Preliminary communication

Thermolysis of $Cp(CO)_nM-CH(CH_3)C_6H_5$ ($n = 2$, M = Fe, Ru; $n = 3$, M = Mo, W). Some vertical trends in transition metal–alkyl bond dissociation energies *

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Abstract

Elucidation of the products and kinetics of thermolysis of the series of compounds, $Cp(CO)_nM-CH(CH_3)C_6H_5$ ($n = 2$, M = Fe, Ru; $n = 3$, M = Mo, W), in benzene, in the absence and presence of free radical traps, yielded the following values of $\Delta H^{\ddagger}$ (kcal/mol) for the homolytic bond dissociation reactions, $Cp(CO)_nM-CH(CH_3)C_6H_5 \rightarrow Cp(CO)_nM\cdot + \cdot CH(CH_3)C_6H_5$: Fe, 29.6; Ru, 34.6; Mo, 26.6; W, 30.6. The corresponding $M-CH(CH_3)C_6H_5$ bond dissociation energies were deduced to be 28, 33, 25 and 29 kcal/mol, respectively.

We have recently elucidated the kinetics and mechanism of thermolysis of $Py(DH)_2Co-CH(CH_3)Ph$ (DH_2 = dimethylglyoxime) and deduced the Co–C bond dissociation energy (BDE, strictly bond dissociation enthalpy) from measurements of $\Delta H^{\ddagger}$ of the homolytic bond dissociation reaction (eq. 1) [1].
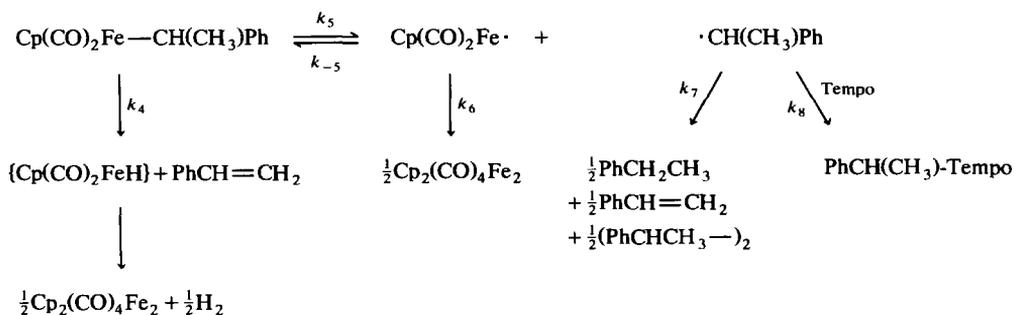
$$Py(DH)_2Co-CH(CH_3)Ph \rightarrow Py(DH)_2Co^{II} + \cdot CH(CH_3)Ph \qquad (1)$$
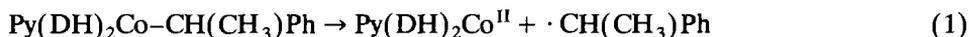
Here we report initial results of an extension of these studies to other metal complexes, notably, $Cp(CO)_nM-CH(CH_3)C_6H_5$ ($n = 2$, M = Fe, Ru; $n = 3$, M = Mo, W) [2**]. These measurements serve to augment significantly the very limited data that presently are available about the systematic dependence of transition metal–alkyl BDE's on the nature of the metal and, especially, about the vertical trends of such BDE's.

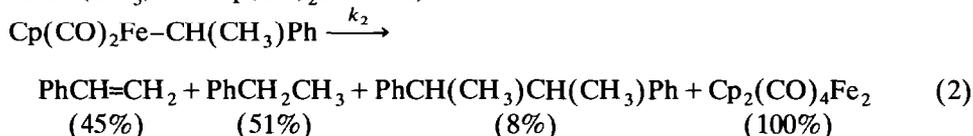Correspondence to: Dr. J. Halpern, Department of Chemistry, The University of Chicago, Chicago, IL 60637, USA.
 * Dedicated to Professor Akio Yamamoto upon his retirement from the Tokyo Institute of Technology and in recognition of his contributions to organometallic chemistry.
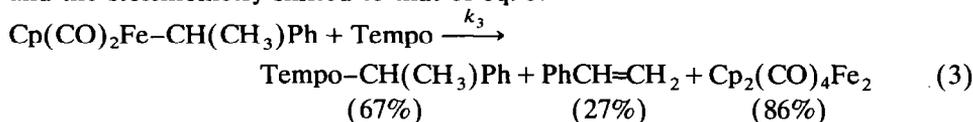** Reference number with asterisk indicates a note in the list of references.

