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Determination of Organo−Cobalt Bond Dissociation Energetics and Thermodynamic Properties of Organic Radicals through Equilibrium Studies

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Abstract: Two methods are described and illustrated for the measurement of organo−cobalt bond homolysis energies through reactions of tetra(*p*-anisyl)porphyrinato cobalt(II), (TAP)$Co^{II\bullet}$, with organic radicals of the form $^{\bullet}C(CH_3)(R)CN$ in the presence of olefins. Thermodynamic values for bond homolysis have been determined directly for (TAP)Co-$C(CH_3)_2CN$ ($\Delta H° = 17.8 \pm 0.5$ kcal mol^{-1}, $\Delta S° = 23.1 \pm 1.0$ cal K^{-1} mol^{-1}) and (TAP)Co-$CH(CH_3)C_6H_5$ ($\Delta H° = 19.5 \pm 0.6$ kcal mol^{-1}, $\Delta S° = 24.5 \pm 1.1$ cal K^{-1} mol^{-1}) from evaluation of the equilibrium constants for the dissociation process ($Co{-}R \rightleftharpoons Co^{II\bullet} + R^{\bullet}$) in chloroform. The bond homolysis enthalpy for (TAP)Co-C_5H_9 ($\Delta H° = 30.9$ kcal mol^{-1}) was determined indirectly by measuring the thermodynamic values for the competition reaction (TAP)Co-$C(CH_3)_2CN + C_5H_8 \rightleftharpoons$ (TAP)Co-$C_5H_9 + CH_2{=}C(CH_3)CN$ ($\Delta H° = 0.9 \pm 0.3$ kcal mol^{-1}) in conjunction with a thermochemical cycle. This indirect approach was also used to evaluate (TAP)Co-$CH(CH_3)C_6H_5$ BDE (20.5 kcal mol^{-1}) which agrees favorably with the value determined directly. When the Co−R bond homolysis enthalpies are known from independent evaluation, these equilibrium measurements provide a method for evaluating relative heats of formation of organic radicals. Application of this approach gives 40.8 kcal mol^{-1} for the heat of formation of $^{\bullet}C(CH_3)_2CN$ in chloroform. Success of these methods is dependent on fast abstraction of $H^{\bullet}$ from the organic radicals by (TAP)$Co^{II\bullet}$ to form (TAP)Co-H and rapid addition of (TAP)Co-H with olefins to form organocobalt complexes. Kinetic-equilibrium simulations utilizing reaction schemes for these processes provide an accurate description of the kinetic profiles and the equilibrium concentrations of solution species when the organic radical species achieve steady state.

Introduction

Bond homolysis enthalpies of many first transition series organo−metal (M−R) species are sufficiently small that the complexes function as effective thermal sources of organic radicals ($R^{\bullet}$). The best current examples of this behavior are for organo−cobalt(III) complexes where Co−R bond homolysis is utilized in producing radical reactions including B_{12} coenzyme dependent processes,[1] numerous organic transformations,[1−4] and controlled radical polymerizations.[2,3] Studies directed toward determining kinetic and thermodynamic parameters for organo−cobalt bond homolysis have provided major contributions in describing the general bond homolysis process[5−7] and defining the factors that contribute to organo-metal bond energies which are required for a more than superficial understanding of the reactivity. Co−R bond enthalpies have frequently been estimated from the activation parameters for radicals entering solution determined by chemical trapping of the organic radicals ($R^{\bullet}$) produced from bond homolysis.[5,6,8−10] This kinetic ap-

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(1) (a) Abeles, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114. (b) Babior, B. M. *Acc. Chem. Res.* **1975**, *8*, 376. (c) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575. (d) Alelyunas, Y. W.; Fleming, P. E.; Finke, R. G.; Pagano, T. G.; Marzilli, L. G. *J. Am. Chem. Soc.* **1991**, *113*, 3781. (e) Gar, C. D.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 4414. (f) Pratt, J. M. *Chem. Soc. Rev.* **1985**, *14*, 161. (g) Stubbe, J. *J. Biol. Chem. 1990*, *265*, 5329.

(2) (a) Gridnev, A. A. *Polymer Science USSR (Engl. Transl.)* **1989**, *31*, 2369. (b) Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V.; Belgovskii, I. M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 879. (c) Gridnev, A. A.; Semeikin, A. S.; Koifman, O. I. *Theor. Exp. Chem. (Engl. Transl.)* **1989**, *25*, 698. (d) Oganova, A. G.; Smirnov, B. R.; Ioffe, N. T.; Enikolopyan, N. S. *Dokl. Phys. Chem. (Engl. Transl.)* **1983**, *268*, 66. (e) Parshall, G. W.; Ittel, S. D. Homogenous Catalysis; Wiley-Interscience: New York, 1992; p 85. (f) Burczyk, A. F.; O'Driscoll, K. F.; Rempel, G. L. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, 22, 3255.

(3) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7943.

(4) (a) Baldwin, J. E.; Moloney, M. G.; Parsons, A. F. *Tetrahedron* **1992**, *48*, 9373. (b) Ali, A.; Harrowven, D. C.; Pattenden, G. *Tetrahedron Lett.* **1992**, *33*, 2851. (c) Harrowven, D. C.; Pattenden, G. *Tetrahedron Lett.* **1991**, *32*, 243. (d) Baldwin, J. E.; Adlington, R. M.; Kang, T. W. *Tetrahedron Lett.* **1991**, *32*, 7093. (e) Branchaud, B. P.; Yu, G.-X. *Tetrahedron Lett.* **1991**, *32*, 3639. (f) Giese, B.; Zehnder, M.; Neuburger, M.; Trach, F. *J. Organomet. Chem.* **1991**, *412*, 415. (g) Yamamoto, K.; Albrecht, S.; Scheffold, R. *Chimia* **1991**, *45*, 86. (h) Brown, K. L. and Zou, X. *J. Am. Chem. Soc.* **1992**, *114*, 9643. (i) Xiang, Z.; Brown, K. L. *J. Am. Chem. Soc.* **1993**, *115*, 6689. (j) Brown, K. L.; Wu, G. Z. *Inorg. Chem.* **1994**, *33*, 4122.

(5) Halpern, J. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series No. 428; American Chemical Society: Washington, DC 1990; pp100−112.

(6) (a) Koenig, T. W.; Hay, B. P.; Finke, R. G. *Polyhedron* **1988**, *1*, 1499. (b) Koenig, T.; Finke, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 2657.

(7) Koenig, T.; Scott, T. W.; Franz, J. A. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series No. 428; American Chemical Society: Washington, DC, 1990; pp 113−132.

(8) (a) Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *Organometallics* **1993**, *12*, 4871. (b) Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* **1993**, 1010.

(9) (a) Tsou, T.-T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623. (b) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124. (c) Kim, S.-H.; Chen, H. L.; Feilchenfeld, N.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3120.

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proach has proven to be a widely applicable, powerful methodology[5,6,8−10] that may be the only means of estimating M−R bond enthalpies for many organo−metal complexes . The precise relationship of an observed activation enthalpy ($\Delta H^{\ddagger}$) to the bond homolysis enthalpy ($\Delta H°$) in solution can be complicated by the occurrence of a solvent caged radical pair intermediate and solvation effects.[6] While these complicating factors probably have a rather small absolute contribution to the activation enthalpy (~2−5 kcal mol^{-1}) they could produce relatively large fractional uncertainty when the derived bond homolysis enthalpies ($\Delta H°$) are small as is the case for Co−R complexes. Direct thermodynamic studies that yield enthalpies and entropies are preferable to kinetic methods but are not yet feasible for most bond homolysis reactions. This article reports on reactions of tetraanisylporphyrinatocobalt(II), (TAP)Co, with organic radicals of the form $^{\bullet}C(CH_3)(R)CN$, and olefins that produce measurable solution equilibria with organo−cobalt complexes, (TAP)Co−R. Analysis of the solution equilibria provide new approaches for determining thermodynamic parameters for organo−metal bond homolysis and relative heats of formation of organic radicals in solution.

Experimental Section

Materials. (TAP)Co (Aldrich) was recrystyallized from chloroform/hexane, and the crystals dried by heating under vacuum. Styrene, cyclopentene, 1-hexyne, and methacrylonitrile (MAN) of 99% purity (Aldrich) were purified by multiple vacuum distillations to remove the stabilizers and degassed by employing at least three freeze−pump−thaw cycles immediately prior to use. All experiments were performed in $CDCl_3$ (Aldrich), which was stored in a vacuum adapted bulb over molecular sieves. Immediately prior to an experiment, $CDCl_3$ was distilled under vacuum and degassed as previously described. AIBN (2,2′-azobis-(isobutyronitrile)) (Wako Chemicals), VAZO-52 (2,2′-azobis(2,4-dimethylpentanenitrile)) (DuPont), and V-70 (2,2′-azobis-(4-methoxy-2,4-dimethylvaleronitrile)) (Wako Chemicals) were used as purchased.

