

I wish to thank the National Institutes of Health Grant GM 069120 for support.

## Appendix

Aspects of controversy concerning the mechanism include (a) the essential requirement of two tyrosine residues in catalysis,<sup>55</sup> (b) different sites for peptide and ester hydrolysis,<sup>55-58</sup> (c) the conclusion that during the catalytic process Tyr-248 moves away from Zn to which it is initially bound,<sup>59</sup> and (d) comments<sup>59-62</sup> on the mechanisms of the X-ray study on relatively active crystals ( $1/3$  of solution activity,<sup>63</sup> reduced by loss of substrate activation<sup>37</sup>) on the basis of experiments<sup>59-62</sup> on relatively inactive crystals ( $1/300$  of that in solution<sup>64,65</sup>) that have different unit cell dimensions.<sup>63</sup>

(55) J. F. Riordan, M. Sokolovsky, and B. L. Vallee, *Biochemistry*, **6**, 3609-3617 (1967).

(56) B. L. Vallee, J. F. Riordan, J. L. Bethune, T. L. Coombs, D. S. Auld, and M. Sokolovsky, *Biochemistry*, **7**, 3547-3556 (1968).

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(63) F. A. Quiocho, C. H. McMurray, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2850-2859 (1972).

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Only side chains of Tyr-248 and Glu-270 can approach atoms of the substrate's scissile peptide (or ester) bond. The conformational changes proposed<sup>66</sup> for Tyr-198 have not been observed in any X-ray diffraction study. While Tyr-198 lies in the extended binding region, it is not near enough to the scissile bond to participate in the catalytic steps.

The binding of an ester analogue (Figure 3) is like that of the peptide (Figure 2) in the region of the active site, and thus offers no support to the proposal of different cleavage sites for esters and peptides.

Crystals that have been grown at pH values of 7.5, 8.0, 8.5, and 9.0 show no binding of Tyr-248 to Zn.<sup>67</sup> Although a few percent would not be detected, the probable value is zero in the unmodified enzyme. The binding of Tyr-248 to Zn in the arsanilazo-Tyr-248 derivative is most probably due to the additional interactions supplied by the arsanilazo group.

Aside from the movements which occur when substrates bind (Figure 5), the structure of the enzyme is the same in several different crystallographic environments in crystals containing about 45% of water. It is therefore likely that the molecular conformations in these crystals are similar to those available in solution on the time scale of rapidly cleaved substrates.

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# Determination and Significance of Transition-Metal-Alkyl Bond Dissociation Energies

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Transition-metal-alkyl bond dissociation energies are of importance in the context of a variety of organometallic, biochemical, and catalytic systems. One such context relates to the stabilities of transition-metal alkyl compounds. Until fairly recently such compounds were relatively rare, giving rise to speculation about the thermodynamic and/or kinetic instability of transition-metal-carbon  $\sigma$  bonds and about the possible origin of such instability.<sup>1-4</sup> It is now apparent that many transition metal alkyl compounds, both binary (homoleptic), i.e., of the type  $MR_n$  (where R is an alkyl group), and complex, i.e., of the type  $L_xMR_n$  (where L is a

ligand such as CO,  $CN^-$ ,  $PR_3$ , etc.), are sufficiently stable to resist decomposition below 100 °C.<sup>4-7</sup> Furthermore, when decomposition does occur, routes other than metal-carbon bond homolysis often intervene, for example, olefin elimination (with  $\beta$ -hydrogen transfer to the metal), reductive elimination, etc.<sup>4-8</sup> The metal-alkyl bond dissociation energies in such cases clearly must exceed ca. 20 kcal/mol but could still lie in a relatively low range.

One context in which transition-metal-alkyl homolytic bond dissociation has been invoked is that of coenzyme  $B_{12}$  promoted enzymatic rearrangements.<sup>9,10</sup>

(1) H. H. Jaffe and G. O. Doak, *J. Chem. Phys.*, **21**, 196 (1953).

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

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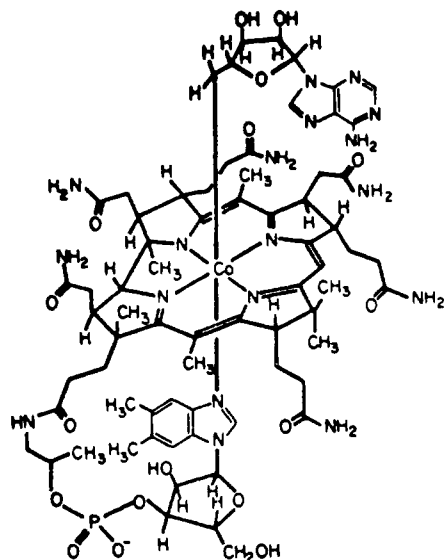
(5) G. Wilkinson, *Science (Washington, D.C.)*, **185**, 109 (1974).

(6) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976).

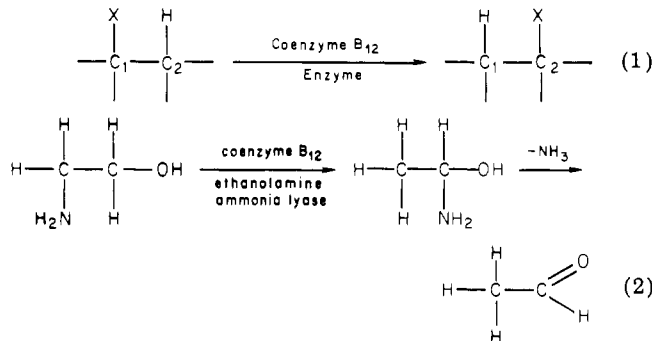
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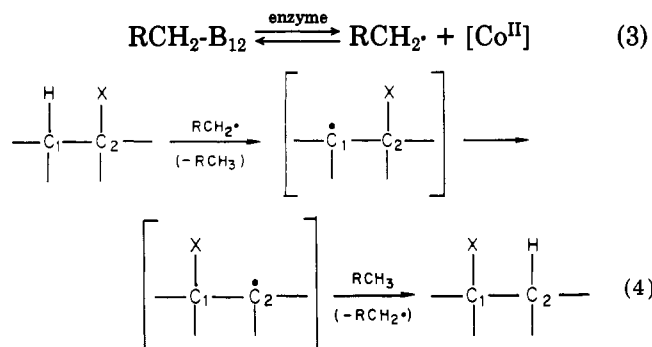
Figure 1. Coenzyme B<sub>12</sub>.

