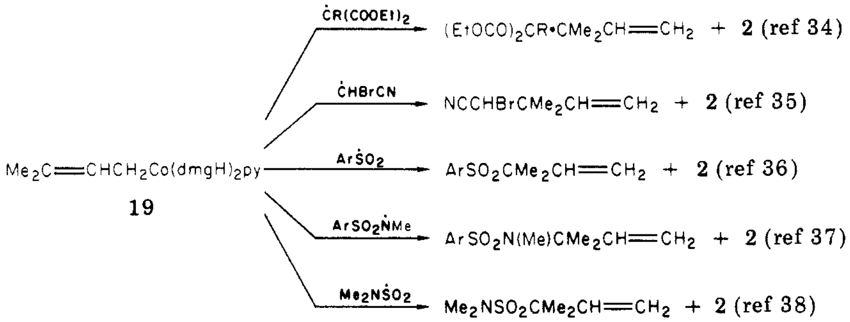
(23) Y. T. Fanchiang and J. M. Wood, *J. Am. Chem. Soc.*, **103**, 5100 (1981).

(24) K = 0.2 at 44 °C. Reference 21. Tfacacen = bis(trifluoroacetylacetonyl)ethylenediamine.

(25) K = 500 at 25 °C. Reference 20. [14]aneN$_4$ = 1,3,8,11-tetraazacyclotetradecane.

(26) C. J. Cooksey, D. Dodd, M. D. Johnson, and B. L. Lockman, *J. Chem. Soc., Dalton Trans.*, 1815 (1978).

Scheme II



chloromethane.[27] Closely related metal-for-metal S_H2' reactions of organoiron complexes have since been postulated by Labinger to account for the photochemical exchange of a phosphine ligand in $(\eta^1\text{-}C_5H_5)Fe(CO)_2(\eta\text{-}C_5H_5)$ catalyzed by traces of the dimer **15** (Scheme I)[28] and by Rosenblum in the case of a (η^1-allyl)(η-cyclopentadienyl)carbonyl(phosphine)iron complex.[29] An exchange similar to that in Scheme I has also been proposed for the reaction of tributyltin radicals with (η^1-cyclopentenyl)- and (η^1-cyclopentadienyl)tin complexes.[30]

S_H2' Reactions of Organocobaloximes with Organic Radicals

It was pointed out by a referee of one of our earlier papers that "the idea that cobaloxime(II) species should be considered as analogs of $\dot{C}H_3$ is an idea of obvious utility, but not one that should be considered inviolate...", i.e., that some care was necessary in comparing the displacement of one inorganic radical by another with an organic S_H2 process. It was thus of special interest to see if similar homolytic displacements could be carried out with conventional organic radicals.

We noted above that the NMR spectrum of **13** was markedly influenced by the presence of bromotrichloromethane and ascribed this to the removal of **2**. This removal takes place through the abstraction of the bromine atom from the polyhalomethane by **2** and capture of the trichloromethyl radical by another molecule of **2** (eq 16 and 17).[31] However, when an

$$Cl_3CBr + Co(dmgH)_2L \rightarrow Cl_3\dot{C} + \underset{\mathbf{17}}{BrCo(dmgH)_2L} \qquad (16)$$

$$Cl_3\dot{C} + Co(dmgH)_2L \rightarrow Cl_3CCo(dmgH)_2L \qquad (17)$$

excess of bromotrichloromethane is added to a solution of complex **13**, a rapid reaction takes place (though there may be an induction period), the products being the bromocobaloxime(III) **17** and the trichlorobutene **18** (R = H). Since 3-substituted allylcobaloximes all give 3-substituted 4,4,4-trichlorobutenes (**18**; R = Me, Ph, etc.), the organic product is clearly formed by the regiospecific attack of the trichloromethyl radical on the γ-carbon of the allyl ligand (eq 19).[32] Thus, in the

$$BrCCl_3 + RCH{=}CHCH_2Co(dmgH)_2L \rightarrow \underset{\mathbf{18}}{Cl_3CCHRCH{=}CH_2} + BrCo(dmgH)_2L \qquad (18)$$

$$Cl_3\dot{C} + RCH{=}CHCH_2Co(dmgH)_2L \rightarrow Cl_3CCHRCH{=}CH_2 + Co(dmgH)_2L \qquad (19)$$

presence of an allylcobaloxime and an excess of bromotrichloromethane, reactions 16 and 19 provide a pair of propagation steps for a chain reaction, and reaction 17 is relegated to a termination step.[33]