Procedures for Determination of k_i for Radical Sources. Weighed quantities of azo radical sources (AIBN, VAZO-52, or V-70) and 7.44 mg of (TAP)Co were placed in a 1.00 mL volumetric flask, and a 0.5 M stock solution of 1-hexyne in $CDCl_3$ was added to give 1.00 mL of solution. After (TAP)Co and the radical source were completely dissolved, the solution sample was transferred to a vacuum adapted NMR tube. After three freeze−pump−thaw cycles, the sample NMR tube was sealed and placed in a constant temperature bath (±0.1 °C). The sample was removed from the bath at a series of times for analysis of the solution concentrations by ^1H NMR (263 K). The concentrations of $(TAP)Co^{II}$ and $(TAP)Co\text{-}C({=}CH_2)(CH_2)_3CH_3$ were monitored by comparison of the meta phenyl proton signal of $(TAP)Co^{II}$ at 9.4 ppm with the pyrrole proton signal of the organometallic at 8.8 ppm.

The rate for free radicals entering solution (V) from the radical source IN is given by the relationship $V = k_i[IN]$, where k_i is the rate constant for free radicals entering solution. The molar concentration of IN is initially established such that it changes by less than one percent during the time required for the kinetic measurements and thus the rate at which radicals enter solution (V) is effectively constant. The rate for free radicals entering solution (V) thus can be evaluated from the slope of the linear plot through the origin of the molar concentration of (TAP)Co−R as a function of time for the specific radical source and temperature of the experiment. The rate constant for free radicals entering solution, k_i, was then calculated from the relationship $k_i = V/[IN]$. The rate constants for V-70 and VAZO-52 were previously reported[12] at the same experimental conditions. Rate constants (k_i) for AIBN were experimentally redetermined at 333 K using the above procedure (k_i (AIBN, 333 K) $= 1.50 \pm 0.01 \times 10^{-5}\ s^{-1}$) and further supported by kinetic simulations for several temperatures. Rate constants (k_i) were also determined at a series of temperatures by using activation enthalpy data for the decompostion of AIBN as reported by the manufacturer (Wako Chemicals USA, Inc.) and scaling the rates of decomposition to experimentally determined rate constants for radicals entering solution. All the data from the above determinations for AIBN were combined and plotted, and the least squares best fit calculated. This best fit "working equation" is accurate to within 5% for the temperature range 270−336 K ($\ln(k_i) = (0.1436 \pm 0.0001) \times T(K) - (58.92 \pm 0.03)$).

Procedures for Equilibrium Measurements. Stock solutions of olefin(s) in $CDCl_3$ were added to a 1.00 mL volumetric flask which contained 7.44 mg of (TAP)Co and radical source (AIBN, VAZO-52, or V-70) and filled to volume. A 0.3−0.5 mL aliquot of this solution was taken as a sample and transferred to a vacuum adapted NMR tube. After three freeze−pump−thaw cycles, the sample NMR tube was sealed and placed in a constant temperature bath (±0.1 °C). The sample was removed at a series of time intervals and the solution concentrations determined by ^1H NMR. This procedure was repeated until the ratio of $[(TAP)Co^{II}]$ to $[(TAP)Co^{III}\text{-}R]$ remained constant which corresponds to having a steady state concentration of radicals ($R^{\bullet}$). The ratio of $(TAP)Co^{II}$ to the $(TAP)Co^{III}$ organometallic derivatives was determined by integrating the meta-phenyl proton signal of $(TAP)Co^{II\bullet}$ ($\delta = 9.4$ ppm) and the pyrrole proton signal of the $(TAP)Co^{III}$ organometallic species ($\delta \approx 8.9$ ppm). The high field ^1H NMR region where the hydrogens in the organic fragment bonded to (TAP)Co occur was further used in characterizing the $(TAP)Co^{III}$ organometallic species by comparison with previously reported peak assignments.[8]

Thermodynamic parameters for the bond dissociation energies reported in this paper were determined by a weighted linear least squares analysis for the plot of $\ln(K_{eq})$ versus $1/T$ (see supporting information for tables of all data).

Results and Analysis

Determination of k_i for Radical Sources. As reported in an earlier paper,[8a] 1-hexyne is an effective (por)Co-H scavenger that forms a very stable vinyl cobalt porphyrin complex such that the rate of $(por)Co\text{-}C({=}CH_2)(CH_2)_3CH_3$ formation equals the rate of free radical production (V)[11,12] which was independently measured with the stable radical 2,2′,6,6′-tetramethylpiperidine-1-oxyl (TEMPO). Since the 1-hexyne procedure is more convenient and shown to trap radicals at the same rate as TEMPO,[8a] the reaction of 1-hexyne was used in determining the rate for radicals entering solution.

$$NC(R)(CH_3)CN{=}NC(CH_3)(R)CN \rightarrow 2\,^{\bullet}CCH_3(R)CN + N_2(g) \quad (1)$$

$$(TAP)Co^{II\bullet} + {}^{\bullet}CCH_3(R)CN \rightleftharpoons (TAP)Co\text{-}H + CH_2{=}C(R)CN \quad (2)$$

$$(TAP)Co\text{-}H + HC{\equiv}C(CH_2)_3CH_3 \rightarrow (TAP)Co\text{-}C({=}CH_2)(CH_2)_3CH_3 \quad (3)$$

Reactions 2 and 3 are fast relative to reaction 1 and therefore, the reaction of radicals entering solution from the radical source (eq 1) is the rate determining step. The equilibrium constant for reaction 3 is sufficiently large such that all (TAP)Co-H is converted into $(TAP)Co\text{-}C({=}CH_2)(CH_2)_3CH_3$ and is the only organocobalt complex observed. Rate constants for radicals entering solution (k_i) from the radical source (IN) were determined by measuring the rate for radicals entering solution

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[10] (a) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197. (b) Martin, B. D.; Finke, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2419. (c) Halpern, J. *Polyhedron* **1988**, *7*, 1483. (d) Derenne, S.; Gaudemer, A.; Johnson, M. D. *J. Organomet. Chem.* **1987**, *322*, 229.

[11] (a) Eastmond, G. C. In *Chemical Kinetics*, v.14A; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1976; Vol. 14A, pp 23−25 and 125−132. (b) Rizzardo, E.; Solomon, D. H. *Polym Bull.* **1979**, *1*, 529. (c) Gridnev, A. A. *Polymer J.* **1992**, *24*, 613.

[12] Wayland, B. B.; Gridnev, A. A.; Ittel, S. D.; Fryd, M. *Inorg. Chem.* **1994**, *33*, 3830.

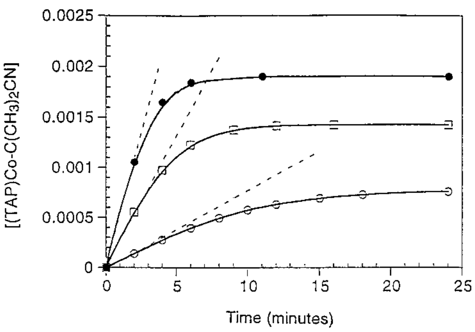

Figure 1. Kinetic profile for the reaction $(TAP)Co^{II\bullet} + {}^{\bullet}C(CH_3)_2CN \rightleftharpoons (TAP)Co\text{-}C(CH_3)_2CN$, where ${}^{\bullet}C(CH_3)_2CN$ radicals are produced by variable initial concentrations of AIBN in $CDCl_3$ at 333 K. ($[(TAP)Co^{II\bullet}]_i = 9.40 \times 10^{-3}$ M). (○) $[AIBN]_i = 0.080$ M (□) $[AIBN]_i = 0.32$ M (●) $[AIBN]_i = 0.64$ M. Dotted line is the total moles per L of ${}^{\bullet}C(CH_3)_2CN$ radicals entering solution from AIBN. Solid lines are calculated by kinetic simulations using the reaction scheme and kinetic parameters given in the Discussion section. ($k_i(AIBN, 333\ K) = 1.50 \times 10^{-5}\ s^{-1}$; $k_t({}^{\bullet}C(CH_3)_2CN, 333\ K) = 1.33 \times 10^{9}\ M^{-1}\ s^{-1}$; $K_5(333K) = 2.20 \times 10^{-7}$).

(V) and the relationship ($V = k_i[IN]$). Values for k_i are found in Tables 1 and 2 of the supporting information.

