

[Hydrotris(3-isopropyl-5-methylpyrazolyl)borato]-iodocobalt(II): Unusual Purification by "Inverse Recrystallization"

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Introduction

In our search for homogeneous oxidation catalysts we are investigating sterically hindered tris(pyrazolyl)borate complexes. For example, hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate (Tp') stabilizes the unusual side-on bonded superoxo-cobalt complex Tp'Co^{II}(O₂).¹ During our study of this complex there arose the need to prepare an analogous molecule with isopropyl groups in place of the *tert*-butyl substituents of the pyrazolyl rings.² As a starting material for this chemistry, we prepared and structurally characterized Tp''Co^{II}I (Tp'' = hydrotris(3-isopropyl-5-methylpyrazolyl)borate). The separation of the latter from its regioisomers takes advantage of a rather unusual solubility effect, termed "inverse recrystallization" in our laboratory. The potential utility of this phenomenon in related systems and our completed investigation of its origin prompt this note.

Experimental Section

Commercial reagents were used as supplied. All manipulations involving cobalt complexes were carried out under nitrogen using a Vacuum Atmospheres inert-atmosphere box or standard Schlenk and high-vacuum techniques. Hydrocarbon and ether solvents were purified by distillation from purple sodium benzophenone ketyl. MeCN was purified by distillation from P₂O₅ and stored over 3A molecular sieves; C₆D₆ was dried with Na and stored over Na/K. CH₂Cl₂ and CD₂Cl₂ were distilled from CaH₂ and stored over 4A molecular sieves.

¹H-NMR spectra were recorded on a Bruker WM-250 NMR. UV/vis/near-IR spectra were obtained using a Bruins Instruments Omega 20 spectrophotometer. IR spectra were obtained on a Mattson Instruments Alpha Centauri FTIR. Magnetic susceptibilities (at room temperature) were measured using a Johnson-Matthey Magnetic Susceptibility balance. Melting points were measured using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

Synthesis of Tp''CoI. A mixture of 3-*i*-Pr-5-Me-pyrazole (7.0 g, 56 mmol) and KBH₄ (0.60 g, 11 mmol) was heated to 210 °C under argon for 12 h under ambient pressure and then for 12 h under reduced pressure in order to distill out all the unreacted pyrazole. The crude glassy product was dissolved in dry THF (50 mL) saturated with KI (1 g, 6 mmol). CoI₂ (7 g, 22 mmol) was added, and the mixture was stirred overnight at room temperature. The solution was then evaporated to dryness, extracted with pentane (5 × 50 mL), and filtered through Celite. Removal of the solvent under vacuum yielded a blue crystalline material (6 g, 10.6 mmol, 95% based on KBH₄). This was a mixture of three regioisomers in a 43/43/14 ratio, respectively, as determined by ¹H NMR (C₆D₆): Tp''CoI (**1a**), -39 (B-H), 9.0 (6 Me), 15.8 (3 Me), 19.6 (3 H_{*i*-Pr}), 81.8 (3 H_{*pz*}); [HB(3-*i*-Pr-5-Me-pz)₂(5-*i*-Pr-3-Mepz)]CoI (**1b**), -39 (B-H), -1.3 (2 Me), 1.2 (1 H_{*i*-Pr}), 7.7 (2 Me), 8.6 (2 Me), 15.3 (2 H_{*i*-Pr}), 16.7 (3 Me), 77.9 (1 H_{*pz*}), 82.7 (2 H_{*pz*}); [HB(3-*i*-Pr-5-Me-pz)(5-*i*-Pr-3-Me-pz)₂]CoI (**1c**), -39 (B-H), -0.7 (2 Me), -0.4 (2 Me), 1.2 (2 H_{*i*-Pr}), 8.0 (2 Me), 13.0 (1 H_{*i*-Pr}), 14.7 (2 Me), 17.6 (1 Me), 81.1 (2 H_{*pz*}), 85.5 (1 H_{*pz*}).