Coenzyme B<sub>12</sub> (5'-deoxyadenosylcobalamin, abbreviated RCH<sub>2</sub>-B<sub>12</sub>), whose structure is depicted in Figure 1, is a cofactor in a variety of enzymatic reactions, a common feature of which is the 1,2 interchange of a H atom and another substituent (OH, NH<sub>2</sub>, etc.) on adjacent carbon atoms (eq 1). A specific example of such a reaction is



the deamination of ethanolamine, catalyzed by ethanolamine ammonia lyase according to eq 2.

A widely accepted mechanism of such coenzyme B<sub>12</sub> dependent rearrangements is depicted by eq 3 and 4.<sup>9,10</sup>



According to this mechanistic interpretation a principal role of the coenzyme is to undergo enzyme-induced cobalt-carbon bond homolysis (eq 3), thereby generating cob(II)alamin (abbreviated [Co<sup>II</sup>]) and a 5'-deoxyadenosyl radical (abbreviated RCH<sub>2</sub>·) which triggers the rearrangement of the substrate by ab-

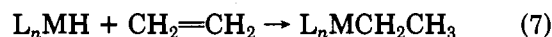
(9) B. M. Babior, *Acc. Chem. Res.*, **8**, 376 (1975).(10) R. H. Abeles and D. Dolphin, *Acc. Chem. Res.*, **9**, 114 (1976).

Table I  
Enthalpies (kcal/mol) of Decomposition of  
Some Organometallic Compounds According to Eq 8

M(CH <sub>3</sub> ) <sub>n</sub>	[D <sub>M-CH<sub>3</sub></sub> ] <sub>mean</sub>	ΔH <sub>g</sub> <sup>o</sup>	ΔH <sub>s</sub> <sup>o</sup>
C(CH <sub>3</sub> ) <sub>4</sub>	85	+170	0
Hg(CH <sub>3</sub> ) <sub>2</sub>	30	-28	-42
Pb(CH <sub>3</sub> ) <sub>4</sub>	35	-30	-77
W(CH <sub>3</sub> ) <sub>6</sub>	38	-27	-229

stracting a H atom from the latter (eq 4). Since these reactions occur under very mild conditions, such a role implies a very weak cobalt-alkyl bond.<sup>11-13</sup>

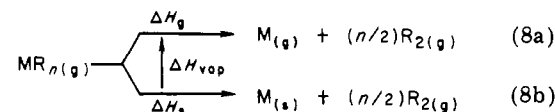
A knowledge of transition-metal-alkyl (and -acyl) bond dissociation energies clearly also is important for an understanding of the thermodynamics of a variety of organometallic processes, including many of importance in catalytic systems,<sup>14,15</sup> such as oxidative addition (eq 5),<sup>16</sup> insertion reactions (eq 6 and 7),<sup>17,18</sup> etc.



Notwithstanding this obviously widespread importance of transition-metal-alkyl bond dissociation energies, few such energies have been determined reliably until recently, reflecting the absence of general methods for their determination. This Account describes some of our recent studies directed at developing such methods and discusses the results obtained through their application.

### Thermodynamic Stabilities of Binary Metal-Alkyl Compounds (MR<sub>n</sub>)

Whereas the evaluation of single metal-alkyl (M-R) bond dissociation energies has, at least until recently, often presented serious difficulties, *mean* M-R bond energies of binary (homoleptic)<sup>6</sup> compounds of the formula MR<sub>n</sub> are readily deduced from their heats of formation.<sup>19,20</sup> This permits the estimation of the "intrinsic" thermodynamic stabilities of such compounds with respect to the reductive elimination of R<sub>2</sub> either in the gas phase to form free M atoms (eq 8a) or on a metal surface to form solid M (eq 8b). The en-



thalpies of the two processes, (ΔH<sub>g</sub> and ΔH<sub>s</sub>, respectively) differ by the enthalpy of atomization of the metal (ΔH<sub>vap</sub>).

Table I summarizes some data pertaining to such decomposition processes. Typical mean metal-alkyl bond energies in such compounds are fairly low, commonly in the range 30-40 kcal/mol. A striking con-

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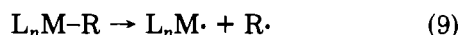
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clusion is that, whereas saturated hydrocarbons are *intrinsically* thermodynamically stable with respect to such decomposition, many organometallic compounds are not. Remarkably, even such familiar and readily handled compounds as lead tetraalkyls are highly unstable thermodynamically (not only with respect to metal deposition but also with respect to decomposition in the gas phase to form Pb atoms) and owe their apparent stabilities to kinetic factors.

It should be noted that there may be considerable discrepancies between such *mean* bond energies and the corresponding individual bond dissociation energies. Thus, for  $\text{Hg}(\text{CH}_3)_2$  (mean  $\text{Hg}-\text{CH}_3$  bond energy = 30 kcal/mol),  $D_{\text{CH}_3\text{Hg}-\text{CH}_3} = 51$  kcal/mol and  $D_{\text{Hg}-\text{CH}_3} = 9$  kcal/mol.<sup>19</sup>

### Approaches to the Determination of Metal-Alkyl Bond Dissociation Energies

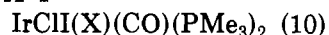
The metal-alkyl bond dissociation energy ( $D_{\text{L}_n\text{M}-\text{R}}$ ) of a compound  $\text{L}_n\text{M}-\text{R}$  corresponds to the endothermicity of the process



In the past, the determination of such bond dissociation energies has not been a straightforward process, and reliable general methods have not been available. Some of the approaches that have been invoked for such determinations, with varying degrees of reliability and generality, are discussed below.