$$Cp(CO)_2Fe-CH(CH_3)Ph \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Cp(CO)_2Fe\cdot \ + \qquad \cdot CH(CH_3)Ph$$

$$\downarrow k_4 \qquad\qquad\qquad\qquad \downarrow k_6 \qquad\qquad k_7\diagup \quad \diagdown\overset{Tempo}{k_8}$$

$$\{Cp(CO)_2FeH\} + PhCH{=}CH_2 \qquad \tfrac{1}{2}Cp_2(CO)_4Fe_2 \qquad \tfrac{1}{2}PhCH_2CH_3 \qquad PhCH(CH_3)\text{-Tempo}$$
$$+ \tfrac{1}{2}PhCH{=}CH_2$$
$$+ \tfrac{1}{2}(PhCHCH_3{-})_2$$

$$\downarrow$$

$$\tfrac{1}{2}Cp_2(CO)_4Fe_2 + \tfrac{1}{2}H_2$$

Scheme 1

The general pattern of thermolysis of this class of compounds is exemplified by that of $Cp(CO)_2Fe-CH(CH_3)Ph$. At 55°C, in C_6D_6 solution the stoichiometry of decomposition of $Cp(CO)_2Fe-CH(CH_3)Ph$ (0.10 M), established by ^1H NMR spectroscopy, conformed to eq. 2 (all yields calculated on the basis of "monomeric" $PhCH(CH_3)$ and $Cp(CO)_2Fe$ units).

$$Cp(CO)_2Fe-CH(CH_3)Ph \overset{k_2}{\longrightarrow}$$

$$PhCH{=}CH_2 + PhCH_2CH_3 + PhCH(CH_3)CH(CH_3)Ph + Cp_2(CO)_4Fe_2 \qquad (2)$$
$$\ \ (45\%) \qquad\quad (51\%) \qquad\qquad (8\%) \qquad\qquad\qquad (100\%)$$

With addition of the free radical trap, Tempo (tetramethylpiperidinyl-1-oxy), the rate of decomposition increased to a limiting value (above $ca.$ 0.03 M Tempo) and the stoichiometry shifted to that of eq. 3.

$$Cp(CO)_2Fe-CH(CH_3)Ph + Tempo \overset{k_3}{\longrightarrow}$$

$$Tempo-CH(CH_3)Ph + PhCH{=}CH_2 + Cp_2(CO)_4Fe_2 \qquad (3)$$
$$(67\%) \qquad\qquad\quad (27\%) \qquad\quad (86\%)$$

In either limiting regime (i.e., with and without trap) the reaction exhibited first order kinetics, i.e.,

$$-d\ \ln[Cp(CO)_2Fe-CH(CH_3)Ph]/dt = k_2 \text{ or } k_3 \qquad (4)$$

Rate measurements (using either ^1H NMR or UV-Vis absorbance at 325 nm to monitor the reaction), encompassing the initial concentration ranges, 1×10^{-4} to 4×10^{-2} M $Cp(CO)_2Fe-CH(CH_3)Ph$ and 2.4×10^{-3} to 8×10^{-1} M Tempo and the temperature range 38 to 67°C, yielded the values: k_2 (60°C) $= 5.0 \times 10^{-4}$ s^{-1}, k_3 (60°C) $= 6.0 \times 10^{-4}$ s^{-1}, $\Delta H_2^{\ddagger} = 26.5 \pm 0.5$ kcal/mol, $\Delta S_2^{\ddagger} = 6 \pm 2$ cal/K-mol, $\Delta H_3^{\ddagger} = 29.5 \pm 0.5$ kcal/mol, $\Delta S_3^{\ddagger} = 15 \pm 2$ cal/K-mol.

The results can be accommodated by the same mechanistic scheme (Scheme 1) as deduced earlier for the decomposition of $Py(DH)_2Co-CH(CH_3)Ph$ [1].

Application of the steady state approximation to this scheme yields:

$$k_2 = k_4 + \cfrac{k_5}{1 + \sqrt{\dfrac{k_{-5}^2}{4k_6k_7}}} \qquad (5)$$

$$k_3 = k_4 + k_5 \qquad (6)$$

Furthermore, at limiting Tempo concentrations (eq. 3):

$$\frac{k_4}{k_5} = \frac{[PhCH{=}CH_2]}{[PhCH(CH_3) - Tempo]} = \frac{27}{67} = 0.41 \text{ at } 60°C \tag{7}$$

Combination of eqs. 4–7 with independently determined values of k_6 and k_7 (1.0×10^9 M^{-1} s^{-1} [3] and 2.4×10^9 M^{-1} s^{-1} [4], respectively) permits all the rate constants in Scheme 1 to be determined, i.e. $k_4 = 1.7 \times 10^{-4}$ s^{-1}; $k_5 = 4.3 \times 10^{-4}$ s^{-1}; $k_{-5} = 1.1 \times 10^9$ M^{-1} s^{-1}, at 60°C.