Equilibrium Measurements for $(TAP)Co^{II}$ with ${}^{\bullet}C(CH_3)_2$-CN. (Tetra(*p*-anisyl)porphyrinato)cobalt(II) (($(TAP)Co^{II\bullet}$ (**1**)) reacts with cyanoisopropyl radicals (${}^{\bullet}C(CH_3)_2CN$ (**2**)) formed thermally from AIBN in $CDCl_3$ to produce the cyanoisopropyl cobalt complex, $(TAP)Co\text{-}C(CH_3)_2CN$ (**3**) (eqs 4 and 5).[13]

$$NC(CH_3)_2CN{=}NC(CH_3)_2CN \rightarrow 2{}^{\bullet}C(CH_3)_2CN + N_2 \tag{4}$$

$$(TAP)Co\text{-}C(CH_3)_2CN \rightleftharpoons (TAP)Co^{II\bullet} + {}^{\bullet}C(CH_3)_2CN \tag{5}$$

Formation of **3** is followed by ^{1}H NMR through the appearance of the characteristic high field resonance associated with the cyanoisopropyl ligand ($\delta(\text{-}C(CH_3)_2CN) = -5.0$). The organometallic complex (**3**) initially forms at a rate equal to the rate at which cyanoisopropyl radicals (**2**) enter solution (Figure 1) and subsequently attains a constant concentration. Steady state concentrations of $(TAP)Co\text{-}C(CH_3)_2CN$ (**3**) and $(TAP)Co^{II\bullet}$ (**1**) were determined by integration of the ^{1}H NMR of the pyrrole and m-phenyl resonances for **3** and **1**, respectively. The ratio of the molar concentrations of $(TAP)Co\text{-}C(CH_3)_2CN$ (**3**) to $(TAP)Co^{II\bullet}$ (**1**) ([**3**]/[**1**]) at steady state was observed to increase linearly with the square root of the molar concentration of the radical source (IN) ($[\mathbf{3}]/[\mathbf{1}] \propto [IN]^{1/2}$) which is directly proportional to the concentration of radicals at steady state ($d[R^{\bullet}]/dt = k_i[IN] - 2k_t[R^{\bullet}]^2 = 0$; $[R^{\bullet}]=(k_i[IN]/2k_t)^{1/2}$ where k_i and k_t are the rate constants for formation and termination of radicals in $CDCl_3$, respectively). Steady state concentrations of radicals in solution were determined from the relationship $[R^{\bullet}] = (V/2k_t)^{1/2}$. For the specific case where AIBN is the radical source, the concentration of free radicals was determined from the relationship $[R_1^{\bullet}] = (V_{(AIBN)}/2k_t(R_1^{\bullet}))^{1/2}$, where $V_{(AIBN)} = k_{i(AIBN)}[AIBN]$ is the rate of free radicals entering solution from AIBN and $k_t(R_1^{\bullet})$ is the radical self-termination rate constant for the cyanoisopropyl radical. Values for k_t were obtained from literature results demonstrating that k_t is diffusion controlled[14] and adapted for the viscosity of deuterated chloroform.[15 b] The viscosity dependence of k_t[14] and the temperature dependence of the viscosity for deuterated chloroform[15] were used to determine $k_t(T)$ for radicals $CDCl_3$ (Table 1). The concentration quotient ([**3**]/[**1**][**2**]) was unaffected by addition of methacrylonitrile and remained constant when the molar concentration of **2** was varied by a factor of 10 which is consistent with reaction 5 attaining equilibrium when the concentration of radical **2** is at steady state. Equilibrium constants for the homolytic dissociation of **3** (reaction 5) were evaluated by this procedure. Revised values for k_i ($k_i(333\ K) = 1.50 \pm 0.01 \times 10^{-5}\ s^{-1}$, $k_i(296\ K) = 7.38 \pm 0.03 \times 10^{-8}\ s^{-1}$) were used in recalculating previously reported equilibrium data for reaction 5[12] and combined with additional new results in determining values for K_5 at 333 K ($2.4 \pm 0.1 \times 10^{-7}$) and 296 K ($7.4 \pm 1.0 \times 10^{-9}$). Equilibrium constants (K_5) were additionally determined at 323 and 311 K from additional new data in an effort to define the thermodynamic parameters for $(TAP)Co\text{-}C(CH_3)_2CN$ more accurately (see supporting information).

Equilibrium Measurements for $(TAP)Co^{II\bullet}$ with ${}^{\bullet}C(CH_3)$-(R)CN and $CH_2{=}C(CH_3)CN$. Complex **3** is formed by reactions of $(TAP)Co^{II\bullet}$ and methacrylonitrile ($CH_2{=}C(CH_3)$-CN) with radicals produced from the azo radical sources VAZO-52 (${}^{\bullet}C(CH_3)(CH_2CH(CH_3)_2)CN$) and V-70 (${}^{\bullet}C(CH_3)(CH_2C$-$(CH_3)_2(OCH_3))CN$) (eq 6–8).

$$NC(R)(CH_3)CN{=}NC(CH_3)(R)CN \rightarrow 2{}^{\bullet}CCH_3(R)CN + N_2(g) \tag{6}$$

$$(TAP)Co^{II\bullet} + {}^{\bullet}CCH_3(R)CN \rightleftharpoons (TAP)Co\text{-}H + CH_2{=}C(R)CN \tag{7}$$

$$(TAP)Co\text{-}H + CH_2{=}C(CH_3)CN \rightleftharpoons (TAP)Co\text{-}C(CH_3)_2CN \tag{8}$$

$$2{}^{\bullet}C(CH_3)_2CN \rightarrow NC(CH_3)_2CC(CH_3)_2CN \tag{9}$$

Reactions of $(TAP)Co^{II\bullet}$ with ${}^{\bullet}CCH_3(R)CN$ radicals from VAZO-52 and V-70 do not produce ^{1}H NMR observable quantities of the organocobalt complexes, $(TAP)Co\text{-}CCH_3(R)$-CN, when the olefin $CH_2{=}C(CH_3)CN$ (0.05–0.50 M) is present. As a result, ${}^{\bullet}CCH_3(R)CN$ functions exclusively as sources of $(TAP)Co\text{-}H$ (eq 7) which can then combine regiospecifically with $CH_2{=}C(CH_3)CN$ to form the Markovnikov product (eq 8). $(TAP)Co\text{-}C(CH_3)_2CN$ and $(TAP)Co^{II\bullet}$ are the only (TAP)-Co containing species observed because $(TAP)Co\text{-}H$ never attains a concentration that is detectable by ^{1}H NMR. Compound **3** initially forms by reaction 8 at a rate that is equal to the rate of radical production from the azo radical sources (Figure 1) which indicates that reactions 7 and 8 are fast relative to 6 and also implies that termination of radicals effectively occurs only through the bimolecular reactions of ${}^{\bullet}C(CH_3)_2CN$ (**2**) (eq 9).

Determination of the molar concentrations of **1** and **3** by integration of the ^{1}H NMR and [**2**] from V and k_t permits evaluation of the equilibrium constants for reaction 5 ($K_5 = [(TAP)Co^{II\bullet}][{}^{\bullet}C(CH_3)_2CN)]/[(TAP)Co\text{-}C(CH_3)_2CN]$).

The temperature dependence of K_5 evaluated by using the three different radical sources (AIBN, VAZO-52, V-70) was used to determine the thermodynamic parameters for the (TAP)-Co-$C(CH_3)_2CN$ homolytic dissociation (Figure 2) ($\Delta H°_5 = 17.8 \pm 0.5$ kcal mol^{-1}; $\Delta S°_5 = 23.1 \pm 1.0$ cal K^{-1} mol^{-1}).

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[13] (a) Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166. (b) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Gonzalez, A. A.; Zhang, K.; Hoff, C. D. *Polyhedron* **1988**, *7*, 1491.

[14] (a) Korth, H. G.; Lommes, P.; Sicking, W.; Sustmann, R. *Int. J. Chem. Kinetics* **1983**, *15*, 267. (b) Zhibin, G.; Combes, J. R.; Menceloglu, Y. Z.; DeSimone, J. M. *Macromolecules* **1993**, 26, 2663.

[15] (a) Handbook of Chemistry and Physics, 71st ed.; CRC Press, Inc.: 1990. (b) Holz, M.; Mao, X.; Seiferling, D.; Sacco, A. *J. Chem. Phys.* **1996**, *104(2)*, 669.