(1) **Thermochemical.** This is, *in principle*, the most direct approach to the determination of bond dissociation energies. The enthalpy of a process such as eq 9 may be evaluated from the enthalpies of formation of  $\text{L}_n\text{M}-\text{R}$ ,  $\text{R}\cdot$ , and  $\text{L}_n\text{M}\cdot$ . The frequent inaccessibility of the latter to measurement constitutes one of the limitations of this approach. Another limitation relates to the fact that the bond dissociation energy, deduced in this way, is obtained as a relatively small difference between large numbers; therefore, the precision of the method, at this stage at least, is somewhat limited. Reported applications include determination of  $\text{R}-\text{Mn}(\text{CO})_5$  bond dissociation energies, e.g., ca. 30 kcal/mol for  $\text{R} = \text{CH}_3$ .<sup>20,21</sup>

Differences in  $\text{L}_n\text{M}-\text{R}$  bond dissociation energies, for different  $\text{R}$ s, can be evaluated more readily and reliably from measurements of the heats of formation of  $\text{L}_n\text{M}-\text{R}$ , since such differences do not depend on the (often inaccessible) heat of formation of  $\text{L}_n\text{M}\cdot$ . Differences in metal-alkyl bond dissociation energies also can be deduced from heats of reaction. Thus, measurements of the enthalpies of oxidative addition of various  $\text{X}-\text{I}$  compounds ( $\text{X} = \text{I}, \text{H}, \text{CH}_3, \text{C}_6\text{H}_5\text{CH}_2$ , etc.) to *trans*- $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$  (eq 10) do yield directly differences



between the resulting  $\text{Ir}-\text{X}$  bond dissociation energies ( $D_{\text{Ir}-\text{X}} - D_{\text{Ir}-\text{I}} \sim 14, 0, -7, -17$ , and  $0$  kcal/mol, for  $\text{X} = \text{H}, \text{CH}_3, i\text{-C}_3\text{H}_7, \text{C}_6\text{H}_5\text{CH}_2$ , and  $\text{C}(\text{O})\text{CH}_3$ , respectively).<sup>22</sup>

(2) **Photochemical.** Determination of the threshold wavelength for the photolytic dissociation of a metal-alkyl bond yields an *upper limit* for the corresponding thermal bond dissociation energy. However, the as-

sumption that this photochemical threshold can be directly identified with the bond dissociation energy does not appear to be warranted.<sup>23,24</sup> Indeed, our estimates of various cobalt-alkyl bond dissociation energies typically yield values (ca. 20–30 kcal/mol)<sup>25–27,29</sup> considerably lower than the photochemical thresholds for the dissociation of such bonds (ca. 50 kcal/mol). This approach, thus, would appear to be of limited utility and reliability for the estimation of bond dissociation energies.

(3) **Equilibrium.** This approach, which will be elaborated below, depends on the determination of the equilibrium constants of reactions of the type depicted by eq 11 which, in certain cases, have been found to  $\text{L}_n\text{M}-\text{CR}_2\text{CR}_2\text{H} \rightleftharpoons \text{L}_n\text{M} + \text{CR}_2=\text{CR}_2 + 1/2\text{H}_2$  (11) exhibit well-behaved reversibility.<sup>25</sup> The corresponding metal-alkyl bond dissociation energies can then be deduced from the enthalpies of reactions yielded by the temperature dependencies of the equilibrium constants.

(4) **Kinetic.** This approach entails determination of the activation enthalpy ( $\Delta H^\ddagger$ ) of the homolytic dissociation process depicted by eq 9 and identification of  $\Delta H^\ddagger$  with the corresponding bond dissociation energy. This identification involves the assumption that the activation enthalpy of the reverse process, namely the recombination of  $\text{L}_n\text{M}\cdot$  and  $\text{R}\cdot$ , is small. This assumption has been confirmed directly in studies on the recombination of  $\text{CH}_3\cdot$  with cob(II)alamin<sup>23</sup> and on combination of various radicals with  $\text{Co}(\text{CN})_5^{3-}$ .<sup>26</sup> Such reactions appear to proceed with rates that are close to diffusion controlled and thus are expected to have activation enthalpies of the order of 2 kcal/mol. Successful application of this approach may be compromised by interference from other accompanying modes of decomposition or by complicating secondary reactions (including recombination to form  $\text{L}_n\text{M}-\text{R}$ ) of the initial radical products. In practice, this leads to the requirement of efficient scavenging of the latter by appropriate radical traps. With these safeguards, this approach would appear to have fairly widespread applicability and reliability.<sup>27</sup>

The above constitute the approaches most obviously applicable to the estimation of metal-alkyl bond dissociation energies of ordinary organometallic compounds, many of which are insufficiently volatile for gas-phase manipulation and must be studied in solution. Other methods, notably those based on ion cyclotron resonance spectroscopy and ion beam techniques, have been developed and applied to the estimation of metal-carbon bond energies in relatively simple ionic (and, in some cases, neutral) species in the gas phase, yielding, for example,  $D_{\text{Co}-\text{CH}_3} = 41$  kcal/mol and  $D_{\text{Co}^+-\text{CH}_3} = 61$  kcal/mol.<sup>28</sup> The overlap of these approaches with the others cited above thus far has been slight, and few direct comparisons of closely related systems are available.

(23) J. F. Endicott and G. J. Ferraudi, *J. Am. Chem. Soc.*, **99**, 243 (1977).

(24) C. Y. Mok and J. F. Endicott, *J. Am. Chem. Soc.*, **100**, 123 (1978).

(25) J. Halpern, F. T. T. Ng, and G. L. Rempel, *J. Am. Chem. Soc.*, **101**, 7124 (1979).