Corroborating results were obtained using $HSnBu_3$ as the radical trap. At limiting trap concentrations (> 0.074 M $HSnBu_3$) the kinetics of decomposition of $Cp(CO)_2Fe-CH(CH_3)Ph$ were virtually identical to those using Tempo as trap, k (60°) = 6.0×10^{-4} s^{-1}, $\Delta H^\ddagger = 29.7$ kcal/mol, $\Delta S^\ddagger = 16$ cal/K-mol. The organic products $PhCH_2CH_3$ (68%) and $PhCH_2CH_2SnBu_3$ (26%) (principally $PhCHDCH_3$ and $PhCHDCH_2SnBu_3$, when $DSnBu_3$ was the trap) are derived from the trapping reactions,

$$PhĊHCH_3 + HSnBu_3 \rightarrow PhCH_2CH_3 + \cdot SnBu_3 \tag{8}$$

$$PhCH{=}CH_2 + HSnBu_3 \rightarrow PhCH_2CH_2SnBu_3 \tag{9}$$
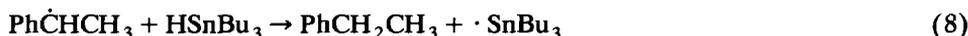
$Cp(CO)_2Ru-CH(CH_3)Ph$ [5*], $Cp(CO)_3Mo-CH(CH_3)Ph$ [5*] and $Cp(CO)_3W-CH(CH_3)Ph$ exhibited essentially similar behavior. In each case, the kinetics, as well as the stoichiometries of reaction, both in the absence and presence of Tempo or $HSnBu_3$, paralleled those for $Cp(CO)_2Fe-CH(CH_3)Ph$, yielding the kinetic parameters in Table 1.

The virtual identity of the activation parameters of k_4 and k_5, for both $Cp(CO)_2Fe-CH(CH_3)Ph$ and $Cp(CO)_3W-CH(CH_3)Ph$, suggests that, as in several earlier related systems, including thermolysis of $py(DH)_2Co-CH(CH_3)Ph$ [1,6], both processes proceed through a common rate-determining step, namely Fe–C homolysis to produce a *geminate* $\overline{Cp(CO)_2Fe\cdot, \cdot CH(CH_3)Ph}$ radical pair. This is followed either by β-H transfer to produce $PhCH{=}CH_2$ or separation to produce a free $\cdot CH(CH_3)Ph$ radical that can be trapped by Tempo [1].

Table 1

Summary of kinetic data

Compound	Temp. range (°C)	Trap	$\Delta H_5^\ddagger$ (kcal/mol) [a]	$\Delta S_5^\ddagger$ (cal/K-mol) [a]	M–C BDE (kcal/mol) [a]
$Cp(CO)_2Fe-CH(CH_3)Ph$ [b]	38–67	Tempo	29.5	15 ⎫	
$Cp(CO)_2Fe-CH(CH_3)Ph$	38–67	$HSnBu_3$	29.7	16 ⎭	28
$Cp(CO)_2Ru-CH(CH_3)Ph$ [c]	144–180	$HSnBu_3$	34.6	5	33
$Cp(CO)_3Mo-CH(CH_3)Ph$	12–33	$HSnBu_3$	26.6	15	25
$Cp(CO)_3W-CH(CH_3)Ph$ [d]	43–65	Tempo	30.5	18 ⎫	
$Cp(CO)_3W-CH(CH_3)Ph$	43–65	$HSnBu_3$	30.8	19 ⎭	29

[a] Estimated standard deviations of $\Delta H_5^\ddagger$ and $\Delta S_5^\ddagger$ are $\pm(0.5$ to $0.6)$ kcal/mol and $\pm(1$ to $2)$ cal/K-mol, respectively. Estimated accuracy of BDE's, ±1.5 kcal/mol. [b] $\Delta H_4^\ddagger = 29.6$ kcal/mol; $\Delta S_4^\ddagger = 15$ cal/K-mol; $\Delta H_5^\ddagger = 29.6$ kcal/mol; $\Delta S_5^\ddagger = 13$ cal/K-mol. [c] In decahydronaphthalene. [d] $\Delta H_4^\ddagger = 30.8$ kcal/mol; $\Delta S^\ddagger = 15$ cal/K-mol; $\Delta H_5^\ddagger = 30.6$ kcal/mol; $\Delta S_5^\ddagger = 18$ cal/K-mol.