Subsequent studies with other free-radical precursors have shown that a wide range of electrophilic radicals react with allylcobaloximes. A selection of reactions of N-, S-, and C-centered radicals with the highly reactive (3-methylbut-2-enyl)cobaloxime (**19**) are shown in Scheme II. This S_H2' reaction is not confined to the organocobaloximes. In fact, the formation of some 4,4,4-trichlorobutene was noted by Kharasch, in the reaction of allyl bromide with carbon tetrahalides, as long ago as 1949, and several similar processes have subsequently been detected as components of more complicated systems.[39] More recently, the displacement of the tributyltin radical from allyltributyltin compounds by trihalomethyl,[40] acyl,[41] and phenyl[30] radicals has been described, as well as the displacement of thiyl and arenesulfonyl radicals by tributyltin radicals during the reduction of allyl sulfides and allyl sulfones,

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[27] There is no evidence that **14** is an intermediate in reaction 15, but it seems likely in view of the reactions of other allyl compounds and of the higher alkenylcobaloximes, described below.

[28] J. A. Labinger and B. D. Fabian, *J. Am. Chem. Soc.*, **101**, 2239 (1979).

[29] M. Rosenblum and P. Waterman, *J. Organomet. Chem.*, **206**, 197 (1981).

[30] U. Schröer and W. P. Neumann, *J. Organomet. Chem.*, **105**, 183 (1976).

[31] The second-order rate constants for the abstraction of a halogen atom from Cl_4C and from $BrCCl_3$ at 25 °C are ca. 1 and 4000 L mol^{-1} s^{-1}, respectively; J. H. Espenson, personal communication.

[32] A. Bury, C. J. Cooksey, T. Funabiki, B. D. Gupta, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1050 (1979).

[33] The fact that **2** neither dimerizes nor disproportionates under the reaction conditions, unlike conventional organic radicals, gives these chain reactions a unique character.

[34] (a) M. Veber, K. N. V. Duong, F. Gaudemer, and A. Gaudemer, *J. Organomet. Chem.*, **177**, 231 (1980); (b) M. Veber, K. N. V. Duong, A. Gaudemer, and M. D. Johnson, *ibid.*, **209**, 393 (1981).

[35] A. Bury, S. T. Corker, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 1*, 645 (1982); A. Bury and M. D. Johnson, *J. Chem. Soc., Chem. Commun.* 498 (1980).

[36] A. E. Crease, B. D. Gupta, M. D. Johnson, E. Bialkowska, K. N. V. Duong, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 1*, 2611 (1979).

[37] M. R. Ashcroft, P. Bougeard, A. Bury, B. D. Gupta, and M. D. Johnson, unpublished work.

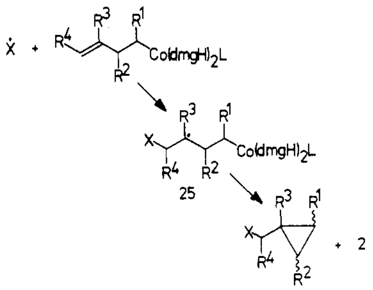
[38] P. Bougeard and M. D. Johnson, *J. Organomet. Chem.*, **206**, 221 (1981).

[39] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949); D. M. Hall, *ibid.*, **32**, 2982 (1967); T. Migita, M. Kosugi, K. Takayama, and Y. Nakawa, *Tetrahedron*, **29**, 51 (1973).

[40] J. Grignon, C. Servens, and M. Peyrere, *J. Organomet. Chem.*, **96**, 225 (1975); M. Kosugi, K. Kurino, K. Takayama, and T. Migita, *ibid.*, **56**, C11 (1973).

