Reaction of 1b with 2a in Benzene under CO. Replacement of the N_2 atmosphere by CO resulted in enhancement of the rate of reaction between **1b** and **2a** (i.e., beyond that corresponding to reaction 14) as reflected in the *additional* term in the rate law corresponding to eq 18 where $k_{19}(75\ ^\circ\mathrm{C}) = 5.8 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$.

$$-\mathrm{d}[\mathbf{1b}]/\mathrm{d}t = (k_{11} + k_{19}[\mathrm{CO}])[\mathbf{1b}] \qquad (18)$$

$$\mathbf{1b} + \mathrm{CO} \xrightarrow{k_{19}} \underset{\mathbf{5b}}{[p\text{-}\mathrm{CH_3OC_6H_4CH_2C({=}O)Mn(CO)_4P}]} \xrightarrow{\mathbf{2a}} \underset{\mathbf{7}}{p\text{-}\mathrm{CH_3OC_6H_4CH_2CHO}} \qquad (19)$$

$$\mathbf{5b} \rightarrow \cdot\mathrm{Mn(CO)_4P} + \underset{\mathbf{6}}{p\text{-}\mathrm{CH_3OC_6H_4CH_2C({=}O)}\cdot} \underset{k_{20}}{\xrightarrow{\mathbf{2a}}} \underset{\mathbf{7}}{p\text{-}\mathrm{CH_3OC_6H_4CH_2CHO}} \qquad (20)$$

This additional contribution to the rate was reflected in the formation of a different product, namely, the aldehyde p-$\mathrm{CH_3OC_6H_4CH_2CHO}$, presumably by the reaction sequence of eq 19. Consistent with this interpretation, the product distribution was found to obey the relation $[p\text{-}\mathrm{CH_3OC_6H_4CH_2CHO}]/[p\text{-}\mathrm{CH_3OC_6H_4CH_3}] = k_{19}[\mathrm{CO}]/k_{11}$, the aldehyde fraction increasing from 0 to 46% when the CO partial pressure was increased from 0 to 1 atm. Since the intermediate **5b** in reaction 19 hardly can contain a vacant coordination site, direct reaction with **2a** seems unlikely, and the free radical mechanism corresponding to eq 20 (i.e., analogous to that of eq 11–13) is favored.[20] This suggests that the Mn—C(=O)R bond dissociation energy is relatively low, probably not exceeding 25 kcal/mol. Attempts to establish this directly by experiments on acylmanganese carbonyl complexes are in progress. Reaction 20 may be considered another[3] model of the aldehyde-forming step in cobalt-carbonyl-catalyzed hydroformylation.[1]

Four distinct pathways, corresponding to the schemes of eq 3 and 4; 7 and 8; 11–13; and 19, respectively, have been identified for binuclear reductive elimination reactions of benzylmanganese carbonyls with hydridomanganese carbonyls. Relatively modest changes in ligands, solvent, or CO concentration may result in essentially complete crossover from one pathway to another. This underlines the danger of assuming the mechanism of such binuclear reductive elimination reactions, the occurrence of which is widespread, without appropriate diagnostic evidence, or of extrapolating from one system or set of conditions to another. While some of the factors influencing the choice of pathway in such reactions have been identified, further elucidation of these factors clearly is called for and our studies designed to achieve this are continuing.

Finally, it is of interest to compare the behavior of these systems with others that have been investigated. The reaction of $\mathrm{HMo(CO)_3Cp}$ with $\mathrm{CH_3Mo(CO)_3Cp}$ to form $\mathrm{CH_3CHO}$ has been shown to follow a pathway analogous to that of eq 7 and 8, while the corresponding reaction with $\mathrm{C_6H_5CH_2Mo(CO)_3Cp}$ appears to proceed, in part, through a free radical pathway analogous to eq 11–13, yielding toluene.[9] On the other hand, the *binuclear* reaction of *cis*-$\mathrm{OsH(CH_3)(CO)_4}$ to form $\mathrm{CH_4}$ appears to proceed through a variant of the mechanistic scheme of eq 7 and 8 in which migratory insertion of CO into the Os–$\mathrm{CH_3}$ bond is followed (for reasons that are puzzling) by reductive elimination of alkane rather than of aldehyde.[2] The mechanism encompassed by eq 3 and 4 finds a parallel in that proposed for the binuclear reductive elimination of H_2 from *cis*-$\mathrm{Os(CO)_4H_2}$.[22]

Acknowledgment. Pertinent preliminary studies on these and related systems were performed in this laboratory by R. L. Sweany (who first identified reaction 1) and M. J. Russell. Support through grants from the National Science Foundation and the National Institutes of Health is gratefully acknowledged. R.S. thanks the Montedison Donegani Institute for a leave of absence.