Table 1. Representative Data[a] for the Determination of Equilibrium Constants for the Homolytic Dissociation of (TAP)Co-$CH(CH_3)C_6H_5$ in $CDCl_3$ at Various Temperatures

IN	*T* (K)	[$Co^{II\bullet}$]/[CoR][b]	V^c ($M\ s^{-1}$)	$2k_t$ ($M^{-1}\ s^{-1}$)	[$R^\bullet$][d]	K^e
AIBN	333	1.378	2.40×10^{-6}	2.67×10^{9}	3.00×10^{-8}	$4.13 \pm 0.49 \times 10^{-8}$
AIBN	323	0.7462	5.71×10^{-7}	2.58×10^{9}	1.49×10^{-8}	$1.11 \pm 0.18 \times 10^{-8}$
AIBN	313	0.6693	1.36×10^{-7}	2.50×10^{9}	7.37×10^{-9}	$4.93 \pm 0.63 \times 10^{-9}$
V-70	303	0.08928	1.86×10^{-6}	2.41×10^{9}	2.78×10^{-8}	$2.48 \pm 0.13 \times 10^{-9}$
V-70	296	0.05134	6.62×10^{-7}	2.35×10^{9}	1.68×10^{-8}	$8.62 \pm 0.32 \times 10^{-10}$

[a] For a complete table of data refer to the supporting information. [b] The ratio of molar concentrations [(TAP)$Co^{II\bullet}$]/[(TAP)Co-$CH(CH_3)C_6H_5$]. [c] $V = k_i[IN]$. [d] $[R^\bullet] = [{}^\bullet CH(CH_3)C_6H_5] = (V/2k_t)^{1/2}$. [e] Equilibrium constants reported are averages based on 2–9 measurements.

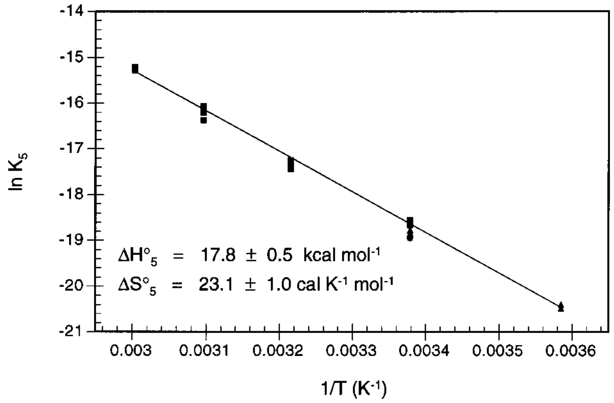


Figure 2. Van't Hoff plot for the homolytic dissociation of (TAP)-Co-$C(CH_3)_2CN$ using initial radical sources (■) AIBN; (●) VAZO-52; or (▲) V-70 (see supporting information for data tables).

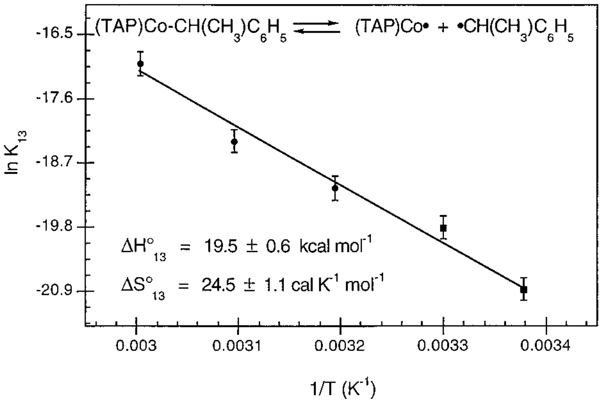


Figure 3. Van't Hoff plot for the homolytic dissociation of (TAP)-Co-$CH(CH_3)C_6H_5$ in $CDCl_3$ (see supporting information for data tables). Radical initiator (■) AIBN; (●) V-70.

Equilibrium Measurements for Reaction of (TAP)$Co^{II\bullet}$ with ${}^\bullet C(CH_3)(R)CN$ and Styrene. Reactions of (TAP)$Co^{II\bullet}$ (**1**) with the radicals produced by AIBN and V-70 in the presence of excess styrene (CH_2=$CH(C_6H_5)$) ([CH_2=$CH(C_6H_5)$] > 10 × [(TAP)$Co^{II\bullet}$]$_i$) result in the formation of the styryl organometallic derivative, (TAP)Co-$CH(CH_3)C_6H_5$ (**5**) (eqs 10–12).

$$IN \rightarrow {}^\bullet C(CH_3)(R)CN\ (R = CH_3,\ CH_2CH(CH_3)_2,\ CH_2C(CH_3)_2OCH_3) \quad (10)$$

$$(TAP)Co^{II\bullet} + {}^\bullet C(CH_3)(R)CN \rightleftharpoons (TAP)Co\text{-}H + CH_2{=}C(R)CN \quad (11)$$

$$(TAP)Co\text{-}H + CH_2{=}CH(C_6H_5) \rightleftharpoons (TAP)Co\text{-}CH(CH_3)C_6H_5 \quad (12)$$

$$(TAP)Co\text{-}CH(CH_3)C_6H_5 \rightleftharpoons (TAP)Co^{II\bullet} + {}^\bullet CH(CH_3)C_6H_5 \quad (13)$$

The styryl complex (**5**) initially forms at a rate equal to the rate that organic radicals enter solution (k_i[IN]) and eventually achieves a steady state concentration. The ratio [**5**]/[**1**] increases linearly with $[IN]^{1/2}$ for each of the initial radical sources and is independent of the molar concentration of styrene when the [CH_2=$CH(C_6H_5)$] is greater than 10 [(TAP)$Co^{II\bullet}$]$_i$. Under these conditions, termination effectively occurs only through bimolecular self termination of styryl radicals and the concentration of styryl radicals, [**6**], is calculated from [**6**] = $(V_{(IN)}/2k_t\text{(styryl)})^{1/2}$, where $V_{(IN)} = k_{i(IN)}[IN]$ is the rate of free radicals entering solution from the radical source (IN) and k_t(styryl) is the radical self-termination rate constant for the styryl radical. The concentration quotient [**5**]/[**1**][**6**] was found to be independent of the choice of IN, [**1**]$_i$ and [**6**], and thus associated with the equilibrium constant (K_{13}) for homolytic bond dissociation of **5** (eq 13).

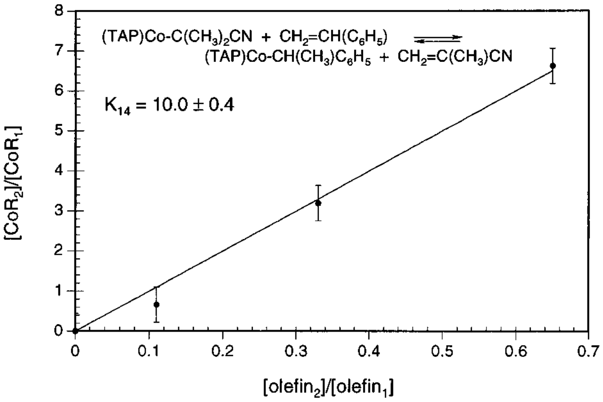


Figure 4. Ratio of the steady state concentrations ([(TAP)Co-$CH(CH_3)C_6H_5$]/[(TAP)Co-$(CH_3)_2CN$]) as a function of the ratio of olefin concentrations ([CH_2=$CH(C_6H_5)$]/[CH_2=$C(CH_3)CN$]). *T* = 333 K, [(TAP)$Co^{II\bullet}$]$_i$ = 9.40 × 10^{-3} M, [AIBN]$_i$ = 0.16 M.

Temperature dependence of K_{13} was used in evaluating the thermodynamic parameters for the bond homolysis of **5** ($\Delta H°_{13} = 19.5 \pm 0.6$ kcal mol^{-1}, $\Delta S°_{13} = 24.5 \pm 1.1$ cal K^{-1} mol^{-1}) (Table 1, Figure 3).

Equilibrium Measurements for Reaction of (TAP)$Co^{II\bullet}$ with ${}^\bullet C(CH_3)_2CN$ and Varying Ratios of [CH_2=$CH(C_6H_5)$] to [CH_2=$C(CH_3)CN$]. In equilibrium experiments where two organometallic species are observable, the equilibrium constant for the reaction CoR_1 + olefin$_2$ ⇌ CoR_2 + olefin$_1$ can be obtained from the experimentally determined ratio of olefins and the measured ratio of molar concentrations of organometallics (CoR_1 and CoR_2). The determination of the equilibrium constant in this case does not require knowledge of the molar concentration of radicals or their rate constants of formation and termination. Equilibrium constants ($K = [CoR_2][olefin_1]/[CoR_1][olefin_2]$) were calculated from the slope of the linear plot through the origin of the ratio of molar concentrations of organometallics as a function of the ratio of molar concentrations of olefins (Figure 4).