[41] M. Kosugi, Y. Shimizu, and T. Migita, *J. Organomet. Chem.*, **129**, C36 (1977).

Scheme III



R^1 =	H	Me	H	H	H	H	CN	CN	CN	CN etc
R^2 =	H	H	Me	H	H	Ph	H	Me	H	H
R^3 =	H	H	H	Me	H	H	H	H	Me	Ph
R^4 =	H	H	H	H	Et	H	H	H	H	H

X = Cl_3C, $ArSO_2$, NCCHBr, etc.

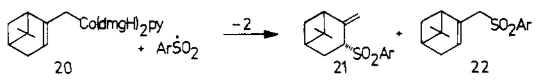
but not sulfoxides, with tributyltin hydride (eq 20 and 21).[42]

$$\dot{Y} + CH_2{=}CHCH_2X \rightarrow YCH_2CH{=}CH_2 + \dot{X} \quad (20)$$

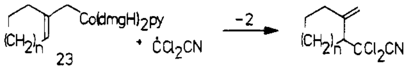
$$Y = Ph, RS, Cl_3C;\ X = Br, Bu_3Sn, RS$$

$$Bu_3\dot{S}n + CH_2{=}CHCHRSO_2Ar \rightarrow Bu_3SnCH_2CH{=}CHR + \dot{S}O_2Ar \quad (21)$$

Exceptions to attack of the allyl ligand at the γ-carbon are rare but have been observed where an allylcobaloxime is sterically hindered. For example, the rather unstable geranylcobaloxime **20** reacts with toluenesulfonyl iodide directly on mixing at ambient temperature to give a mixture of the two sulfones **21** and **22**, the latter being formed by attack on the α-carbon of the allyl ligand.[37] With the less hindered analogue **23** (n = 1 or 2) the *exo*-methylene compound is the main product (eq 23). A further, understandable, exception is the attack at the ϵ-carbon of the sorbylcobaloxime **24** (eq 24).[37]



(22)



(23)

$$Ar\dot{S}O_2 + \underset{\textbf{24}}{MeCH{=}CHCH{=}CHCH_2Co(dmgH)_2py} \rightarrow ArSO_2CHMeCH{=}CHCH{=}CH_2 + 2 \quad (24)$$

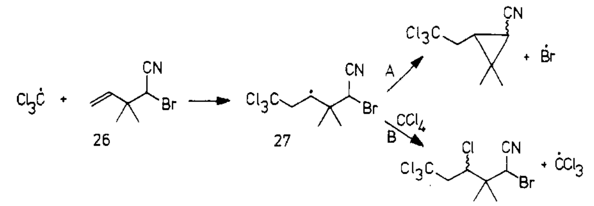
Attack at the γ-carbon of allenyl- and propargylcobaloximes is also common, but the conditions needed are more forcing and the yields are lower. The presence of imidazole as the axial ligand is advantageous, though these complexes are somewhat less soluble in methylene chloride, the solvent most commonly used for these reactions (eq 25 and 26, ref 32 and 34, respectively).

$$Me_2C{=}C{=}CHCo(dmgH)_2imid + \dot{C}Cl_3 \rightarrow Cl_3CCMe_2C{\equiv}CH + Co(dmgH)_2imid \quad (25)$$

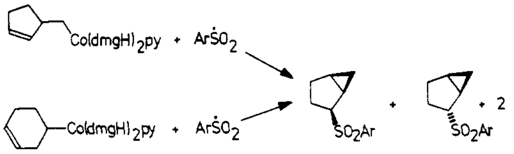
$$PhC{\equiv}CCH_2Co(dmgH)_2py + \dot{C}H(COOEt)_2 \rightarrow (EtOCO)_2CH{-}CPh{=}C{=}CH_2 + 2 \quad (26)$$

