Figure 1. Decoupled ^{13}C NMR spectra: (A) poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (4) (125 MHz); (B) (*E*)-1,4-bis(methyldiphenylsilyl)-1-buten-3-yne (2) (22.5 MHz).

resulting substance was reprecipitated twice from benzene-ethanol to give a light yellow polymer in 73% yield. The polymer thus obtained is soluble in common organic solvents such as benzene, toluene, chlorocarbons, and ethers and melts at 90–95 °C without decomposition. Molecular weight of 4 was determined to be $\overline{M_w}$ = 117 000 relative to polystyrene standards ($\overline{M_w}/\overline{M_n}$ = 6.1). The presence of the (disilanylene)butenyne structure in the polymer backbone was confirmed by its ^{13}C NMR spectrum. Thus, the ^{13}C NMR spectrum of 4 shows resonances at 91.2, 91.3, 91.5, 91.6, 109.81, 109.84, 109.9 ppm and 125.8, 125.9, 142.5, 142.8 ppm, due to ethynylic and ethylenic carbons, respectively. These chemical shifts are consistent with those of product 2 as shown in Figure 1. The existence of four nonequivalent resonances for methylsilyl carbons of 4 indicates that the C–H bond activation by a rhodium complex occurs in the ethynyl group of the starting monomer and of the polymeric systems.

Recently, it has been reported that the reaction of α,ω-bis(ethynyldimethylsilyl)-substituted compounds involving 1,2-diethynyltetramethyldisilane[6] with a tungsten chloride catalyst resulted in formation of polyenes arising from cyclopolymerization.[7] In the present case, however, 1,2-diethynyltetramethyldisilane (5) reacted with a rhodium catalyst at room temperature to give poly[(tetramethyl-

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(8) Compound 6: mp >300 °C; ^1H NMR (δ in CDCl$_3$) 0.13 (3 H, s, MeSi), 0.23 (3 H, s, MeSi), 0.22 (3 H, s, MeSi), 0.29 (3 H, s, MeSi), 5.90 (1 H, d, J = 19 Hz, olefinic proton), 5.96 (1 H, d, J = 19 Hz, olefinic proton); ^{13}C NMR (δ in CDCl$_3$) –4.6, –4.5, –3.0, –2.9 (MeSi), 92.8, 93.0, 108.0 (C≡C), 123.9, 124.1, 144.7, 145.0 (C=C); IR $\nu_{C≡C}$ 2149 cm^{-1}; UV (film) λ_{max} 293 nm.

disilanylene)butenyne-1,4-diyl] (6) whose molecular weight was calculated to be $\overline{M_w}$ = 28 000 by GPC ($\overline{M_w}/\overline{M_n}$ = 13.0).

Polymers 4 and 6 can be cast to a thin film by spin coating of their methylene chloride solution. The polymers exhibit strong absorption at near 290 nm and are photoactive in the ultraviolet. Irradiation of thin solid films of 4 and 6 with a low-pressure mercury lamp in air led to the disappearence of the absorption at near 290 nm indicating that homolytic scission of silicon–silicon bonds in the polymer backbone occurred, as observed in the photolysis of poly[*p*-(disilanylene)phenylene].[9]

To our surprise, when the films of 4 and 6 were doped by exposure to vapor of SbF$_5$, the conducting films were obtained. The conductivity determined by the four-probe method showed to be 1.09 S·cm^{-1} for 4 and 0.02 S·cm^{-1} for 6, respectively.[10]

(9) Nate, K.; Ishikawa, I.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673.
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Iodinolysis of the Co–C Bond in *trans*-Bis(dimethylglyoximato)alkyl(4-cyanopyridine)cobalt(III) Complexes: Evidence for a Bimolecular Oxidative Mechanism