(26) J. Halpern, *Pure Appl. Chem.*, **51**, 2171 (1979), and references cited therein.

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(21) D. L. S. Brown, J. A. Connor, and H. A. Skinner, *J. Organomet. Chem.*, **81**, 403 (1974).

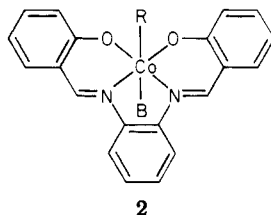
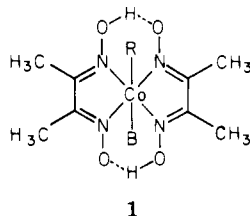
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Table II  
Equilibrium and Kinetic Data for the Decomposition of Some  
[L(DH)<sub>2</sub>Co-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>] Compounds in Acetone According to Eq 12<sup>29</sup>

L	10 <sup>6</sup> K <sub>12</sub> (25 °C), M <sup>3/2</sup>	ΔH <sub>12</sub> <sup>o</sup> , kcal/mol	ΔS <sub>12</sub> <sup>o</sup> , cal/(mol K)	D <sub>Co-R</sub> , kcal/mol	10 <sup>4</sup> k <sub>12</sub> (25 °C), s <sup>-1</sup>	ΔH <sub>12</sub> <sup>‡</sup> , kcal/mol	ΔS <sub>12</sub> <sup>‡</sup> , 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	52.2	19.5	7.3	21.6	-0.2
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

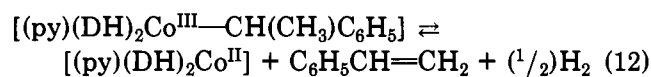
### Cobalt-Alkyl Bond Dissociation Energies

We have recently developed procedures for applying methods 3 and 4 cited above and have tested their validity.<sup>25,27,29</sup> The application of these procedures is illustrated below and some results are reported and discussed. The examples cited emphasize cobalt-alkyl compounds in view of the relevance of such compounds as coenzyme B<sub>12</sub> analogues and because an appropriate selection of compounds convenient for such studies is readily accessible.<sup>9-13</sup> In particular, our measurements of cobalt-alkyl bond dissociation energies have encompassed alkylbis(dimethylglyoximate)cobalt(III) compounds (1, abbreviated R-Co(DH)<sub>2</sub>L, where DH = dimethylglyoxime) and alkyl(*N,N'*-disalicylidene-*o*-phenylenediamine)cobalt(III) compounds (2, abbreviated R-Co(Saloph)L or Co-R). Both classes of com-



pounds have been widely invoked, in a variety of contexts, as coenzyme B<sub>12</sub> analogues.<sup>11,13</sup>

(1) **Equilibrium Method.** We have found that for certain organocobalt compounds, exemplified by [(py)(DH)<sub>2</sub>Co-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>] (py = pyridine), decomposition according to eq 12 attains a measurable equilibrium under mild conditions (10–40 °C in solvents such as acetone or toluene), permitting the spectrophotometric determination of the equilibrium constant K<sub>12</sub> (1.3 × 10<sup>-5</sup> M<sup>3/2</sup> at 25 °C).<sup>25</sup> The temperature



$$K_{12} = \frac{[(\text{py})(\text{DH})_2\text{Co}^{\text{II}}][\text{C}_6\text{H}_5\text{CH}=\text{CH}_2][\text{H}_2]^{1/2}}{[(\text{py})(\text{DH})_2\text{Co}^{\text{III}}-\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5]} \quad (13)$$

dependence of K<sub>12</sub> yielded the corresponding values of ΔH<sub>12</sub><sup>o</sup> (22.1 kcal/mol) and ΔS<sub>12</sub><sup>o</sup> (+52 cal/(mol K)).

From the available data for the heats of formation of C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub> (ΔH<sub>f</sub><sup>o</sup><sub>25</sub> = 35.2 kcal/mol)<sup>30a</sup> and of the C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>· radical (ΔH<sub>f</sub><sup>o</sup><sub>25</sub> = 33 kcal/mol),<sup>30b</sup> the cobalt-carbon bond dissociation energy of [(py)(DH)<sub>2</sub>Co-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>] (i.e., ΔH<sup>o</sup> for eq 15) can be

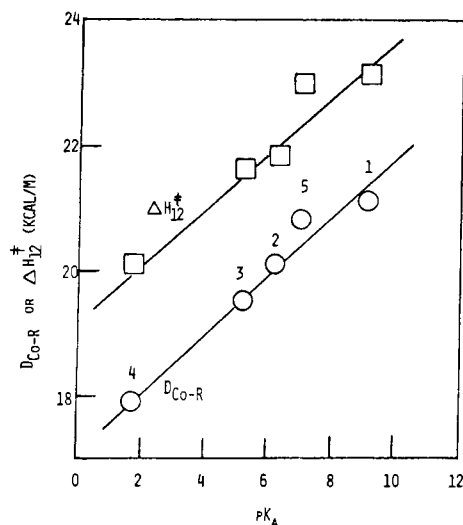
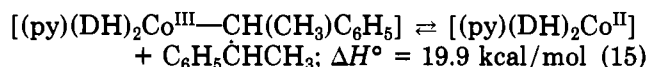
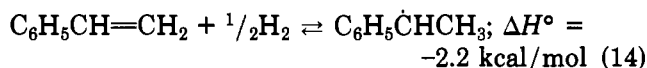
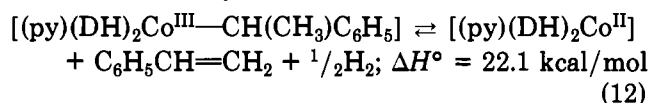


Figure 2. Dependence of D<sub>Co-R</sub> and ΔH<sub>12</sub><sup>‡</sup> for the decomposition of [L(DH)<sub>2</sub>Co-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>] on the basicity (pK<sub>a</sub>) of L. L = 4-aminopyridine (1); 4-methylpyridine (2); pyridine (3); 4-cyanopyridine (4); imidazole (5).

deduced to be 19.9 kcal/mol by using the following thermochemical cycle:



It should be noted that this determination of the cobalt-carbon bond dissociation energy rests entirely upon thermodynamic considerations and is independent of the mechanism of reaction 12.