In our search for new methods of preparation of synthetic pyrethroid precursors, we also investigated the possibility that cyclopropanes might be prepared by the attack of an organic radical at the terminal unsaturated carbon of a but-3-enyl ligand, followed by an intramolecular homolytic displacement at the α-carbon (Scheme III). The formation of the cyclopropane would thus be the rather special case of an S_H2 at saturated carbon mentioned above.[2] The reaction does indeed occur readily and a wide range of substituted cyclopropyl carbinyl sulfones and (trichloroethyl)cyclopropanes have been synthesized by thermal and photochemical reactions of toluenesulfonyl halides, trichloromethanesulfonyl chloride, and other radical precursors, with a series of substituted but-3-enylcobaloximes.[34b,35,43] It has also been demonstrated that the same type of process can occur with but-3-enyliron complexes.[44]

Scheme IV

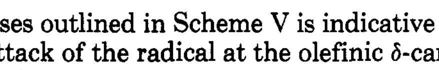


Scheme V



Support for the formation of an intermediate organocobaloxime radical (**25**) comes indirectly from the course of reaction of the but-3-enyl bromide **26** with trichloromethyl radical precursors (Scheme IV). The intermediate **27**, formed by attack of the trichloromethyl radical at the δ-carbon of **26**, undergoes a unimolecular intramolecular displacement of a bromine atom (path A), except when the concentration of the radical precursor is sufficiently high to make the bimolecular halogen abstraction (path B) dominant.[35]

Spiro and fused cyclopropane/cycloalkane systems can also by synthesized by the reaction of appropriate cycloalkenylcobaloximes with free-radical precursors, especially toluenesulfonyl iodide (eq 27 and Scheme V).[37] The formation of two isomers in each of the processes outlined in Scheme V is indicative of the fact that attack of the radical at the olefinic δ-carbon is not stereoselective but can take place either on the opposite side to or on the same side as the departing radical **2**.



(27)

S_H2 Attack at the α-Carbon of Benzyl Ligands

All of the above reactions of allyl and but-3-enyl compounds, except that of the geranylcobaloxime, take place initially by attack of an electrophilic radical at a nucleophilic olefinic carbon. Our attempts to induce an S_H2 displacement at the α-carbon of an alkyl chain under the same conditions were not successful. However, when trichloromethanesulfonyl chloride was used as the radical precursor and the reactions were carried out under tungsten light at 0–10 °C, primary and sec-

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[42] Y. Ueno, S. Aoki, and M. Okawara, *J. Am. Chem. Soc.*, **101**, 5414 (1979); Y. Ueno and M. Okawara, *ibid.*, **101**, 1893 (1979).

[43] M. R. Ashcroft, A. Bury, C. J. Cooksey, A. G. Davies, B. D. Gupta, M. D. Johnson, and H. Morris, *J. Organomet. Chem.*, **195**, 89 (1980).

[44] A. Bury, M. D. Johnson, and M. J. Stewart, *J. Chem. Soc., Chem. Commun.*, 622 (1980).

ondary alkylcobaloximes gave excellent yields of the corresponding alkanesulfonyl chlorides, by the sequence of nonchain processes shown in eq 28–31.[45]

$$\mathrm{RCo(dmgH)_2py} \rightarrow \dot{\mathrm{R}} + \mathbf{2} \qquad (28)$$

$$\dot{\mathrm{R}} + \mathrm{SO_2} \rightarrow \mathrm{R\dot{S}O_2} \qquad (29)$$

$$\mathrm{\dot{R}SO_2} + \mathrm{Cl_3CSO_2Cl} \rightarrow \mathrm{RSO_2Cl} + \mathrm{Cl_3C\dot{S}O_2} \qquad (30)$$

$$\mathrm{Cl_3C\dot{S}O_2} \rightarrow \mathrm{Cl_3\dot{C}} + \mathrm{SO_2} \qquad (31)$$