Reactions of (TAP)$Co^{II\bullet}$ with ${}^\bullet C(CH_3)_2CN$ from AIBN in the

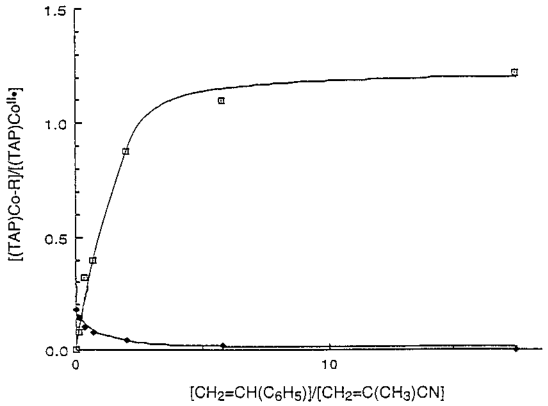


Figure 5. Steady state molar concentration ratios (◆) [(TAP)Co-C(CH$_3$)$_2$CN]/[(TAP)Co$^{II\bullet}$]) and (□) [(TAP)Co-CH(CH$_3$)C$_6$H$_5$]/[(TAP)-Co$^{II\bullet}$]) as a function of the ratio of olefins ([CH$_2$=CH(C$_6$H$_5$)]/[CH$_2$=C(CH$_3$)CN]). $T = 333$ K, [AIBN]$_i$ = 0.16 M. Solid curves are the calculated concentration ratios from kinetic-equilibrium simulations using the rate and equilibrium constants given in the Experimental Section.

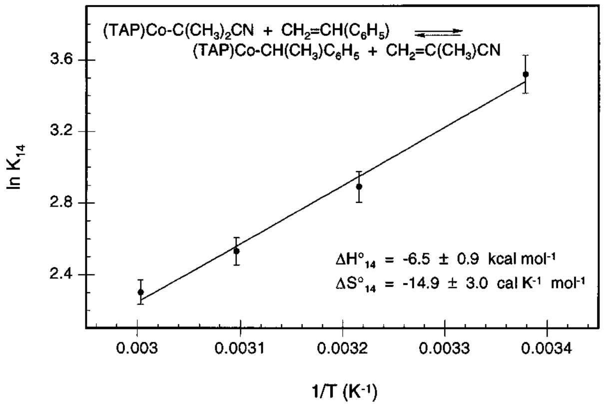


Figure 6. Van't Hoff plot for reaction 14 ((TAP)Co-C(CH$_3$)$_2$CN + CH$_2$=CH(C$_6$H$_5$) ⇌ (TAP)Co-CH(CH$_3$)C$_6$H$_5$ + CH$_2$=C(CH$_3$)CN) using AIBN as the initial radical source.

presence of molar ratios of CH$_2$=C(CH$_3$)CN (**7**) to CH$_2$=CH-(C$_6$H$_5$) (**8**) in the range of 0.1−18 result in ^{1}H NMR observable steady state concentrations of both (TAP)Co-CH(CH$_3$)C$_6$H$_5$ (**5**) and (TAP)Co-C(CH$_3$)$_2$CN (**3**). As the ratio of molar concentrations of styrene to methacrylonitrile ([**8**]/[**7**]) increases, the ratio of steady state concentrations [**3**]/[**1**] decreases, and [**5**]/[**1**] increases until the limiting value is achieved when **3** is no longer observable (Figure 5). These observations indicate that both the styryl and cyanoisopropyl radicals have significant concentrations that maintain simultaneous equilibria for reactions 5 and 13 and that both radicals contribute significantly to bimolecular radical termination events.

The ratio [**5**]/[**3**] at a fixed temperature is invariant to the concentration of radicals and varies linearly with the ratio of olefin concentrations, [**8**]/[**7**]. Plots of [**5**]/[**3**] versus [**8**]/[**7**], including the origin, have a slope corresponding to the equilibrium constant for reaction 14 (K_{14} = [**5**][**7**]/[**3**][**8**]) (Figure 4). Observation that reaction 14 is at equilibrium provides indirect experimental evidence that equilibrium concentrations of (TAP)Co-H (**4**) occur when the organic radicals concentrations are at steady state (eqs 8 and 12) (eq 14 = eq 12 − eq 8).

$$\text{(TAP)Co-C(CH}_3)_2\text{CN} + \text{CH}_2\text{=CH(C}_6\text{H}_5) \rightleftharpoons \text{(TAP)Co-CH(CH}_3)\text{C}_6\text{H}_5 + \text{CH}_2\text{=C(CH}_3)\text{CN} \quad (14)$$

Temperature dependence of K$_{14}$ (Figure 6) provides thermodynamic parameters for reaction 14 ($\Delta H°_{14} = -6.5 \pm 0.9$ kcal mol^{-1}, $\Delta S°_{14} = -14.9 \pm 3.0$ cal K^{-1} mol^{-1}).

Reactions of (TAP)Co$^{II\bullet}$ with $^\bullet$C(CH$_3$)$_2$CN, Methacrylonitrile, and Cyclopentene. Solutions containing (TAP)Co$^{II\bullet}$, CH$_2$=C(CH$_3$)$_2$CN, and cyclopentene (C$_5$H$_8$) react with radicals produced from AIBN to form ^{1}H NMR observable steady state concentrations of both (TAP)Co-C(CH$_3$)$_2$CN (**3**) and (TAP)-Co-C$_5$H$_9$ (**9**). Both **3** and **9** attain steady state concentrations which requires that reactions 8 and 15 are at

$$\text{(TAP)Co-H} + \text{C}_5\text{H}_8 \rightleftharpoons \text{(TAP)Co-C}_5\text{H}_9 \quad (15)$$

equilibrium. Summing the reverse of 8 with reaction 15 gives eq 16 which describes the observable equilibrium stoichiometry for the system when both cyclopentene and methacrylonitrile are present. Equilibrium constants for reaction 16

$$\text{(TAP)Co-C(CH}_3)_2\text{CN} + \text{C}_5\text{H}_8 \rightleftharpoons \text{(TAP)Co-C}_5\text{H}_9 + \text{CH}_2\text{=C(CH}_3)\text{CN} \quad (16)$$

were evaluated by using ^{1}H NMR to measure the molar concentrations of the organometallic species in combination with the experimentally established ratio of cyclopentene to methacrylonitrile (K_{16} = [(TAP)Co-C$_5$H$_9$][CH$_2$=C(CH$_3$)CN]/[(TAP)-Co-C(CH$_3$)$_2$CN][C$_5$H$_8$]). The ratio of the molar concentrations of (TAP)Co-C$_5$H$_9$ to (TAP)Co$^{II\bullet}$ was observed to increase linearly with the increase in the ratio of the molar concentrations of cyclopentene to methacrylonitrile, but the ratio [(TAP)Co-C(CH$_3$)$_2$CN]/[(TAP)Co$^{II\bullet}$] remains constant as the ratio of olefins was varied. The system is at steady state which requires that reaction 5 ((TAP)Co$^{II\bullet}$ + $^\bullet$C(CH$_3$)$_2$CN ⇌ (TAP)Co-C(CH$_3$)$_2$-CN) and reaction 17 are both at equilibrium and thus K_5 and K_{17} must be fulfilled at each different olefin ratio.

$$\text{(TAP)Co-C}_5\text{H}_9 \rightleftharpoons \text{(TAP)Co}^{II\bullet} + {}^\bullet\text{C}_5\text{H}_9 \quad (17)$$

Absence of a measurable change in the ratio [(TAP)Co-C(CH$_3$)$_2$CN]/[(TAP)Co$^{II\bullet}$] indicates that the concentration of $^\bullet$C(CH$_3$)$_2$CN is effectively constant as the olefin ratio is changed. The linear increase in the ratio [(TAP)Co-C$_5$H$_9$]/[(TAP)Co$^{II\bullet}$] with an increase in the olefin ratio ([C$_5$H$_8$]/[CH$_2$=C(CH$_3$)CN]) means that the molar concentration of $^\bullet$C$_5$H$_9$ is increasing linearly. Equilibrium concentrations of both $^\bullet$C(CH$_3$)$_2$CN and $^\bullet$C$_5$H$_9$ occur in solution but the total concentration of radicals in solution ([$^\bullet$C(CH$_3$)$_2$CN] + [$^\bullet$C$_5$H$_9$]) must effectively be equal to the concentration of $^\bullet$C(CH$_3$)$_2$CN radicals. This implies that the coupling of cyanoisopropyl radicals is effectively the only radical termination process that need be considered in this specific case. This is an example of the limiting case where the difference in the organo−cobalt bond dissociation enthalpies is sufficiently large that the organic radical concentration in solution is dominated by homolysis of the Co−R complex with the smaller dissociation enthalpy which in this case is (TAP)-Co-C(CH$_3$)$_2$CN.