Values of the thermodynamic parameters and Co-C bond dissociation energies for various [L(DH)<sub>2</sub>Co-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>] compounds, containing different axial ligands L, determined by this procedure, are listed in Table II.<sup>29</sup> The Co-C bond dissociation energies span the range 17.9 to 21.2 kcal/mol. For the series of complexes containing para-substituted pyridines as the axial ligands, for which the steric influences presumably are constant, the Co-C bond dissociation energy increases with the basicity of the axial ligand L according to the trend depicted in Figure 2. This is not unexpected since dissociation of the Co-C bond according to eq 15 involves a decrease in the formal oxidation state of cobalt from +3 to +2. 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. Analogous reasoning has been invoked to explain the increase in reactivity

(29) F. T. T. Ng, G. L. Rempel, and J. Halpern, *J. Am. Chem. Soc.*, **104**, 621 (1982).

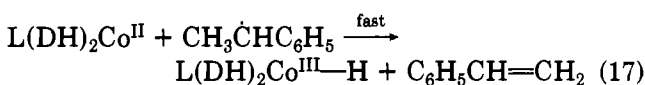
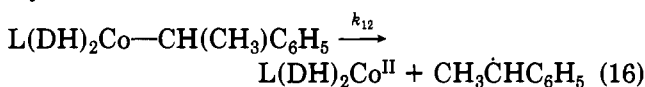
(30) (a) D. S. Stull, E. F. Westrum and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969; (b) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

Table III  
Kinetic Data for the Decomposition of Some [R-Co(Saloph)L] Compounds According to Scheme I<sup>27</sup>

R	$k_0(70^\circ\text{C}), \text{s}^{-1}$	$\Delta H_0^\ddagger, \text{kcal/mol}$	$\Delta S_0^\ddagger, \text{cal/(mol K)}$	$k_1(70^\circ\text{C}), \text{s}^{-1}$	$\Delta H_1^\ddagger, \text{kcal/mol}$	$\Delta S_1^\ddagger, \text{cal/(mol K)}$	$(k_{-1}/k_2)_{70^\circ\text{C}}$	$D_{\text{Co-R}}, \text{kcal/mol}$
$\text{CH}_2\text{CH}_2\text{CH}_3$	$1.0 \times 10^{-5}$	23.4	-15.1	$4.7 \times 10^{-4}$	27.1	2.6	10	25
$\text{CH}(\text{CH}_3)_2$	$1.9 \times 10^{-3}$	19.8	-15.5	$5.7 \times 10^{-2}$	21.8	-2.9	93	20
$\text{CH}_2\text{C}(\text{CH}_3)_3$				$3.4 \times 10^{-2}$	20.3	-6.2	8	18
$\text{CH}_2\text{C}_6\text{H}_5$				$1.2 \times 10^{-2}$	23.6	1.3	70	22

of  $\text{Co}^{\text{II}}(\text{DH})_2\text{L}$  complexes toward organic halides with increasing basicity of L.<sup>31</sup>

(2) **Kinetic Method.** The systems just described also provide a test of the validity of the kinetic approach to the determination of bond dissociation energies. Although the Co-C bond dissociation energies listed in Table II were deduced by a method that does not depend on the mechanism of reaction 12, a plausible mechanism encompasses the sequence of steps depicted by eq 16-18, the rate-determining step being the homolysis of the Co-C bond. Kinetic measurements con-



firmed that these decomposition reactions obey first-order kinetics, i.e.,  $-\text{d}[\text{L}(\text{DH})_2\text{Co}-\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5]/\text{d}t = k_{12}[\text{L}(\text{DH})_2\text{Co}-\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5]$ , and yielded the values of  $\Delta H_{12}^\ddagger$  and  $\Delta S_{12}^\ddagger$  listed in Table II (see also Figure 2). The finding that the values of  $\Delta H_{12}^\ddagger$  are consistently about 2 kcal/mol higher than the corresponding Co-R bond dissociation energies lends strong support to this mechanistic interpretation and implies that measurements of  $\Delta H^\ddagger$  for reactions analogous to eq 12 (or other reactions whose rates are determined by Co-C bond homolysis) can be used to deduce the corresponding Co-C bond dissociation energies in cases where the reactions do not achieve measurable equilibria.

Preliminary results of such kinetic measurements on other  $\text{L}(\text{DH})_2\text{Co}-\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  compounds, for example, 2-substituted pyridines or tertiary phosphines, indicate that bulky axial ligands significantly weaken the Co-C bond and promote decomposition according to reaction 12.<sup>32</sup> When L is a tertiary phosphine the value of  $k_{12}$  increases markedly (and the value of  $\Delta H_{12}^\ddagger$  correspondingly decreases) with the cone angle<sup>33</sup> of L, e.g., from  $1.0 \times 10^{-4} \text{ s}^{-1}$  at  $25^\circ\text{C}$  ( $\Delta H_{12}^\ddagger = 26 \text{ kcal/mol}$ ) for L = dimethylphenylphosphine (cone angle  $122^\circ$ ), through  $1.9 \times 10^{-2} \text{ s}^{-1}$  ( $\Delta H_{12}^\ddagger = 19 \text{ kcal/mol}$ ) for L = triphenylphosphine (cone angle  $145^\circ$ ) to ca.  $0.5 \text{ s}^{-1}$  for L = tricyclohexylphosphine (cone angle  $170^\circ$ ). Such a dependence is consistent with the lengthening of Co-C bonds by bulky axial ligands revealed by structural studies on related organocobalt compounds.<sup>34</sup>

The kinetic approach also has been applied to the determination of cobalt-alkyl bond energies in some organocobalt Schiff base compounds, R-Co(Saloph)L (2, abbreviated Co-R, L = pyridine).<sup>27</sup> Such com-

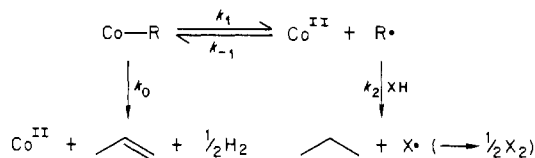
(31) J. Halpern and P. Phelan, *J. Am. Chem. Soc.*, **94**, 1985 (1972).