Registry No. 1a, 80105-78-8; **1b**, 80105-79-9; **1c**, 14049-86-6; **2a**, 16972-33-1; **2b**, 80105-80-2.

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[20] The formation of aldehyde **7** according to route 20 requires that the hydrogen abstraction step, $\mathbf{6} + \mathbf{2a} \xrightarrow{k_{20}} \mathbf{7} + \mathrm{Mn(CO)_5}$, be fast compared with the decarbonylation of **6**, i.e., $\mathbf{6} \rightarrow p\text{-}\mathrm{CH_3OC_6H_4CH_2}\cdot + \mathrm{CO}$. The rate constant of the corresponding decarbonylation of $\mathrm{C_6H_5CH_2(CO)}\cdot$ to $\mathrm{C_6H_5CH_2}\cdot + \mathrm{CO}$ has been estimated to be ca. $5 \times 10^7\ \mathrm{s^{-1}}$ at room temperature.[21] A similar decarbonylation rate constant for **6** would require that $k_{20} > 5 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$. This is significantly higher than our estimate[16] of ca. $10^6\ \mathrm{M^{-1}\ s^{-1}}$ for k_{12} but is not considered incompatible with the latter since $\mathrm{HMn(CO)_5}$ is expected to be a much better H donor than $\mathrm{HMn(CO)_4P}$.

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Ligand Effects on Transition-Metal-Alkyl Bond Dissociation Energies

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The importance of transition-metal–alkyl bond dissociation energies in various organometallic, biochemical, and catalytic contexts has been widely recognized.[1] Notwithstanding this, few such bond energies have been determined reliably,[2] and the factors that influence the strengths of such bonds and the stabilities of transition-metal–alkyl compounds still are unclear and controversial.[3] We report here the first systematic determinations of the influence of ligand variation on transition-metal–carbon bond dissociation energies. Our results, which relate to a series of organocobalt compounds, are of particular interest in view of the relevance of such compounds as vitamin $\mathrm{B_{12}}$ coenzyme models and of the role widely accorded to cobalt–carbon bond homolysis in coenzyme $\mathrm{B_{12}}$-promoted reactions.[4-6] Our results also bear on the mechanism of olefin elimination from organocobalt compounds for which alternative interpretations have been advanced.[7,8]

Our studies involve determination of the cobalt–carbon bond dissociation energies, using a procedure that we previously described,[9] of a series of (α-phenylethyl)cobalt compounds, $[\mathrm{L(DH)_2Co\text{-}CH(CH_3)C_6H_5}]$ (where $\mathrm{DH_2}$ = dimethylglyoxime and L is an axial ligand such as pyridine, a 4-substituted pyridine, or imidazole). This involves determination of the equilibrium constant (K_1) and enthalpy (ΔH_1°) of the reversible reaction corresponding to reaction 1. In combination with available data for

$$[\mathrm{L(DH)_2Co^{III}CH(CH_3)C_6H_5}] \rightleftarrows [\mathrm{L(DH)_2Co^{II}}] + \mathrm{C_6H_5CH{=}CH_2} + {}^1/{}_2\mathrm{H_2}\ (\Delta H_1^\circ) \qquad (1)$$

$$\mathrm{C_6H_5CH{=}CH_2} + {}^1/{}_2\mathrm{H_2} \rightleftarrows \mathrm{C_6H_5\dot{C}HCH_3}\ (\Delta \mathrm{H}_2^\circ) \qquad (2)$$

$$[\mathrm{L(DH)_2Co^{III}CH(CH_3)C_6H_5}] \rightleftarrows [\mathrm{L(DH)_2Co^{II}}] + \mathrm{C_6H_5\dot{C}HCH_3}\ (\Delta H_3^\circ \sim D_{\mathrm{Co-R}}) \qquad (3)$$

the heats of formation of $\mathrm{C_6H_5CH{=}CH_2}$ (ΔH_f° = 35.2 kcal/mol)[10] and the $\mathrm{C_6H_5\dot{C}HCH_3}$ radical (ΔH_f° = 33 kcal/mol)[11] (yielding $\Delta H_2^\circ = -2.2$ kcal/mol for reaction 2), the cobalt–carbon