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Summary: The iodinolysis of 4CNpyCo(DH)$_2$R (4CNpy = 4-cyanopyridine; R = CH$_3$, CH$_2$CH$_3$, CH$_2$CH$_2$CH$_3$, CH-(CH$_3$)$_2$, CH$_2$C$_6$H$_5$, CH$_2$CF$_3$) in benzene solution is first-order with respect to both the concentration of organocobalt-(III) complex and iodine. The appearance of a transient EPR signal due to an organocobalt(IV) intermediate and the strong correlation of the logarithm of the pseudo-first-order rate constants for iodinolysis with reversible oxidation potentials along with other pertinent observations strongly suggest that the rate-limiting step of the reaction is oxidation of the six-coordinate organocobalt-(III) complex by iodine.

The mechanism of the cleavage of cobalt–carbon (Co–C) bonds in vitamin B$_{12}$ model compounds by molecular halogens has been the object of intense study[1,2] ever since it was demonstrated that iodinolysis of the Co–C bond in coenzyme B$_{12}$ and [CH$_3$Co(CN)$_5$]$^{3-}$ gives 5′-iodo-5′-deoxy-

(1) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105.
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Table I. Rate Constants for Reaction 1 (L = 4CNpy)[a] and EPR Parameters[b] for the Corresponding [4CNpyCo(DH)₂R]⁺

R	k,[c] 10^4 s⁻¹	k,[d] 10^3 M⁻¹ s⁻¹	g	A_{iso}^{Co}, 10^4 cm⁻¹
$CH_2C_6H_5$	61.3	15.3	2.030	12.0
$CH(CH_3)_2$	60.6	15.2	2.029	12.4
$CH_2CH_2CH_3$	46.8	11.7	2.025	12.0
CH_2CH_3	25.2	6.3	2.030	12.0
CH_3	8.2	2.1	2.024	11.3
CH_2CF_3	0.005	0.0013	e	e

[a] In benzene solution, 305 ± 0.5 K; [4CNpyCo(DH)₂R] = 0.040 M, [I₂] = 0.40 M. [b] In benzene solution, ambient temperature; relative to external DPPH. [c] Pseudo-first order rate constant; average of three trials; standard deviation is ca. ±10%. [d] Second-order rate constant; standard deviation is ca. ±10%. [e] Not observed.
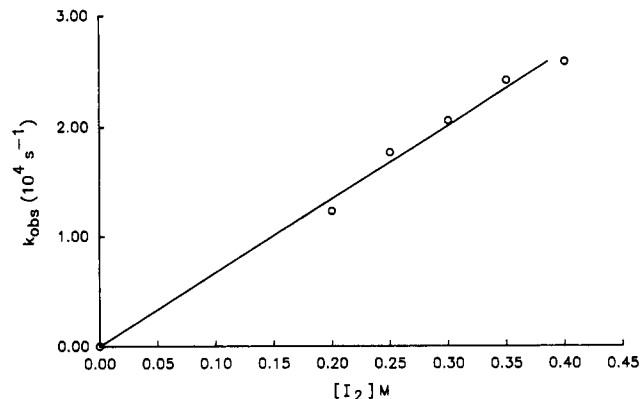
adenosine[3] and CH_3I,[4] respectively. For strong oxidizing agents such as Cl_2, Br_2, and ICl, oxidation of the organocobalt(III) complex to an organocobalt(IV) intermediate is inferred either from product and stereochemical analyses[5-8] and/or by detection of EPR signals characteristic of Co(IV) cationic complexes.[9,10] For the weaker oxidizer I_2, an emerging body of evidence suggests that single electron-transfer processes also may play a significant role in iodinolyses of the Co–C bond.[11,12]

Recently, some of us reported upon the determination of absolute Co–C bond disruption enthalpies in the bis-(dimethylglyoximato)alkyl(pyridine)cobalt(III) system[13] using iodinolytic[14] solution thermochemical techniques (see eq 1, L = pyridine (py), DH = the monoanion of dimethylglyoxime, and R = alkyl ligand). Although the

$$LCo(DH)_2R + I_2 \rightarrow LCo(DH)_2I + RI \qquad (1)$$

exact mechanism of reaction 1 is immaterial to the thermodynamic calculations, we were intrigued by a report by Okamoto et al.[11a] that the rate-determining step for reaction 1 in benzene solution (for L = py and R = substituted benzyl) is slow dissociation of the py ligand, as determined from kinetic analyses of visible absorption spectra. Subsequent rapid oxidation of the five-coordinate complex by I_2 is postulated on the basis of product analyses.