(32) F. T. T. Ng, G. L. Rempel, and J. Halpern, unpublished results.

(33) C. A. Tolman, *Chem. Rev.*, **77**, 3131 (1977).

(34) L. Randaccio, N. Bresciani-Pahor, P. J. Toscano, and L. G. Marzilli, *J. Am. Chem. Soc.*, **102**, 7372 (1980); **103**, 6347 (1981), and references cited therein.

Scheme I

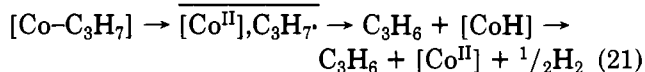


pounds were found to undergo thermal decomposition at conveniently measurable rates in pyridine solution at temperatures below  $100^\circ\text{C}$  in the presence of efficient radical traps such as the hydrogen donor, *n*- $\text{C}_8\text{H}_{17}\text{SH}$  (abbreviated XH). When R = *n*-propyl or isopropyl (i.e., an alkyl containing a  $\beta$ -hydrogen atom) the reaction yielded a mixture of propene and propane, exhibiting the kinetics (eq 19) and product distribution (eq 20) corresponding to Scheme I where  $\text{CoR} = (\text{py})(\text{Saloph})\text{Co}-\text{C}_3\text{H}_7$  and  $\text{Co}^{\text{II}} = \text{py}(\text{Saloph})\text{Co}^{\text{II}}$ .<sup>27</sup>

$$-\text{d} \ln [\text{CoR}] / \text{d}t = k_{\text{obsd}} = k_0 + \frac{k_1 k_2 [\text{XH}]}{k_{-1} [\text{Co}^{\text{II}}] + k_2 [\text{XH}]} \quad (19)$$

$$\frac{[\text{CH}_2=\text{CH}-\text{R}]}{([\text{CH}_3-\text{CH}_2-\text{R}] + [\text{CH}_2=\text{CH}-\text{R}])} = k_0/k_{\text{obsd}} \quad (20)$$

The probable mechanism of the olefin-elimination step corresponding to  $k_0$  is that depicted by eq 21, i.e.,  $\beta$ -hydrogen transfer between the  $\text{C}_3\text{H}_7\cdot\text{Co}^{\text{II}}$  geminate radical pair, followed by rapid decomposition of the resulting cobalt hydride. Such  $\beta$ -hydrogen abstraction



has been shown to be fast in closely related systems and, in one case, to occur within the cage lifetime of such a radical pair.<sup>35</sup> In any event, since  $k_0$  is small compared with  $k_1$  (in no case greater than ca. 3%), its interpretation does not seriously affect the interpretation of the major  $k_1$ -derived radical pathway. For R = neopentyl or benzyl (i.e., lacking a  $\beta$ -hydrogen atom) the olefin-producing path was absent. Accordingly, the organic products were exclusively neopentane and toluene, and the kinetics conformed to eq 19 with  $k_0 = 0$ .

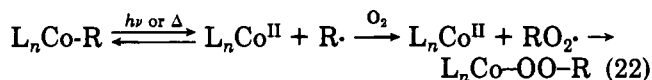
The results of these kinetic measurements are summarized in Table III,<sup>27</sup> together with the Co-R bond dissociation energies ( $D_{\text{Co-R}}$ ), deduced from  $\Delta H_1^\ddagger$  on the assumption that recombination of  $\text{Co}^{\text{II}}$  and R $\cdot$  is diffusion controlled; i.e., that  $\Delta H_{-1}^\ddagger \sim 2 \text{ kcal/mol}$ , hence  $D_{\text{Co-R}} \sim \Delta H_1^\ddagger - 2 \text{ kcal/mol}$ . The resulting values of  $D_{\text{Co-R}}$  span the range 18-25 kcal/mol. While the trend, in part (e.g., *n*-propyl > benzyl), parallels that for other alkyl bond dissociation energies (e.g., R-H), the low values of  $D_{\text{Co-R}}$  for isopropyl and neopentyl, compared with benzyl, attest to the importance of steric effects in such cobalt complexes, an inference underscored by the results of structural investigations on related or-

(35) R. L. Sweany and J. Halpern, *J. Am. Chem. Soc.*, **99**, 8335 (1977).

ganocobalt compounds.<sup>34</sup> In this context our results suggest that neopentyl is at least as sterically demanding as isopropyl. The unusual reactivities reported recently for certain neopentylplatinum compounds also may reflect such sterically induced destabilization.<sup>36</sup>

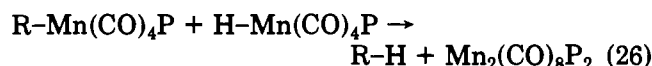
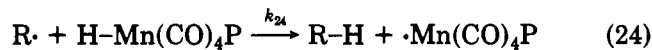
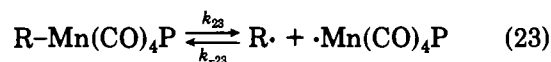
The relatively small difference (ca. 3 kcal/mol) between the Co-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and Co-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> bond dissociation energies, compared with the difference (ca. 10 kcal/mol) between the corresponding H-CH<sub>2</sub>CH<sub>2</sub>C-H<sub>3</sub> and H-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> bond dissociation energies, suggests enhanced stabilization of the metal-benzyl bond, possibly related to the stability of the benzyl carbanion. Similar indications of enhanced metal-benzyl bond stability are provided by the unfavorable equilibrium for CO insertion into C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-Mn(CO)<sub>5</sub> compared with CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-Mn(CO)<sub>5</sub> or CH<sub>3</sub>-Mn(CO)<sub>5</sub>.<sup>37</sup>