On the other hand, though some α-toluenesulfonyl chloride is formed, in the reaction of benzylcobaloximes with trichloromethanesulfonyl chloride the major product is the corresponding (trichloroethyl)benzene (eq 32),[46] which is also formed in the reaction with

$$\dot{\mathrm{X}} + \mathrm{ArCH_2Co(dmgH)_2py} \rightarrow \mathrm{ArCH_2X} + \mathbf{2} \qquad (32)$$

$$\mathrm{X} = \mathrm{Cl_3C},\ \mathrm{ArSO_2}$$

bromotrichloromethane at 55–90 °C. Similarly, toluenesulfonyl iodide reacts with benzylcobaloximes to give good yields of the benzyl tolyl sulfone, the key step being the homolytic attack of the sulfonyl radical at the α-carbon of the benzyl ligand.[37] The yield of sulfone or (trichloroethyl)arene is dependent on the nature of substitutents in the benzene ring, being high ($\geq$85%) in the case of methyl substituents but low ($\leq$50%) in the case of nitro substituents. The preponderence of attack at the α-carbon over aromatic carbon is even evident in the case of the (9-anthracenylmethyl)cobaloxime **28**, for which only path A (Scheme VI) can be detected.[37]

Homolytic attack at the benzylic carbon has also been invoked to account for the formation of "crossed" products in the apparent insertion of sulfur dioxide into the carbon–metal bonds of a mixture of benzylcobaloximes and benzylrhodoximes in liquid sulfur dioxide.[47] It was proposed that the reaction of **2**, formed by homolysis of a molecule of benzylcobaloxime, with the solvent gives the novel metallosulfonyl radical **29**, which can then attack the α-carbon of *either* the benzylcobaloxime *or* the benzylrhodoxime to give the apparent insertion product **30** or **31**. In the formation of **31**, it is the rhodoxime(II) radical **32** that is displaced and that can then react further with sulfur dioxide to give the related metallosulfonyl radical **33**, capable of further displacement at the α-carbon of either substrate as in eq 38.[48]

$$\mathrm{ArCH_2Co(dmgH)_2py} \rightarrow \mathrm{Ar\dot{C}H_2} + \mathbf{2} \qquad (33)$$

$$\mathbf{2} + \mathrm{SO_2} \rightarrow \underset{\mathbf{29}}{\mathrm{py(dmgH)_2Co\dot{S}O_2}} \qquad (34)$$

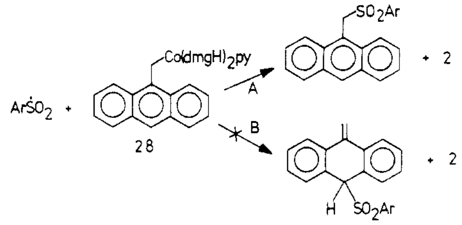
$$\mathrm{py(dmgH)_2Co\dot{S}O_2} + \mathrm{ArCH_2Co(dmgH)_2py} \rightarrow \underset{\mathbf{30}}{\mathrm{py(dmgH)_2CoSO_2CH_2Ar}} + \mathbf{2} \qquad (35)$$

$$\mathrm{py(dmgH)_2Co\dot{S}O_2} + \mathrm{PhCH_2Rh(dmgH)_2py} \rightarrow \underset{\mathbf{31}}{\mathrm{py(dmgH)_2CoSO_2CH_2Ph}} + \underset{\mathbf{32}}{\mathrm{\dot{R}h(dmgH)_2py}} \qquad (36)$$

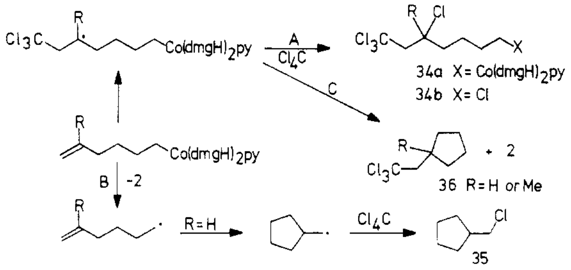
$$\mathbf{32} + \mathrm{SO_2} \rightarrow \underset{\mathbf{33}}{\mathrm{py(dmgH)_2Rh\dot{S}O_2}} \qquad (37)$$

$$\mathbf{33} + \mathrm{ArCH_2Co(dmgH)_2py} \rightarrow \mathrm{py(dmgH)_2RhSO_2CH_2Ar} + \mathbf{2} \qquad (38)$$