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Table I. Summary of Equilibrium and Kinetic Data[a]

L	10^6K_1 (25 °C), $M^{3/2}$	$\Delta H°_1$, kcal/mol	$\Delta S°_1$, kcal/mol·K	D_{Co-R}, cal/mol	10^4k_1 (25 °C), s^{-1}	$\Delta H^{\ddagger}_1$, kcal/mol	$\Delta S^{\ddagger}_1$, cal/mol·K
4-aminopyridine	5.5	23.4	54.3	21.2	4.0	23.1	3.8
4-methylpyridine	13.6	22.3	52.5	20.1	6.0	21.8	0.9
pyridine	19.5	21.7	52.1	19.5	7.3	21.6	−0.2
pyridine[b]	13.6[b]	22.1[b]	51.9[b]	19.9	7.8[b]	21.2[b]	−1.4[b]
4-cyanopyridine	47.2	20.1	47.5	17.9	13.1	20.1	−3.9
imidazole	4.0	23.0	52.5	20.8	1.7	23.0	1.9

[a] Typical experimental errors: $\Delta H°_1$, $\Delta H^{\ddagger}_1$, ±0.5 kcal/mol; $\Delta S°_1$, $\Delta S^{\ddagger}_1$, ±1.5 cal/mol·deg. [b] In toluene; all other measurements in acetone.

bond dissociation energy can readily be deduced from the following thermochemical cycle which yields $D_{Co-R} \sim \Delta H_3° = \Delta H_1° + \Delta H_2°$.[12]

Measurements of K_1 (defined by eq 4) were made, as previously

$$K_1 = \frac{[L(DH)_2Co^{II}][C_6H_5CH{=}CH_2][H_2]^{1/2}}{[L(DH)_2Co^{III}CH(CH_3)C_6H_5]} \quad (4)$$

described,[9] in acetone (and, in one case, also toluene) solution and typically encompassed the concentration ranges $3 \times 10^{-5} - 1.5 \times 10^{-4}$ M [LCo(DH)$_2$CH(CH$_3$)C$_6$H$_5$], [L(DH)$_2$Co^{II}], and $C_6H_5CH{=}CH_2$ and ca. 4×10^{-3} M (1 atm) H_2 (varied in one case from 0.3–1 atm). Values of $\Delta H_1°$ and $\Delta S_1°$ were determined from the temperature dependence of K_1, measured over a temperature interval of at least 20 °C in the range 10 – 37 °C. Measurements of the kinetics of reaction 1 under similar conditions, performed spectrophotometrically as described earlier,[9] yielded values of k_1 (defined by $-d \ln [L(DH)_2CoCH(CH_3)C_6H_5]/dt = k_1$), $\Delta H^{\ddagger}_1$, and $\Delta S^{\ddagger}_1$. The results of the equilibrium and kinetic measurements are summarized in Table I. Neither the equilibrium nor kinetic parameters appeared to be sensitive to solvent variation, as revealed by the comparisons of acetone and toluene in Table I for L = pyridine.

The values of D_{Co-R} in Table I range from 17.9 to 21.2 kcal/mol. For the series of ligands examined the cobalt–carbon bond dissociation energy increases systematically with basicity of the ligand L, as depicted in Figure 1. While this contrasts with the commonly observed trans-labilizing influence of strongly electron-donating ligands such as H^- or CH_3^- in substitution reactions proceeding by *heterolytic* ligand dissociation,[13,14] such a trend is consistent with the decrease in the oxidation state of cobalt from +3 to +2 that accompanies *homolytic* dissociation of the Co–C bond according to reaction 3. By favoring the higher oxidation state, more basic ligands should accordingly stabilize the organocobalt compound and reduce the driving force for Co–C bond homolysis (reaction 3). Analogous reasoning has previously been invoked to explain the *increase* in reactivity for oxidative addition of organic halides to [L(DH)$_2$Co^{II}] complexes with increasing basicity of L.[15]