In this contribution, we report upon our kinetic results for reaction 1 in benzene solution with L being 4-cyanopyridine (4CNpy) and R encompassing a wider structural range of alkyl groups than in the Okamoto[11a] study utilizing ¹H NMR spectroscopy. Changes in concentration of reactant and product complexes were monitored via the

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(13) Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166.
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Figure 1. k_{obs} for reaction 1 (L = 4CNpy; R = CH_2CH_3) versus concentration of iodine. The concentration of complex in each case was 0.020 M; each point is the average of at least three trials; T = 305 ± 0.5 K.
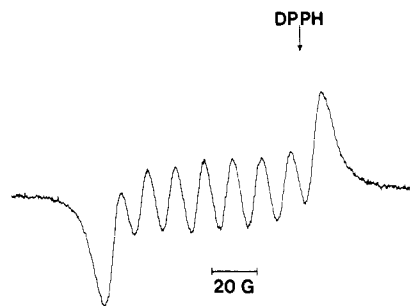
Figure 2. The EPR spectrum observed during the reaction of 4CNpyCo(DH)₂CH₂C₆H₅ with excess I_2 in benzene solution at ambient temperature. Microwave frequency was 9.26 GHz at 3.5 mW power, while the modulation amplitude was 0.82 G at 100 kHz. Other alkyl cobalt(III) complexes gave comparable spectra when reacted with I_2 (see Table I).

intense DH–CH₃ resonances in the spectra. 4CNpy rather than py was employed in the present investigation because rates were conveniently slow over the entire range of alkyl ligands facilitating the NMR technique. In addition, the DH–CH₃ resonances of the starting organocobalt(III) complexes with L = py, unlike their 4CNpy counterparts, were severely broadened throughout the duration of the reaction with I_2, which significantly limited the accuracy of the kinetic analyses in these cases.

Pseudo-first-order (10 times excess of I_2) rate constants for reaction 1 (L = 4CNpy; R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2C_6H_5$, $CH(CH_3)_2$, CH_2CF_3) are collected in Table I. The reactions were first-order in organocobalt(III) complex for at least 2.5–3.0 half-lives (correlation coefficients (r) were generally greater than 0.995), cleanly giving 4CNpyCo(DH)₂I and alkyl iodide as determined by ¹H NMR spectral comparisons to authentic samples. Exclusion of dioxygen has virtually no effect on the rates. For R = CH_2CH_3, a plot of k_{obs} versus [I₂] (see Figure 1) is linear (slope = 6.72 × 10⁻³ M⁻¹ s⁻¹; r = 0.996) and passes through the origin (intercept = −1.7 × 10⁻⁶). Similar results were obtained for R = $CH_2C_6H_5$ (slope = 2.04 × 10⁻² M⁻¹ s⁻¹; intercept = −5.8 × 10⁻⁴) with somewhat more scatter (r = 0.97) due to the intrinsically faster reactions.

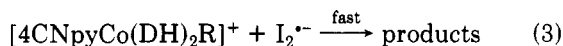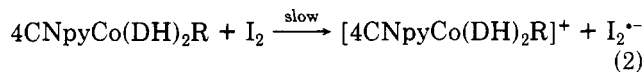In addition, a small steady-state eight-line ($I = \frac{7}{2}$ for ⁵⁹Co) EPR signal that has g and A_{iso}^{Co} values characteristic for low-spin bis(glyoximato)cobalt(IV) cationic complexes at room temperature[9,10,15] develops in all cases immediately after the reactants are mixed (see Figure 2 and Table I).