Scheme VI



Scheme VII



A most important step forward in the study of the S_H2 reaction has been made by Espenson.[49] He has determined the rate constant for the reaction of the 1-hydroxyisopropyl radical, derived from the thermolysis of the (1-hydroxyisopropyl)pentaaquachromium(III) ion (eq 39), at the α-carbon of both benzylcobaloxime and its conjugate acid in aqueous solution, which gives 2-hydroxy-2-methyl-1-phenylpropane in quantitative yield (eq 40). The values obtained, $k_2 = 7 \times 10^6$ and 1.9×10^7 L mol^{-1} s^{-1}, respectively, show that the carbon–cobalt bond is weakened when one of the dioximato ligands is protonated.

$$\mathrm{Me_2C(OH)Cr(H_2O)_5^{2+}} \rightleftharpoons \mathrm{Me_2\dot{C}OH} + \mathrm{Cr(H_2O)_5^{2+}} \qquad (39)$$

$$\mathrm{Me_2\dot{C}OH} + \mathrm{PhCH_2Co(dmgH)_2aq} \rightarrow \mathrm{Me_2C(OH)CH_2Ph} + \mathbf{2} \qquad (40)$$

S_H2 Attack of Organic Radicals at the α-Carbon of Substituted Alkylcobaloximes

The devil's advocate might say that the benzylic carbon was also a rather special case of saturated carbon. However, displacements at the α-carbon of an alkyl chain can be the dominant process under appropriate conditions if the homolytic displacement is intramolecular and if a five-membered cyclic product is formed.[50] Thus, the thermal and photochemical reactions of hex-5-enylcobaloxime with a large excess of carbon tetrachloride gives mainly the expected pentachloroheptane **34b** through addition to the double bond and subsequent cleavage of the carbon–cobalt bond of **34a** (Scheme VII, path A). The photochemical reaction in the presence of a low concentration of carbon tetrachloride gives mainly the cyclopentylmethyl chloride **35** through homolysis of the carbon–cobalt bond, cyclization of the hexenyl radical, and chlorine atom abstraction (Scheme VII, path B). However, the thermal reaction in the presence of a low concentration of carbon tetrachloride gives a higher yield of (trichloro-

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[45] P. Bougeard, M. D. Johnson, and G. M. Lampman, *J. Chem. Soc., Perkin Trans 1*, 849 (1982).

[46] P. Bougeard, B. D. Gupta, and M. D. Johnson, *J. Organomet. Chem.*, **206**, 211 (1981).

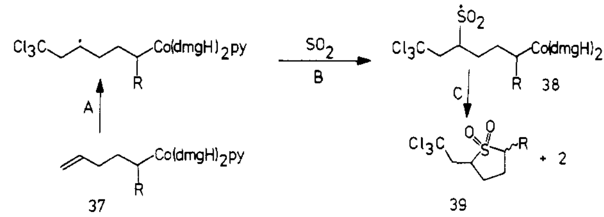
[47] A. E. Crease and M. D. Johnson, *J. Am. Chem. Soc.*, **100**, 8013 (1978).

[48] It is thus possible to accelerate the "insertion" of SO_2 into a primary carbon–cobalt bond by adding a trace of a benzylcobaloxime.

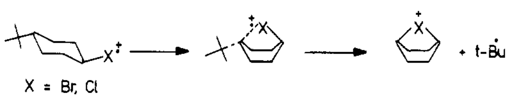
[49] R. C. Hatton, J. H. Espenson, and A. Bakac, *J. Am. Chem. Soc.*, **104**, 3531 (1982).

[50] M. R. Ashcroft, P. Bougeard, A. Bury, C. J. Cooksey, M. D. Johnson, and J. M. Hungerford, *J. Org. Chem.*, submitted for publication.

Scheme VIII



Scheme IX



ethyl)cyclopentane (**36**, R = H) through attack of a trichloromethyl radical at the terminal unsaturated carbon followed by the intramolecular homolytic displacement of **2** by attack of the secondary radical center on the α-carbon (Scheme VII, path C).