While our determinations of the cobalt–carbon bond dissociation energies rest wholly on thermodynamic considerations and are independent of the mechanism of reaction (1) our results do provide some insights into the latter. From Table I and Figure 1 it is apparent that the trend of activation enthalpies ($\Delta H_1^{\ddagger}$) for reaction 1 closely parallels the corresponding trend of Co–R bond dissociation energies. This is consistent with, and strongly supportive of, the mechanism depicted by reaction 5 according to

$$\begin{gathered}[L(DH)_2CoCH(CH_3)C_6H_5] \rightleftarrows \\ [L(DH)_2Co^{II}] + CH_3\dot{C}HC_6H_5 \rightarrow [L(DH)_2CoH] + \\ C_6H_5CH{=}CH_2 \rightarrow [L(DH)_2Co^{II}] + {}^1/{}_2H_2 + C_6H_5CH{=}CH_2 \end{gathered} \quad (5)$$

which reaction 1 proceeds through homolysis of the Co–C bond

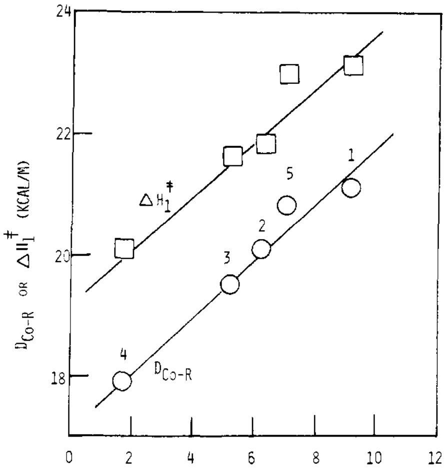

Figure 1. Dependence of D_{Co-R} and $\Delta H_1^{\ddagger}$ on the bascity (pK_a) of L. L = (1) 4-aminopyridine; (2) 4-methylpyridine; (3) pyridine; (4) 4-cyanopyridine; (5) imidazole.

followed by rapid β-hydrogen abstraction and decomposition of the resulting cobalt hydride, the latter two processes having previously been demonstrated to be rapid in closely related systems.[1,16] Indeed, it is probable that the β-hydrogen abstraction occurs within the solvent cage of the geminate $\overline{[L(DH)_2Co^{II}],\cdot CH(CH_3)C_6H_5}$ radical pair.[17] Since recombination of Co^{II} complexes with organic radicals has been demonstrated to be diffusion controlled,[1,18] and hence expected to exhibit an activation enthalpy of ca. 2 kcal/mol, this interpretation predicts that $\Delta H_1^{\ddagger}$ should consistently be about 2 kcal/mol greater than D_{Co-R}. The results in Table I and Figure 1 are in excellent accord with this. Since reaction 1 proceeds with rates close to those predicted for the pathway depicted by reaction 5, there would appear to be little, if any, contribution from a concerted[7,8] olefin elimination pathway. Indeed, such a pathway for 18-electron cobalt(III) complexes should be disfavored on orbital symmetry grounds.

The trends depicted in Table I and Figure 1 presumably reflect primarily electronic effects since the ligands involved in the comparison are sterically similar. We are currently extending these studies to other axial ligands, L, to examine the influence of steric, as well as additional electronic, parameters. Preliminary results indicate that bulky axial ligands, such as 2-substituted pyridines and bulky tertiary phosphines,[19] weaken the Co–C bond and promote decomposition according to reaction 1. This is consistent with the lengthening of the Co–C bond by bulky trans-axial ligands revealed by structural studies on related organocobalt compounds.[20]

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(12) The applicability of this method appears to be limited to secondary or tertiary alkyl cobalt compounds and, as previously noted,[9] to compounds for which reaction 1 attains equilibrium at relatively low temperatures in view of a slow competing irreversible reduction of [LCo^{II}(DH)$_2$].

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(19) Preliminary results on a series of [LCo(DH)$_2$CH(CH$_3$)C$_6$H$_5$] complexes, where L is a tertiary phosphine, reveal a large systematic increase in k_1 with the cone angle of the phosphine, from 1.0×10^{-4} s^{-1} at 25 °C for L = dimethylphenylphosphine (cone angle 122°) to ca. 0.5 s^{-1} for L = tricyclohexylphosphine (cone angle 170°).