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The signal persists during the reaction, then diminishes in intensity, and finally vanishes at completion. Neither solutions of pure organocobalt(III) complex, nor solutions of I_2, by themselves exhibit this EPR signal.

One possible mechanism in accord with the above observations would involve rate-determining oxidation of the six-coordinate organocobalt(III) complex by I_2 followed by rapid collapse inside the solvent cage to products:[16]

$$4CNpyCo(DH)_2R + I_2 \xrightarrow{\text{slow}} [4CNpyCo(DH)_2R]^+ + I_2{}^{\bullet-} \tag{2}$$

$$[4CNpyCo(DH)_2R]^+ + I_2{}^{\bullet-} \xrightarrow{\text{fast}} \text{products} \tag{3}$$

Besides the agreement with the overall second-order rate law and the appearance of the EPR signal, we note the following arguments. For R = CH_3, an essentially identical rate constant $(7.71 \pm 0.24 \text{ s}^{-1})$ was calculated employing Co–CH_3 and CH_3I resonances in the kinetic analysis rather than DH–CH_3 resonances, which along with the other available evidence suggests that both $4CNpyCo(DH)_2I$ and CH_3I form quickly in step(s) subsequent to the rate-determining step. The rate of reaction 1 in $CHBr_3$ solution for analogous conditions and concentrations of reactants (L = 4CNpy; R = CH_3 or CH_2CH_3) is ca. 3–4 times faster than that found in benzene solution.[17a] Such a result might be expected in going from benzene to the more polar $CHBr_3$ if formation of charged intermediates occurs in the slow step of the reaction.[17b] Both benzene and $CHBr_3$ should be essentially noncoordinating in this particular system. For reaction 1 with L = 4CNpy and R = $CH_2C_6H_5$, an eight-line EPR signal develops in $CHBr_3$ that is nearly identical $(g = 2.030, A_{iso}{}^{Co} = 11.8 \times 10^{-4} \text{ cm}^{-1})$ to that found in benzene solution, implying that a similar mode of reaction is occurring in both solvents.

No dependence of the rate upon [4CNpy] was noted for R = CH_2CH_3 or $CH_2C_6H_5$ for up to 4 times excess of added 4CNpy in benzene solution. Furthermore, there is no correlation of the pseudo-first-order rate constants for reaction 1 and known rate constants[18,19] for dissociative ligand exchange for this system in CH_2Cl_2 solution (see eq 4). For instance, the rate constants of iodinolysis for

$$4CNpyCo(DH)_2R + L \rightarrow LCo(DH)_2R + 4CNpy \tag{4}$$
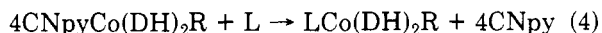
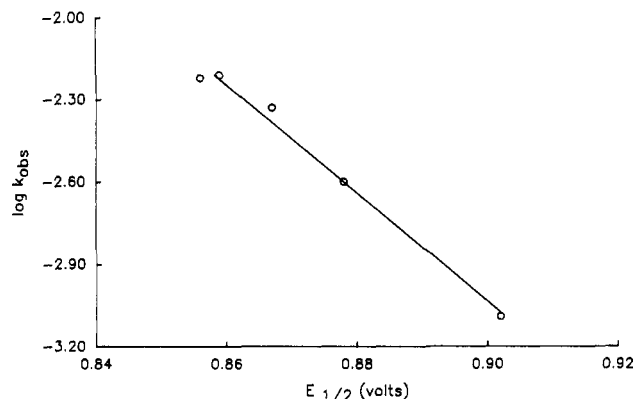$4CNpyCo(DH)_2R$ (R = $CH_2C_6H_5$, $CH(CH_3)_2$) are virtually identical, although for the same complexes the rate con-