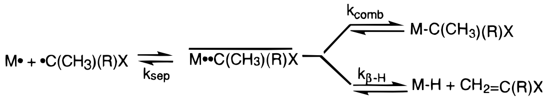
Equilibrium constants for reaction 16 (K_{16}) are obtained from the slope for plots of [(TAP)Co-C$_5$H$_9$]/[(TAP)Co-C(CH$_3$)$_2$CN] versus [C$_5$H$_8$]/[CH$_2$=C(CH$_3$)CN] that include the origin. The temperature dependence of K_{16} was used to determine the thermodynamic parameters, $\Delta H°_{16} = +0.9 \pm 0.3$ kcal mol^{-1}, $\Delta S°_{16} = -4.6 \pm 1.0$ cal K^{-1} mol^{-1} (Figure 7). Experimental values for $\Delta H°_{16}$ (+0.9 kcal mol^{-1}) and $\Delta H°_5$ (−17.8 kcal mol^{-1}) in conjunction with thermochemical data for the reactions of H$^\bullet$ with CH$_2$=C(CH$_3$)CN and C$_5$H$_8$ provides a thermochemical cycle for estimating the bond dissociation enthalpy for (TAP)Co-C$_5$H$_9$ ($\Delta H°_{17} \cong 30.9$ kcal mol^{-1}).

Simulations of Kinetic Equilibrium Measurements. Simulation of the concentration versus time profiles and the equilibrium concentration of (TAP)Co species when the radical concentrations are at steady state were obtained by use of the computer program GEAR adapted by T. E. Beukelman and F. G. Weigert from HAVCHM, written by R. N. Stabler and J. Chesick (*Int. J. Chem. Kinet.* **1978**, *10*, 461−469). The Macintosh version of GEAR and "Mac Kinetics" was designed and edited by W. S. Leipold, J. F. Weiher, and R. J. McKinney (copyright: E. I. DuPont de Nemours, Inc. 1992).

All simulations were done for reactions using AIBN as the initial radical source with an initial concentration of 9.40 × 10^{-3} M for $(TAP)Co^{II\bullet}$ at $T = 333$ K where $k_i(\text{AIBN}) = 1.50 \times 10^{-5}$, $k_t({}^\bullet C(CH_3)_2CN) = 1.33 \times 10^9$ and $K_5 = 2.38 \times 10^{-7}$. Scheme 1 is capable of accurately describing the concentration versus time profiles and the equilibrium constants for reactions involving $(TAP)Co^{II\bullet}$ species.

Discussion

The encounter of a metallo-radical ($M^\bullet$) with an organic radical (${}^\bullet C(CH_3)(R)X$) in solution produces an intermediate solvent caged radical pair ($\overline{M^{\bullet\bullet}C(CH_3)(R)X}$) which can combine to form an organometallic complex ($M\text{-}C(CH_3)(R)X$), separate back into freely diffusing radicals ($M^\bullet + {}^\bullet C(CH_3)(R)X$) and react by $M^\bullet$ abstracting a β-hydrogen from ${}^\bullet C(CH_3)(R)X$ to form a metal hydride (M−H) and an olefin ($CH_2{=}C(R)X$).[5] All three



of these processes that are associated with the intermediate radical pair can be very fast. Combining of the metal and organic radicals occurs with only an entropy barrier, separation into freely diffusing radicals is usually diffusion controlled with a small enthalpy barrier dependent on viscosity,[7] and β-H abstraction often occurs at a competitive rate with separation.[5]

Scheme 1 describes the minimum set of equations needed to describe the observed solution stoichiometry resulting from reactions that occur in a system that initially contains $(TAP)Co^{II\bullet}$, a source (IN) of organic radicals ($R_1^\bullet$) and two olefins

Scheme 1

$$\text{I-1} \quad \text{IN} \rightarrow R_1^\bullet$$

$$\text{I-2} \quad Co^\bullet + R_1^\bullet \rightleftharpoons Co{-}R_1$$

$$\text{I-3} \quad Co{-}R_1 + \text{olefin}_2 \rightleftharpoons Co{-}R_2 + \text{olefin}_1$$

$$\text{I-4} \quad Co{-}R_2 \rightleftharpoons Co^\bullet + R_2^\bullet$$

$$\text{I-5} \quad 2\,R_1^\bullet \rightarrow R_1\text{-}R_1$$

$$\text{I-6} \quad 2\,R_2^\bullet \rightarrow R_2\text{-}R_2$$

$$\text{I-7} \quad R_1^\bullet + R_2^\bullet \rightarrow R_1\text{-}R_2$$

(olefin$_1$, olefin$_2$). Caged radical pairs ($\overline{Co^{\bullet\bullet}R}$) and a cobalt hydride (Co−H) function as intermediates in the formation and interconversion of the observed organometallic complexes (Co−R_1, Co−R_2) (Scheme 1), but they never achieve sufficient concentration to make significant contributions to the observed equilibrium distribution of the cobalt species in solution. When the organic radical species attain steady state concentrations through initiation and termination (I-1, I-5−I-7), reactions I-2−I-4 are at equilibrium, and the concentrations of solution species can be used to evaluate the equilibrium constants for Co−R bond homolysis. Scheme 1 is sufficient for accurate simulation of the concentration versus time profiles for the directly observed species ($Co^\bullet$, Co−R_1, Co−R_2) and calculation of equilibrium concentrations using values from Table 1. The capability for this system to attain equilibrium for all of the (TAP)Co containing species is primarily a consequence of rapid reversible abstraction of $H^\bullet$ from organic radicals by $(TAP)Co^{II\bullet}$ to form (TAP)Co-H and the subsequent fast addition of (TAP)Co-H to olefins. Interconversion of organometallic species (Co−R) by reactions with olefins that attain equilibrium (eq I-3, (TAP)Co−R_1 + olefin$_2$ ⇌ (TAP)Co−R_2 + olefin$_1$) is one observable consequence of the fast formation and reaction of an intermediate cobalt hydride.

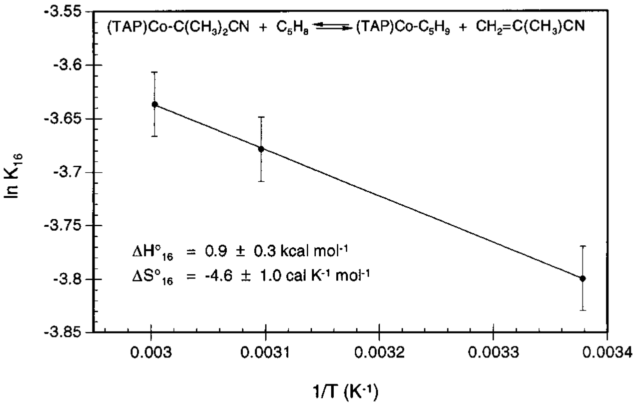


Figure 7. Van't Hoff plot for reaction 16 ($(TAP)Co\text{-}C(CH_3)_2CN + C_5H_8 \rightleftharpoons (TAP)Co\text{-}C_5H_9 + CH_2{=}C(CH_3)CN$) using AIBN as the initial radical source.

Direct Method for the Determination of Equilibrium Constants and Thermodynamic Parameters for M−R Bond Homolysis. Scheme 2 describes the simple case where an organic radical ($R^\bullet$) produced from a radical source (IN) reacts with a metallo-radical ($M^\bullet$) to form an organometallic complex (M−R) and terminates through a bimolecular process. When

Scheme 2

$$\text{II-1} \quad \text{IN} \xrightarrow{k_1} R^\bullet$$

$$\text{II-2} \quad M^\bullet + R^\bullet \rightleftharpoons M{-}R$$

$$\text{II-3} \quad 2R^\bullet \xrightarrow{k_t} R{-}R$$

the organic radical ($R^\bullet$) achieves steady state ($d[R^\bullet]/dt = k_i[\text{IN}] - 2k_t[R^\bullet]^2 = 0$) the organometallic complex (M−R) attains equilibrium with $M^\bullet$ and $R^\bullet$. The concentration of $R^\bullet$ is determined from k_i and k_t ($[R^\bullet] = (k_i[\text{IN}]/2k_t)^{1/2}$), as previously discussed, and if the $[M^\bullet]$ and [M−R] can be measured, then the equilibrium constant for homolytic dissociation of M−R can be directly evaluated. This simple case is illustrated by measurement of the thermodynamics of $(TAP)Co\text{-}C(CH_3)_2CN$ bond homolysis where AIBN is the direct source of ${}^\bullet C(CH_3)_2CN$ ($\Delta H° = 17.7 \pm 0.6$ kcal mol^{-1}, $\Delta S° = 22.8 \pm 1.0$ cal K^{-1} mol^{-1}). This method is most effective for organometallics with relatively weak bonds (M−R < 25 kcal mol^{-1}).