All the Co-alkyl bond dissociation energies determined in these studies, both for R-Co(DH)<sub>2</sub>L compounds (Table II) and R-Co(Saloph)L compounds (Table III), lie in the range 18–25 kcal/mol. Comparable values have recently been estimated for some alkylcobalamins by a similar kinetic procedure.<sup>38</sup> These lie in an appropriately low range to be consistent with, and supportive of, the proposed role of Co-C bond homolysis in coenzyme B<sub>12</sub> promoted reactions according to eq 3 and 4. Co-C bond homolysis probably also is involved in other reactions of organocobalt compounds, for example, the photochemical or thermal insertion of O<sub>2</sub> according to eq 22.<sup>39,40</sup>



### Other Transition-Metal-Carbon Dissociation Energies

Only a few other transition-metal-alkyl bond energies have been determined reliably, although the approaches described above, particularly the kinetic method, would appear to be fairly widely applicable to other systems. Using this method, the Mn-C bond dissociation energy in *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-Mn(CO)<sub>4</sub>P(*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (abbreviated R-Mn(CO)<sub>4</sub>P) has recently been determined to be 25 kcal/mol, from kinetic measurements on reaction 26 which has been shown to proceed by the mechanistic sequence of eq 23–25 ( $\Delta H_{23}^\ddagger = 27$  kcal/mol).<sup>41</sup> Indirect evidence has been cited in support of



(36) P. Foley, R. DiCosimo, and G. M. Whitesides, *J. Am. Chem. Soc.*, **102**, 6713 (1980).

(37) (a) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962); (b) "Abstracts of Papers", Seventh International Conference on Coordination Chemistry, Stockholm, Sweden, 1962, p 296.

(38) G. N. Schrauzer and J. Grate, *J. Am. Chem. Soc.*, **103**, 541 (1981).

(39) (a) C. Giannotti, A. Gaudemer, and C. Fontaine, *Tetrahedron Lett.*, 3209 (1970); (b) K. N. V. Duong, C. Fontaine, M. C. Giannotti, and A. Gaudemer, *Tetrahedron Lett.*, 1187 (1981); (c) C. Fontain, K. N. V. Duong, C. Merienne, A. Gaudemer, and C. Giannotti, *J. Organomet. Chem.*, **38**, 167 (1972); (d) C. Giannotti, C. Fontaine, and A. Gaudemer, *Ibid.*, **39**, 381 (1972).

(40) F. R. Jensen and R. C. Kiskis, *J. Am. Chem. Soc.*, **97**, 5825 (1975).

the conclusion that the corresponding acyl-manganese bond dissociation energy in *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C(O)Mn(CO)<sub>4</sub>P(*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> also probably does not exceed 25 kcal/mol.<sup>41</sup> The conclusion that Ir-alkyl and Ir-acyl bond dissociation energies are comparable also has been reached on the basis of measurements of the enthalpies of oxidative addition of alkyl and acyl iodides to IrCl(CO)(PMe<sub>3</sub>)<sub>2</sub>.<sup>22</sup> This conclusion also can be inferred from the modest equilibrium constants for the insertion of CO into metal-alkyl bonds, e.g., of CH<sub>3</sub>Mn(CO)<sub>5</sub>.<sup>18</sup> Thermochemical measurements have yielded a value of ca. 30 kcal/mol for the Mn-C bond dissociation energy of CH<sub>3</sub>-Mn(CO)<sub>5</sub>.<sup>21</sup>

On the basis of the data presently available it appears that transition-metal-alkyl bond dissociation energies are fairly low, i.e.,  $\leq 30$  kcal/mol. The range of compounds for which such determinations have been made is fairly limited, but does encompass Co and Mn compounds with a wide variety of ligands. It thus seems reasonable to infer that metal-alkyl bond dissociation energies in this range are typical at least for coordinatively saturated (18 electron) alkyl compounds of the first row (3d) transition metals. The finding that M-H bond dissociation energies tend to be fairly constant (ca. 60 kcal/mol for a wide range of transition metal hydrides, e.g., H-Co(CO)<sub>4</sub>, H-Co(CN)<sub>5</sub><sup>3-</sup>, H-Mn(CO)<sub>5</sub>, etc.,<sup>26</sup> suggests that it is also reasonable to anticipate a similar uniformity of transition-metal-alkyl bond energies. At this stage there is virtually no reliable information about metal-alkyl bond dissociation for organometallic compounds of the early transition metals (groups 3–6) or of the second and third row (4d and 5d) elements. It is quite possible that stronger metal-alkyl bonds will be found in such compounds.

As noted above, the typical range of values of 20–30 kcal/mol for Co-R bond dissociation energies of coordinately saturated cobalt compounds compares with characteristic values of ca. 60 kcal/mol for the corresponding M-H bond dissociation energies. This difference seems large in the light of the corresponding difference of ca. 15–20 kcal/mol in organic compounds, e.g.,  $D_{CH_3-H} \sim 100$  kcal/mol compared with  $D_{CH_3-CH_3} \sim 85$  kcal/mol. The electronic reasons for this are not obvious, and it is possible that steric factors are, at least in part, responsible. The sensitivity of Co-R bond dissociation energies to steric influences already has been cited. It is possible that steric factors contribute to M-R bond weakening even in relatively uncrowded alkyl compounds such as CH<sub>3</sub>-Mn(CO)<sub>5</sub>. Such an inference also would be consistent with the somewhat higher metal-alkyl bond dissociation energies found in coordinately unsaturated metal alkyls such as the "bare" gas phase molecule Co-CH<sub>3</sub> ( $D_{Co-R} \sim 41$  kcal/mol) and in the smaller differences between M-R and M-H dissociation energies reported for such molecules ( $D_{Co-H} \sim 39$  kcal/mol).<sup>28a</sup>

### Implications for the Thermodynamics of Organometallic Reactions

A knowledge of M-H, M-R, and M-C(O)R bond dissociation energies permits the enthalpies of various organometallic reactions, such as those depicted by eq 5–7, to be estimated. On the basis of the limited data

(41) M. J. Nappa, R. Santi, S. P. Diefenbach, and J. Halpern, *J. Am. Chem. Soc.*, **104**, 619 (1982).