Figure 3. Log k_{obs} for reaction 1 (L = 4CNpy) versus $E_{1/2}$ (Co-(III)/Co(IV)) for $H_2OCo(DH)_2R$.[23,24] Points are (from left to right): R = $CH(CH_3)_2$, $CH_2C_6H_5$, $CH_2CH_2CH_3$, CH_2CH_3, and CH_3.

stants for ligand exchange differ by nearly 2 orders of magnitude.[18,19] While accurate rate measurements for the reaction of $LCo(DH)_2CH_3$ (L = pyridine or 1-methylimidazole) with I_2 using the ^1H NMR technique are precluded by significant broadening of the DH–CH_3 ^1H NMR resonances of the starting complexes, the reactions are over within a minimum of 5–10 min as estimated by total disappearance of any integrated intensity for the starting organocobalt(III) complex. Likewise, disappearance of the Co(IV) signal in the EPR spectra occurs within the same time frame. These reaction time periods are considerably shorter than for L = 4CNpy (5 half-lives = 70 min). The corresponding relative dissociative ligand exchange constants for $LCo(DH)_2CH_3$ are 164 (L = 4CNpy), 32 (py), and 1 (1MeIm).[19] This series also argues against prior rate determining dissociation of the ligand trans to the alkyl ligand in these cases, since we would predict the 4CNpy complex to react with I_2 the most quickly from the observed order.

Co–C bond cleavage apparently is not important in the rate-determining step as well since there is nearly a 9 kcal/mol difference in bond disruption enthalpies for $pyCo(DH)_2R$ (R = $CH_2C_6H_5$ and $CH(CH_3)_2$)[13] and essentially no variation in iodinolysis rate constants for $4CNpyCo(DH)_2R$ (R = $CH_2C_6H_5$ and $CH(CH_3)_2$). Although the Co–C bond disruption enthalpies for the $4CNpyCo(DH)_2R$ complexes are not known and likely are not precisely the same as for the analogous py complexes,[20] we would expect approximately parallel values in the two series, since 4CNpy and py are sterically similar based upon relevant crystal structure determinations.[19] Direct electrophilic attack of I_2 on the alkyl ligand also appears unlikely since the order of increasing rate found here is opposite to that observed for S_E2 electrophilic cleavage in analogous complexes by Hg^{2+} ion.[21,22]

On the other hand, excellent linear correlation $(r = 0.994)$ between log k_{obs} for reaction 1 and reversible oxidation potentials[23,24] for the corresponding $H_2OCo(DH)_2R$ complexes is evident in Figure 3. Similar observations have been reported recently for other alkyl cobalt(III) complexes and ferrocenyl compounds in acetonitrile solu-

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(16) (a) Equation 3 likely occurs as a sequence of reactions rather than as a single step. One plausible route to the observed products involves nucleophilic cleavage of the Co–R bond:[7]

$$I_2{}^{\bullet-} \rightarrow I^{\bullet} + I^- \tag{3a}$$

$$[4CNpyCo(DH)_2R]^+ + I^- \rightarrow [4CNpyCo(DH)_2] + RI \tag{3b}$$

$$[4CNpyCo(DH)_2] + \tfrac{1}{2}I_2 \rightarrow [4CNpyCo(DH)_2I] \tag{3c}$$

Alternatively, another possible mechanism includes homolytic cleavage of the Co–C bond:[16b]

$$[4CNpyCo(DH)_2R]^+ \rightarrow [4CNpyCo(DH)_2]^+ + R^{\bullet} \tag{3d}$$

$$R^{\bullet} + I_2{}^{\bullet-} \rightarrow RI + I^- \tag{3e}$$

$$[4CNpyCo(DH)_2]^+ + I^- \rightarrow [4CNpyCo(DH)_2I] \tag{3f}$$

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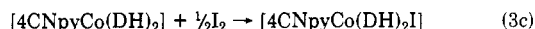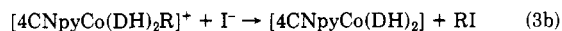(20) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 621.