When a convenient source for the radical ($R_2^\bullet$) of the organometallic (M−R_2) is not available then a different initial radical ($R_1^\bullet$) sometimes may be employed as described in Scheme 3. Application of this approach is limited to systems where β-H abstraction from $R_1^\bullet$ by $M^\bullet$ and addition of M-H to olefin$_2$ are fast compared with the rate at which $R_1^{\bullet}$ is produced from the radical source (IN). By adding sufficient olefin$_2$, $M-R_2$ can be made to be the only observed organometallic and $R_2^{\bullet}$ is effectively the only radical involved in termination. When these conditions are fulfilled, the concentration of $R_2^{\bullet}$ ($[R_2^{\bullet}] = (k_i[\mathrm{IN}]/2k_t(R_2^{\bullet}))^{1/2}$) can be used in conjunction with the observed $[M^{\bullet}]$ and $[M-R_2]$ to evaluate equilibrium constants for $M-R_2$ bond homolysis. Good agreement between equilibrium constants for (TAP)Co-C(CH$_3$)$_2$CN bond homolysis determined using V-70 and VAZO-52 as sources of the initial radicals $^{\bullet}C(CH_3)(C(CH_3)_2OCH_3)CN$ and $^{\bullet}C(CH_3)(CH_2CH(CH_3)_2)CN$ respectively, with those obtained using AIBN as a direct source for $^{\bullet}C(CH_3)_2CN$ illustrate the usefulness of this methodology[8] (Table 2, supporting information). This approach was further applied in measuring the (TAP)Co-styryl bond dissociation energetics ($\Delta H° = 19.5 \pm 0.6$ kcal mol^{-1}, $\Delta S° = 24.5 \pm 1.1$ cal K^{-1} mol^{-1}) (Table 1, Figure 3) where a convenient direct source of the styryl radical ($^{\bullet}CH(CH_3)C_6H_5$) is not available. This procedure permits the use of a series of initial radical sources that produce a wide range of steady state radical concentrations at a fixed temperature and allows expansion of the temperature region where measurable equilibria are obtained.

Scheme 3

$$\text{III-1}\quad \mathrm{IN} \rightarrow R_1^{\bullet}$$

$$\text{III-2}\quad M^{\bullet} + R_1^{\bullet} \rightleftharpoons M-R_1$$

$$\text{III-3}\quad M-R_1 + \text{olefin}_2 \rightleftharpoons M-R_2 + \text{olefin}_1$$

$$\text{III-4}\quad M-R_2 \rightleftharpoons M^{\bullet} + R_2^{\bullet}$$

$$\text{III-5}\quad 2R_2^{\bullet} \rightarrow R_2\text{-}R_2$$

The direct methods for determining M−R bond homolysis enthalpies by evaluation of the equilibrium constants is limited by the capability of obtaining steady state concentrations of radicals ($R_2^{\bullet}$) where the concentrations of both $M-R_2$ and $M^{\bullet}$ can be experimentally determined. Relatively stable radical sources can provide steady state concentrations of radicals down to approximately 10^{-13} M which should permit NMR measurement of M−R bond dissociation enthalpies in excess of 30 kcal mol^{-1}.

Indirect Determination of M−R Bond Homolysis Enthalpies. Thermodynamic parameters for M−R bond homolysis can also be obtained by determining equilibrium constants for the competition reaction ($M-R_1 + \text{olefin}_2 \rightleftharpoons M-R_2 + \text{olefin}_1$) (Scheme 3) for use in conjunction with a thermochemical cycle. Application of this approach to estimate the (TAP)Co-CH(CH$_3$)C$_6$H$_5$ bond dissociation enthalpy is illustrated in Scheme 4. Using published values for the heats of formation of organic radicals and olefins,[16] Scheme 4 yields a value of 20.5 kcal mol^{-1} for the (TAP)Co-CH(CH$_3$)C$_6$H$_5$ BDE (Scheme 4) compared with 19.5 kcal mol^{-1} from the direct equilibrium constant evaluation method. This level of agreement is better than expected considering that the heats of formation of organic radicals are generally quoted with error limits greater than ±2 kcal mol^{-1}.

Scheme 4

$$\mathrm{(TAP)Co\text{-}CH(CH_3)C_6H_5 + CH_2{=}C(CH_3)CN \rightleftharpoons (TAP)Co\text{-}C(CH_3)_2CN + CH_2{=}CH(C_6H_5)} \qquad \Delta H° = 6.5\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{(TAP)Co\text{-}C(CH_3)_2CN \rightleftharpoons (TAP)Co^{II\bullet} + {}^{\bullet}C(CH_3)_2CN} \qquad \Delta H° = 17.8\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{{}^{\bullet}C(CH_3)_2CN \rightleftharpoons CH_2{=}C(CH_3)CN + H^{\bullet}} \qquad \Delta H° = 50.5\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{CH_2{=}CH(C_6H_5) + H^{\bullet} \rightleftharpoons {}^{\bullet}CH(CH_3)C_6H_5} \qquad \Delta H° = -54.3\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{(TAP)CoCH(CH_3)C_6H_5 \rightleftharpoons (TAP)Co^{II\bullet} + {}^{\bullet}CH(CH_3)C_6H_5} \qquad \Delta H° = +20.5\ \mathrm{kcal\ mol^{-1}}$$

Scheme 5

$$\mathrm{(TAP)Co\text{-}C_5H_9 + CH_2{=}C(CH_3)CN \rightleftharpoons (TAP)Co\text{-}C(CH_3)_2CN + C_5H_8} \qquad \Delta H° = -0.9\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{(TAP)Co\text{-}C(CH_3)_2CN \rightleftharpoons Co^{II\bullet} + {}^{\bullet}C(CH_3)_2CN} \qquad \Delta H° = 17.8\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{{}^{\bullet}C(CH_3)_2CN \rightleftharpoons CH_2{=}C(CH_3)CN + H^{\bullet}} \qquad \Delta H° = 50.5\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{C_5H_8 + H^{\bullet} \rightleftharpoons {}^{\bullet}C_5H_9} \qquad \Delta H° = -36.5\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{(TAP)Co\text{-}C_5H_9 \rightleftharpoons (TAP)Co^{II\bullet} + {}^{\bullet}C_5H_9} \qquad \Delta H° \cong 30.9\ \mathrm{kcal\ mol^{-1}}$$

When the Co−R$_2$ bond dissociation enthalpy is relatively large, as in the case of (TAP)Co-C$_5$H$_9$, the equilibrium constant for bond homolysis cannot be directly evaluated because the concentration of $R_2^{\bullet}$ at steady state results in nearly complete conversion of (TAP)Co$^{II\bullet}$ to (TAP)Co−R$_2$ such that the equilibrium concentration of (TAP)Co$^{II\bullet}$ becomes too small for observation by ^{1}H NMR. For this case, determination of the enthalpy change for I-3 ($Co-R_1 + \text{olefin}_2 \rightleftharpoons Co-R_2 + \text{olefin}_1$) can be used in conjunction with a thermochemical cycle to estimate the Co−R$_2$ BDE when enthalpies of formation for olefins and radicals are available. The system initially comprised of (TAP)Co^{II}, AIBN, methacrylonitrile, and cyclopentene produces observable equilibrium concentrations of (TAP)Co$^{II\bullet}$, (TAP)Co-C(CH$_3$)$_2$CN, and (TAP)Co-C$_5$H$_9$ and serves to illustrate the application of this case. Determination of the equilibrium constants for reaction I-3 ((TAP)(Co-C(CH$_3$)$_2$CN + C$_5$H$_8$ $\rightleftharpoons$ (TAP)Co-C$_5$H$_9$ + CH$_2$=C(CH$_3$)CN) at several temperatures yields a value of 0.9±0.3 kcal mol^{-1} for the enthalpy change (Figure 7) which can be used in conjunction with the (TAP)Co-C(CH$_3$)$_2$CN bond dissociation enthalpy (17.8 kcal mol^{-1}) and thermochemical parameters for the olefins and organic radicals ($\Delta H_f(C_5H_8) = 8.7$ kcal mol^{-1};[15] $\Delta H_f(^{\bullet}C_5H_9) = 24.3$ kcal mol^{-1})[17] to provide an estimate for the (TAP)Co-C$_5$H$_9$ BDE (30.9 kcal mol^{-1}) (Scheme 5). The reliability of the (TAP)Co-C$_5$H$_9$ BDE estimated by this procedure is limited primarily by the accuracy of thermodynamic parameters available for organic radicals. This method is potentially applicable for the entire range of M−R bond dissociation enthalpies, but is limited to M−R complexes where rapid reversible β-H

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[16] $\Delta H_f(^{\bullet}C(CH_3)_2CN) = 39.8$ kcal mol^{-1};[22] $\Delta H_f(^{\bullet}CH(CH_3)C_6H_5) = 33$ kcal mol^{-1};[18,19] $\Delta H_f(H^{\bullet}(g)) = 52.1$ kcal mol^{-1};[15] $\Delta H_f(CH_2{=}(CH_3)CN) = 38.2$ kcal mol^{-1};[21] $\Delta H_f(CH_2{=}CH(C_6H_5)) = 35.2$ kcal mol^{-1}.[20]

[17] Furuyama, S.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1970**, *2*, 93.

abstraction from $R^•$ by $M^•$ occurs and the heats of formation of olefins and organic radicals ($R^•$) are known.