Table IV  
Estimated Enthalpies of Some Oxidative  
Addition and Insertion Reactions (R = alkyl)

reaction	$\Delta H^\circ$ , (kcal/mol)
$M + H_2 \rightarrow MH_2$	-16
$M + RH \rightarrow MHR$	+14
$M + R\overset{\text{O}}{\parallel}CH \rightarrow MHC(O)R$	0
$M + R_2 \rightarrow MR_2$	+25
$M-H + CO \rightarrow MCHO$	+15
$M-R + CO \rightarrow MC(O)R$	-8
$M-H + CH_2=CH_2 \rightarrow M-CH_2CH_3$	-9
$M-R + CH_2=CH_2 \rightarrow M-CH_2CH_2R$	-24

presently available and discussed above, the following would appear to be reasonably typical values at least for coordinately saturated compounds of the first transition series, such as  $XMn(CO)_5$ :  $D_{M-H} = 60$  kcal/mol;  $D_{M-R}$  (R =  $CH_3$  or primary alkyl) = 30 kcal/mol;  $D_{M-C(O)R}$  (presumably including  $D_{M-C(O)H}$ ) = 25 kcal/mol. These values may be used to estimate the enthalpies of the various oxidative addition and insertion reactions listed in Table IV.

The conclusions yielded by the data in Table IV appear to be consistent with available experimental evidence. Three of the four reactions that are concluded to be thermodynamically favorable (i.e., oxidative addition of  $H_2$ ,<sup>16</sup> CO insertion into M-R,<sup>18</sup> and olefin insertion into M-H<sup>42</sup>) are familiar and widespread processes. The estimated  $\Delta H^\circ$  (-8 kcal/mol) for the insertion of CO into R-Mn(CO)<sub>5</sub> agrees well with the reported experimental values for such reactions.<sup>37</sup> The conclusion that olefin insertion into M-R bonds is exothermic to the extent of ca. 24 kcal/mol, and hence is thermodynamically favorable, clearly is reliable (since the M-R bond is conserved). Accordingly, failure of such reactions to occur readily must reflect kinetic barriers. The oxidative addition of RC(O)-H, which is predicted to be thermodynamically "marginal", does appear to be accessible, for example, in the oxidative addition of formaldehyde to  $[Os(CO)_2(PPh_3)_2]$  or  $[Ir(PPh_3)_4]^+$ ,<sup>43</sup> and as the initial step of the facile decarbonylation of aldehydes by metal complexes.<sup>44</sup> Three processes are predicted to be unfavorable thermodynamically, namely the oxidative addition of (unstrained) saturated C-C bonds, the oxidative addition of saturated hydrocarbon C-H bonds, and the insertion of CO into M-H bonds. In keeping with this, attempts to realize such reactions generally have been unsuccessful, although a few special cases recently have been reported.<sup>45</sup> The last two reactions commonly are found

to proceed readily *in the reverse direction*,<sup>46,47</sup> confirming that they are thermodynamically unfavorable. Oxidative addition of saturated C-C bonds has been realized for strained hydrocarbons such as cyclopropane, where the otherwise unfavorable thermodynamic barrier presumably is compensated by the relief of strain energy.<sup>48,49</sup>

### Concluding Remarks

Hardly any transition-metal bond dissociation energies have been determined reliably until recently, and only recently have fairly widely applicable methods for the determination of such energies been developed. The limited data thus far accumulated, principally for coordinately saturated transition metal-alkyl compounds of the first transition series (especially Co and Mn), suggest that the dissociation energies of such metal-alkyl bonds are characteristically low, i.e.,  $\leq 30$  kcal/mol. This confirms longstanding views about the "weakness" of transition metal-alkyl bonds.

Although other processes (e.g.,  $\beta$  elimination of olefins or reductive elimination) often intervene as preferred modes of decomposition of organo-transition-metal compounds (i.e., rather than metal-carbon bond homolysis), the weakness of transition metal-alkyl bonds does result in the accessibility of free-radical pathways in organometallic chemistry.<sup>26,50</sup> One important manifestation of this is the role of cobalt-carbon bond homolysis in coenzyme B<sub>12</sub> promoted rearrangements.<sup>9-13</sup> Free-radical mechanisms also have been identified in various catalytic processes such as hydrogenation,<sup>35,51</sup> and recent evidence suggests that such mechanisms are more widespread than has generally been appreciated.<sup>26</sup>

At this stage there is a clear need for the determination of transition metal-alkyl bond dissociation energies for a wider range of organometallic compounds, including those of the early transition metals and of the second and third periods.

*The research on which this Account is based was supported by the National Institutes of Health (AM 13339) and by the National Science Foundation (CHE78-01192).*

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(51) H. M. Feder and J. Halpern, *J. Am. Chem. Soc.*, **97**, 7186 (1975).

(42) H. C. Clark, C. Jablonski, J. Halpern, A. Montovani, and T. A. Weil, *Inorg. Chem.*, **13**, 1541 (1974).

(43) (a) G. R. Clark, C. E. L. Headford, K. Marsden and W. R. Roper, *J. Am. Chem. Soc.*, **101**, 503 (1979); (b) D. L. Thorn, *ibid.*, **102**, 7109 (1980); (c) D. L. Thorn, *Organometallics*, **1**, 197 (1982).

(44) K. Ohno and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 99 (1968).