(20) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7372 and earlier work cited therein.

Dimethylglyoxime and related compounds of cobalt have been invoked widely as vitamin B_{12} analogues.[6,21] The relatively low Co–C bond dissociation energies identified in these studies are consistent with and supportive of the proposed role of Co–C bond homolysis in coenzyme B_{12} promoted reactions.[4-6] Our results also serve to identify some of the factors that influence Co–C bond dissociation energies in such compounds and which may, thus, be involved in promoting the Co–C bond homolysis step.

Acknowledgment. Support of this research through grants from the National Institutes of Health (AM 13339), the National Science Foundation (CHE 78-01192), and the Natural Sciences and Engineering Research Council Canada (A 6069) is gratefully acknowledged.

Registry No. $py(DH)_2Co\text{-}CH(CH_3)C_6H_5$, 37824-58-1; $4\text{-}NH_2\text{-}py(DH)_2Co\text{-}CH(CH_3)C_6H_5$, 80227-63-0; $4\text{-}CH_3\text{-}py(DH)_2Co\text{-}CH(CH_3)C_6H_5$, 80227-64-1; $4\text{-}CN\text{-}py(DH)_2Co\text{-}CH(CH_3)C_6H_5$, 80227-65-2; $Im(DH)_2Co\text{-}CH(CH_3)C_6H_5$, 80227-66-3.

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Kinetic Determination of Transition-Metal–Alkyl Bond Dissociation Energies: Application to Organocobalt Compounds Related to B_{12} Coenzymes

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Despite their widespread significance for various organometallic, biochemical, and catalytic processes,[1] few transition-metal–alkyl bond dissociation energies have been determined reliably, reflecting in considerable degree the limited applicability of the methods available for such determinations.[2,3] The studies described in this communication reveal conclusively that the thermal decomposition of certain organocobalt compounds proceeds via homolytic cobalt–carbon bond dissociation and demonstrate that the dissociation energies of such bonds can be deduced from kinetic measurements. Interest in the results of these studies is enhanced by the relevance of these organocobalt compounds as coenzyme B_{12} analogues[4,5] and by the further potential of the method for the determination of other transition-metal–alkyl bond dissociation energies.

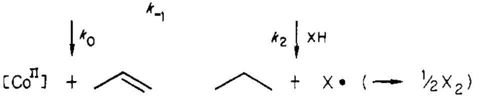
Our studies relate to the thermal decompositions of organocobalt Schiff base compounds [py(saloph)Co–R] (where py = pyridine, saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamine and R = alkyl or benzyl), which were found to proceed at conveniently measurable rates in pyridine solution[6] at temperatures below 100 °C in the presence of an efficient radical trap such as the hydrogen donor, $n\text{-}C_8H_{17}SH$ (abbreviated XH). When R = *n*-propyl or isopropyl (i.e., an alkyl containing a β hydrogen), the reaction yielded a mixture of propene and propane, exhibiting the kinetics and product distribution corresponding to Scheme I where $[Co^{III}R]$ = $[py(saloph)Co\text{–}C_3H_7]$ and $[Co^{II}]$ = $[py(saloph)Co^{II}]$.[7,8]

Table I. Product Distribution from the Decomposition of $[py(saloph)Co\text{–}CH(CH_3)_2]$ at 62.7 °C in Pyridine Solution Containing 1.3×10^{-3} M $[Co^{II}]$

$10^3[n\text{-}C_8H_{17}SH]$, M	10^3k_{obsd}, s^{-1}	$(C_3H_6)_{calcd}$,[a] %	$(C_3H_6)_{obsd}$, %
0	1.4	72	71
1.9	3.3	30	27
3.8	5.0	20	17
5.8	6.5	15	12
9.6	9.6	10	8

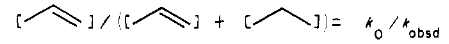
[a] Percent $(C_3H_6)_{calcd} = (100k_0/k_{obsd})$ where $k_0 = 1.00 \times 10^{-3}$ s^{-1}.