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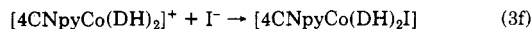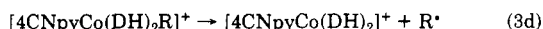
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tion.[11b] As expected for a slow initial single electron transfer, a large rate retardation (3–4 orders of magnitude) is observed for the complex with the weakly electron-donating CH_2CF_3 group.[25] In addition, it might be expected that $LCo(DH)_2CH_3$ might be more easily oxidized for more basic ligands (L = py and 1MeIm) than for poorer electron donors (L = 4CNpy), thus leading to the observed higher rates for the former compounds.

At this time it is difficult to reconcile completely these results with the earlier study by Okamoto et al.[11a] involving the interaction of I_2 with $pyCo(DH)_2(CH_2C_6H_4R-p)$ in benzene. A priori, a five-coordinate Co(III) complex would be expected to be much less susceptible to oxidation than the corresponding six-coordinate compound.[19] We note that in an investigation of the iodinolysis of alkylcobalamins by I_2 in aqueous solution,[11c] the base-on form was found to be 16 times more reactive than the base-off form. We feel that it is unlikely that the change from py to 4CNpy is responsible for an alteration in mechanism caused by a possible inner-sphere interaction of the I_2 electrophile with the cyano group. Previous investigations[26,27] involving uncoordinated 4CNpy in CCl_4 solution have indicated that this should have low probability. Further, in our hands the rates do not parallel known dissociative ligand exchange kinetic data (vide supra).[18,19]

A possible explanation might be that for L = py the oxidation reaction analogous to eq 2 proceeds relatively to completion before decomposition to products in subsequent slower step(s). The severely broadened ^1H NMR spectra in the L = py or 1MeIm cases lend support to this scenario. If the Co–C bond cleavage then proceeds without direct intervention of I_2 (most likely either through a nucleophilic attack on $[4CNpyCo(DH)_2R]^+$ by I^- formed from $I_2^{\bullet-}$ in the ion pair within the solvent cage[6,7] or via radical processes[16]), then the zero-order behavior with respect to

$[I_2]$ can be explained. In the L = 4CNpy case, oxidation (eq 2) is rate limiting so that overall second-order kinetics are observed, since this reaction step requires I_2. We have not observed any inverse dependence upon $[I_2]$ due to reaction of I^- with excess I_2 to give I_3^- as was reported for the reaction of alkylcobalamins with I_2 in aqueous solution.[11c] This may be a result of ion pair formation in the nonpolar benzene,[28] which is followed by rapid collapse to products.

The rate retardation due to added py was noted by Okamoto et al.[11a] at relatively large excesses of py, where [py] was 2–10 times greater than $[I_2]$ and 60–300 times greater than the concentration of the organocobalt(III) complex. A 1:1 py:I_2 complex with formation constant equal to 60–80 is known to form in CCl_4.[26,27] Presumably, this molecular complex is not likely to be electrophilic and could possibly tie up sufficient amounts of I_2 to retard the oxidation reaction rate.

In summary, the reaction of $4CNpyCo(DH)_2R$ (R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2C_6H_5$, $CH(CH_3)_2$, CH_2CF_3) with I_2 in benzene solution was found to be first-order in both organocobalt(III) complex and I_2. The detection of a small concentration of Co(IV) complex via EPR spectroscopy, combined with the linear correlation between log k_{obs} and reversible oxidation potentials and other relevant observations, strongly suggests that rate-limiting single electron transfer (probably outer-sphere in nature[11b,25,29]) from the six-coordinate organocobalt(III) complex to I_2 occurs. Further work is in progress to attempt to delineate steps in the mechanism subsequent to electron transfer.

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