Estimation of the Enthalpy of Formation of $^•C(CH_3)_2CN$. Observable equilibrium concentrations of (TAP)Co-$C(CH_3)_2$-CN, (TAP)Co-$CH(CH_3)C_6H_5$, and (TAP)$Co^{II•}$ occur for the system produced from (TAP)$Co^{II•}$, AIBN, methacrylonitrile, and styrene which permits evaluation of the equilibrium constants and thermodynamic parameters for III-3 ((TAP)Co-$CH(CH_3)$-C_6H_5 + $CH_2{=}C(CH_3)CN \rightleftharpoons$ (TAP)Co-$C(CH_3)_2CN$ + $CH_2{=}CH$-(C_6H_5) ($\Delta H° = 6.5$ kcal mol^{-1}). This system illustrates how equilibrium measurements for reaction type III-3 can be used to evaluate relative heats of formation for organic radicals when the Co−R bond dissociation enthalpies are known from an independent measurement (Scheme 6). The Co−R bond dissociation enthalpies for (TAP)Co-$C(CH_3)_2CN$ (17.8 kcal mol^{-1}) and (TAP)Co-$CH(CH_3)C_6H_5$ (19.5 kcal mol^{-1}), determined by the direct method, $\Delta H°$ for III-A (6.5 kcal mol^{-1}), and thermodynamic parameters for the styryl radical, styrene, and methacrylonitrile[16,18−21] can be used in evaluating the heat of formation for the cyanoisopropyl radical ($\Delta H_f(^•C(CH_3)_2CN$) = 40.2 kcal mol^{-1}) through Scheme 6 ($\Delta H_f(^•C(CH_3)_2CN) = \Delta H°$(III-E) (−50.1 kcal mol^{-1}) + $\Delta H_f(H^•)$ (52.1 kcal mol^{-1}) + $\Delta H_f(CH_2{=}C(CH_3)CN)$ (38.2 kcal mol^{-1}) = 40.8 kcal mol^{-1}).

Scheme 6

$$\text{III-A}\quad \text{(TAP)Co-}CH(CH_3)C_6H_5 + CH_2{=}C(CH_3)CN \rightleftharpoons \text{(TAP)Co-}C(CH_3)_2CN + CH_2{=}CH(C_6H_5)\qquad \Delta H° = 6.5\ \text{kcal mol}^{-1}$$

$$\text{III-B}\quad \text{(TAP)Co}^• + {}^•CH(CH_3)C_6H_5 \rightleftharpoons \text{(TAP)Co-}CH(CH_3)C_6H_5\qquad \Delta H° = -19.5\ \text{kcal mol}^{-1}$$

$$\text{III-C}\quad \text{(TAP)Co-}C(CH_3)_2CN \rightleftharpoons \text{(TAP)Co}^{II•} + {}^•C(CH_3)_2CN\qquad \Delta H° = 17.8\ \text{kcal mol}^{-1}$$

$$\text{III-D}\quad CH_2{=}CH(C_6H_5) + H^• \rightleftharpoons {}^•CH(CH_3)C_6H_5\qquad \Delta H° = -54.3\ \text{kcal mol}^{-1}$$

$$\text{III-E}\quad H^• + CH_2{=}C(CH_3)CN \rightleftharpoons {}^•C(CH_3)_2CN\qquad \Delta H° = -49.5\ \text{kcal mol}^{-1}$$

The enthalpy of formation for $^•C(CH_3)_2CN$ in $CDCl_3$ evaluated through Scheme 6 ($\Delta H_f(^•C(CH_3)_2CN) = 40.8$ kcal mol^{-1}) compares favorably with the value of 39.8 kcal mol^{-1} determined in the gas phase from low pressure pyrolysis experiments.[22] The accuracy of $\Delta H_f(^•C(CH_3)_2CN)$ determined by this procedure is limited primarily by the quality of thermodynamic data available for the styryl radical.

Halpern has used a combination of kinetic and equilibrium thermodynamic methods for a cobalt−styryl bond homolysis to corroborate a heat of formation of 33 kcal mol^{-1} for the styryl radical by an approach closely related to that employed for evaluating $\Delta H_f(^•C(CH_3)_2CN)$ in this article. Mutual consistency of the solution equilibrium and gas phase heats of formation for the styryl and cyanoisopropyl radicals illustrate the efficacy of the organometallic equilibria methods. Minimally, the organometallic equilibrium approach can be used in choosing the more probable gas phase heats of formation from among the often conflicting reports for organic radicals.[18,23] The solution organometallic method is limited to organic radicals with β-hydrogens and requires an independent measurement of the organometal bond dissociation enthalpy, but systematic application of this approach could substantially advance the scope of reliable heats of formation for organic radicals in solution.

Summary

Equilibria that occur in the reactions of tetra(*p*-anisyl)-porphyrinatocobalt(II), (TAP)$Co^{II•}$, with organic radicals of the form $^•C(CH_3)(R)CN$ in the presence of olefins are used to illustrate several approaches for determining thermodynamic values for organo−metal bond homolysis and heat of formation values for organic radicals in solution. Equilibrium constants for the dissociation process (Co−R $\rightleftharpoons$ $Co^{II•}$ + $R^•$) in $CDCl_3$ were directly evaluated and used in determining thermodynamic values for organo−cobalt bond homolysis of (TAP)Co-$C(CH_3)_2$-CN ($\Delta H° = 17.8 \pm 0.5$ kcal mol^{-1}, $\Delta S° = 23.1 \pm 1.0$ cal K^{-1} mol^{-1}) and (TAP)Co-$CH(CH_3)C_6H_5$ ($\Delta H° = 19.5 \pm 0.6$ kcal mol^{-1}, $\Delta S° = 24.5 \pm 1.1$ cal K^{-1} mol^{-1}). Equilibria of the general form $M{-}R_1$ + olefin$_2$ $\rightleftharpoons$ $M{-}R_2$ + olefin$_1$ were observed to occur and alternately used in evaluating either an organo−metal bond homolysis enthalpy or a heat of formation of an organic radical ($R^•$) through the use of a thermochemical cycles. The (TAP)Co-C_5H_9 bond dissociation enthalpy was found to be too large for accurate evaluation by the direct equilibrium method, but was amenable to estimation indirectly by using thermodynamic values for the reaction (TAP)Co-$C(CH_3)_2CN$ + C_5H_8 $\rightleftharpoons$ (TAP)Co-C_5H_g + $CH_2{=}C(CH_3)CN$ ($\Delta H° = 0.9 \pm 0.3$ kcal mol^{-1}) in conjunction with the heats of formation of the olefins and organic radicals ((TAP)Co-C_5H_9 (BDE = 30.9 kcal mol^{-1})). When independent determinations of the Co−R bond dissociation enthalpies are available, relative heats of formation of organic radicals ($R_1^•$, $R_2^•$) can be derived. The observed enthalpy change for the reaction (TAP)Co-CH-$(CH_3)C_6H_5$ + $CH_2{=}C(CH_3)CN$ $\rightleftharpoons$ (TAP)Co-$C(CH_3)_2CN$ + $CH_2{=}CH(C_6H_5)$ ($\Delta H° = 6.5$ kcal mol^{-1}) in combination with the directly observed (TAP)Co−R bond dissociation enthalpies and $\Delta H_f(^•CH(CH_3)C_6H_5)$ (33 kcal mol^{-1}) was used in evaluating the cyanoisopropyl radical heat of formation ($\Delta H_f(^•C(CH_3)_2$-CN) = 40.8 kcal mol^{-1}). Internal consistency of these results and favorable comparisons with prior gas phase and solution measurements of the heats of formation for the styryl and cyanoisopropyl radicals are indicative of the efficacy for obtaining reliable heats of formation of organic radicals by this equilibrium organometallic approach. Systematic application of these equilibrium methods could substantially broaden the scope and reliability for both organo−metal bond dissociation enthalpies and thermodynamic properties of organic radicals in solution.

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Supporting Information Available: A listing of figures and data tables for all the equilibrium studies discussed (14 pages). See any current masthead page for ordering and Internet access instructions.

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(18) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(19) Ng, F. T. T.; Rempel, G. L.; Mancuso, C.; Halpern, J. *Organometallics* **1990**, *9*, 2762.

(20) Prosen, E. J.; Rossini, F. P. *J. Research Nat'l. Bur. Stds.* **1945**, *34*, 59−63.

(21) Benson, S. W. In *Thermochemical Kinetics*; Wiley, New York, NY, 1968.

(22) King, K. D.; Goddard, R. D. *J. Phys. Chem.* **1976**, *80*, 546.

(23) Robaugh, D. A.; Stein, S. E. *J. Chem. Kinet.* **1984**, *13*, 445.