Surprisingly, in the corresponding thermal reaction of (5-methylhex-5-enyl)cobaloxime with solvent carbon tetrachloride at 80 °C for 48 h, the *sole* organic product is the (trichloroethyl)cyclopentane **36** (R = Me), formed through the homolytic attack of a *tertiary* carbon radical at the primary α-carbon.

No four-membered cyclic products are formed in the corresponding reactions of pent-4-enylcobaloximes with carbon tetrachloride, but both the thermal and photochemical reactions of a number of substituted pent-4-enylcobaloximes with trichloromethanesulfonyl chloride give good yields of the corresponding (trichloroethyl)sulfolanes **39** (Schene VIII). As in many of the above reactions, the attack of the trichloromethyl radical takes place at the terminal olefinic carbon, and in the presence of sulfur dioxide, derived either from the reagent or added purposely to the solution, a sulfonyl radical (**38**) is then formed that can undergo an intramolecular homolytic attack on the α-carbon to give the observed sulfolane (Scheme VIII). In the thermal reaction of (*R*)-hex-5-en-2-ylcobaloxime (**37**, R = Me) with trichloromethanesulfonyl chloride and sulfur dioxide, the main product is a mixture of *cis*- and *trans*-**39** (R = Me), *each in substantial enantiomeric excess*, the small loss of stereospecificity being ascribable to racemization of the substrate during reaction. The homolytic displacement (C in Scheme VIII) thus takes place with *either* retention *or* inversion of configuration at the α-carbon. An earlier observation[51] that fragmentation of the molecular ions derived from *trans*-4-*tert*-butylcyclohexyl halides occurs through an intramolecular homolytic displacement of an alkyl radical by attack of the halogenium ion radical at carbon (Scheme IX) suggests that the inversion process is preferred. Cyclic and acyclic S_H2 displacements of halogen atoms by halogenium ion radicals in the gas phase have also been detected.[52]

Scheme X

$$\dot{X} + R{-}M \rightleftharpoons X\!:^- + R{-}\dot{M}^+ \xrightarrow{S_N2} X{-}R + \dot{M}$$

Conclusions

The above discussion clearly establishes that the attack of free radicals on carbon ligands is an interesting and useful reaction of some potential in organic synthesis. However, there is one important aspect of the mechanism that is the subject of some contention. Even though it seems well-established from product, stereochemical, kinetic, and thermodynamic studies that the displacement of one paramagnetic metal complex by an identical or near-identical complex does proceed through a concerted homolytic displacement reaction, the displacement of a paramagnetic metal complex by a greatly dissimilar radical, such as a carbon or sulfur-centered radical, may take place by a two-stage process in which an electron transfer is followed by a *heterolytic* displacement (Scheme X). The validity of the label S_H2 for some of these reactions will thus remain in doubt until further detailed studies of the redox characteristics of the radicals and substrates have been determined, accurate kinetic studies have been carried out, and a careful search has been made for intermediates. An extension of the detailed work[49] on nonchain processes would thus be invaluable. Three aspects of the scope of the reaction merit further examination. (a) What other ligands, especially heteroatom containing ligands isoelectronic with allyl, allenyl, pentenyl etc., are susceptible to attack by radicals? Preliminary work suggests that isothiocyanato ligands may provide a route to organic thiocyanates.[37] (b) While organocobaloximes are useful substrates, the equatorial dioximato ligands themselves are a little too susceptible to attack by radical reagents. It would be useful to survey the influence of different, especially inert, equatorial ligands on the character of the displacement reaction. (c) The number of radicals that have so far been shown to be effective has been limited, in part as outlined in b above. However, it seems likely, from a comparison with mass spectrometric studies, that other radicals, particularly cation radicals, may also be effective in promoting displacement reactions at saturated carbon.

I am most grateful to my many frineds who have discussed much of the above work with me over the last few years and to my many students, research assistants and colleagues mentioned by name in the references, without whose efforts this subject would barely have existed.

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[51] M. M. Green, R. J. Giguere, and J. R. P. Nicholson, *J. Am. Chem. Soc.*, **100**, 8010 (1978).

[52] R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 5964 (1977).