Scheme I



According to Scheme I, the kinetics of the reaction should conform to eq 1 and the product distribution to eq 2. Kinetic measurements,[10] typically encompassing the initial concentration ranges ca. 5×10^{-4} M CoR, $0\text{–}2 \times 10^{-3}$ M Co^{II}, and $0\text{–}2 \times 10^{-2}$ M $n\text{-}C_8H_{17}SH$, yielded excellent linear plots (Figure 1) of $(k_{RAD})^{-1}$ vs. $[Co^{II}]$ and $(k_{RAD})^{-1}$ vs. $[C_8H_{17}SH]^{-1}$, in accord with eq 3, which is derived by rearrangement of eq 1 (k_{RAD} corresponding to the contribution to the overall rate constant of the free radical path initiated by the Co–R bond homolysis step, i.e., k_1).

$$\frac{-\mathrm{d}\ln\,[Co^{III}R]}{\mathrm{d}t} = k_{obsd} = k_0 + \frac{k_1k_2[XH]}{k_{-1}[Co^{II}] + k_2[XH]} \tag{1}$$



(2)

$$(k_{obsd} - k_0)^{-1} = (k_{RAD})^{-1} = (1/k_1) + [k_{-1}[Co^{II}]/(k_1k_2[XH])] \tag{3}$$

Values of k_0 were determined by extrapolation of k_{obsd} to limiting high Co^{II} (and low XH) concentrations, and values of k_1 and k_{-1}/k_2 were deduced from the intercepts and slopes of plots exemplified by those in Figure 1. Table I records the excellent agreement that was obtained between the observed product distribution and that calculated from the rate data according to eq 2. For R = neopentyl or benzyl (i.e., lacking a β hydrogen), the olefin-producing path was absent; accordingly, the organic products were exclusively neopentane and toluene, respectively, and the kinetics conformed to eq 1 and 3, with $k_0 = 0$. The results of the kinetic measurements are summarized in Table II which also lists activation parameters derived from the temperature dependence, measured at three to five temperatures over a 10–20 °C interval (43–63 °C for R = isopropyl; 77–97 °C for *n*-propyl; 54–69 °C for neopentyl; 55–65 °C for benzyl).[10]

The kinetic behavior and product distribution clearly establish the validity of Scheme I and define the kinetics of the cobalt–carbon bond homolysis step corresponding to k_1. The mechanism of the olefin-elimination step corresponding to k_0 is less clear. While a "concerted"[9,11] elimination cannot be ruled out, a more likely pathway appears to be that depicted by eq 4, i.e., β-hydrogen

$$[Co^{III}\text{–}C_3H_7] \rightarrow \overline{[Co^{II}],C_3H_7\cdot} \rightarrow C_3H_6 + [CoH] \rightarrow C_3H_6 + [Co^{II}] + {}^1/_2H_2 \tag{4}$$

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[1] Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171 and references therein.

[2] Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71 and references therein.

[3] Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124.

[4] Halpern, J. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 2 and references therein.

[5] Halpern, J. In "Vitamin B_{12}"; Dolphin, D., Ed.; Wiley: New York, in press.

[6] Pyridine was used as solvent to eliminate complications due to possible dissociation of the axially coordinated pyridine ligand.

[7] Qualitatively similar results were obtained for organocobalt complexes of other Schiff bases including *N,N'*-bis(salicylidene)ethylenediamine (salen) and bis(acetylacetone)ethylenediamine (bae) and using other radical traps including 1,4-cyclohexadiene, R_3SnH, and copper(II).

[8] Our *demonstration* that $[py(saloph)Co\text{–}CH(CH_3)_2]$ decomposes predominantly via homolytic Co–C bond cleavage contrasts with the assertion[9] that isopropylcobalamin decomposes by a concerted olefin elimination path.

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[10] The kinetics were monitored spectrophotometrically, following the disappearance of [CoR], at ca. 650 nm. The quantitative conversion of CoR to Co^{II} was confirmed spectrophotometrically. The organic products, i.e., propene, propane, neopentane, toluene, and $(n\text{-}C_8H_{17}S)_2$ were determined by VPC and found to conform to the reported stoichiometry. Except where otherwise noted, the precision of the measured kinetic parameters is estimated to be rate constants, ±5%; $\Delta H^{\ddagger}$, ±1kcal/mol; $\Delta S^{\ddagger}$, ±3 cal/mol·K.

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