Accordingly, $\Delta H_3^{\ddagger}$ (for the combination of rate constants k_4 and k_5) may be identified with homolytic dissociation of the $Cp(CO)_nM–CH(CH_3)Ph$ bonds. As elaborated and justified elsewhere [8], the M–C BDE may be deduced from $\Delta H_3^{\ddagger}$ (which, in the case tested, is identical to $\Delta H_5^{\ddagger}$; see Table 1) by subtracting therefrom $\Delta H^{\ddagger}$ for recombination of $Cp(CO)_nM\cdot$ and $\cdot CH(CH_3)Ph$, i.e., $\Delta H_{-5}^{\ddagger}$. Since such recombination reactions typically are close to diffusion controlled (e.g., $k_{-5} = 1 \times 10^9$ M^{-1} s^{-1} for $Cp(CO)_2Fe–CH(CH_3)Ph$; see above), $\Delta H_{-5}^{\ddagger}$ may be approximated by $\Delta H^{\ddagger}$ of viscous flow which, for solvents such as benzene, is *ca.* 1–2 kcal/mol [8b]. Applying this correction yields the $Cp(CO)_nM–CH(CH_3)Ph$ BDE's listed in Table 1. These range from 25 to 33 kcal/mol.

The most significant feature of the results yielded by this study is the consistent increase of *ca.* 4–5 kcal/mol in the M–C BDE for each vertical step, i.e., in going from Fe to Ru and from Mo to W. While the trend is consistent with widespread qualitative experience, these are among the first quantitative data that bear directly on this theme, particularly for the later transition elements.

Also of interest is the significantly higher $Cp(CO)_2Ru–CH(CH_3)Ph$ BDE (33 kcal/mol) compared with that of $Cp(CO)_3Mo–CH(CH_3)Ph$ (25 kcal/mol). While electronic factors may also contribute to this difference, the trend is consistent with other demonstrations of an inverse dependence of metal–alkyl BDE's on steric crowding [9]. Extension of these measurements to variously substituted Cp ligands and other alkyl groups should provide further insights into this theme.

References and notes

1 F.T.F. Ng, G.L. Rempel, C. Mancuso and J. Halpern, Organometallics, 9 (1990) 2762.
2 Attention is directed to several earlier qualitative studies of the thermolysis of $Cp(CO)_nM–R$ compounds (a) C.U. Pittman and R.F. Felis, J. Organomet. Chem., 72 (1974) 399; (b) W.D. Jones, J.M. Huggins and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 4415; (c) W.D. Jones and R.G. Bergman, J. Am. Chem. Soc., 101 (1979) 5447; (d) J.A. McCleverty and G. Wilkinson, J. Chem. Soc. (1963) 4096; (e) A.N. Nesmeyanov, Y.A. Chapovskii, B.V. Lokshin, A.V. Kisin and L.G. Makarova, Akad. Nauk SSSR, 171 (1966) 637; (f) P.A. Wegner and G.P. Sterling, J. Organomet. Chem., 162 (1978) C31.
3 J.V. Caspar and T.J. Meyer, J. Am. Chem. Soc., 102 (1980) 7794.
4 O. von Brede, W. Helmstreit and R. Mehnert, J. Prakt. Chem., 316 (1974) 402.
5 The synthesis of these compounds paralleled the literature synthesis of the known compound $Cp(CO)_3W–CH(CH_3)Ph$ [7], in each case via the alkylation of $[Cp(CO)_nM]^-$ by $Br–CH(CH_3)Ph$. The syntheses and characterizations are detailed in C. Mancuso, Ph.D. Dissertation, The University of Chicago, 1990.
6 (a) T.T. Tsou, M. Loots and J. Halpern, J. Am. Chem. Soc., 104 (1982) 623; (b) S.H. Kim, H.L. Chen, N. Feilchenfeld and J. Halpern, J. Am. Chem. Soc., 110 (1988) 3120.
7 (a) S.C.H. Su and A. Wojcicki, Organometallics, 2 (1983) 1296; (b) B. Klein, R.J. Kazlauskas and M.S. Wrighton, Organometallics, 1 (1982) 1338.
8 (a) J. Halpern, Polyhedron, 7 (1988) 1483, and references therein; (b) J. Halpern, ACS Symposium Series, 428 (1990) 100 and references therein.
9 (a) F.T.T. Ng, G.L. Rempel and J. Halpern, Inorg. Chim. Acta, 77 (1983) L165; (b) M.K. Geno and J. Halpern, J. Am. Chem. Soc., 109 (1987) 1238.