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Purification of Tp''CoI by "Inverse Recrystallization". The isomeric mixture obtained above was suspended in 20 mL of acetonitrile at room temperature, and the suspension was then cooled to -30 °C. The resulting greenish-yellow homogeneous solution was allowed to warm back to room temperature, at which point a blue solid crystallized. This was collected by filtration, and its ¹H-NMR showed an enrichment in the desired Tp''CoI (**1a**) at the expense of the other regioisomers: the ratio was now 74/21/5 (for comparison, one conventional recrystallization from pentane yielded a mixture with the proportions 45/24/31). The recrystallization was repeated twice, to finally afford isomerically pure Tp''CoI as big, blue cubic crystals (1.26 g, yield = 20%). Mp: 212 °C dec. IR (KBr): 2524 (ν_{BH}) cm⁻¹. MS (EI): *m/e* 567 (M⁺, 0.4%), 440 (100%). μ_{eff}(RT) = 5.0(1) μ_B. Anal. Calcd for C₂₁H₃₄BCoIN₆: C, 44.47; H, 6.04; N, 14.82. Found: C, 44.40; H, 6.33; N, 14.84.

Variable-Temperature ¹H-NMR. In the drybox an NMR tube equipped with a J-Young valve was charged with 37 mg (0.065 mmol) of isomerically pure Tp''CoI. A 0.36-mL volume of CD₂Cl₂ was then vacuum transferred into the tube, and three sets of NMR spectra were recorded at various temperatures with 0, 5.7, and 12.7 molar equiv of CH₃CN (relatively to Tp''CoI), also added by vacuum transfer. ¹H-NMR (CD₂Cl₂, 191.5 K; see Figure 2A): 137 (3H, H_{*pz*}), 42.5 (3H, -CH(CH₃)₂), 24 (18H, -CH(CH₃)₂), 19.5 (9H, -CH₃), -94 (1H, BH). ¹H NMR (CD₂Cl₂, 5.7 equiv of CH₃CN, 191.5 K; see Figure 2B): 177 (1H, BH), 83 (3H, H_{*pz*}), 74 (9H, -CH₃), 2.02 (free CH₃CN), -23 (9H, coordinated CH₃CN), -61 (18H, -CH(CH₃)₂), -195 (3H, -CH(CH₃)₂). The relative integration of the resonances provided the relative ratio of the blue and yellow species and free acetonitrile as a function of the temperature. Absolute concentrations were corrected for the thermal contraction of the solvent.

Results and Discussion

Heating of KBH₄ with an excess of 3-isopropyl-5-methylpyrazole yielded a mixture of regioisomeric tris(pyrazolyl)borates, as previously reported.² Whereas the larger difference in steric bulk between the *tert*-butyl and methyl substituents of the Tp' ligand accounts for the formation of a single isomer with the bulkier *tert*-butyl groups occupying all 3-positions, in the case of Tp'' the relatively smaller difference between isopropyl and methyl groups results in a lack of regioselectivity. Thus, reaction of the mixture of tris(pyrazolyl)borates with an excess of cobaltous iodide produced a mixture of regioisomeric cobalt complexes in 95% yield. ¹H NMR analysis of the crude pentane extract from this reaction revealed a multitude of isotropically shifted resonances expected of tetrahedral Co(II) complexes. However, the distinct resonances of the protons in the pyrazolyl 4-position (at ca. 80 ppm) indicated the presence of three major isomers **1a-c**, formed in a ratio of ca. 3:3:1. On the basis of their NMR spectra, we assigned to them the structures [hydrotris(3-isopropyl-5-methylpyrazolyl)borato]iodocobalt(II) (Tp''CoI, **1a**), [hydrobis(3-isopropyl-5-methylpyrazolyl)(5-isopropyl-3-methylpyrazolyl)borato]iodocobalt(II) (**1b**), and [hydrido(3-isopropyl-5-methylpyrazolyl)bis(5-isopropyl-3-methylpyrazolyl)borato]iodocobalt(II) (**1c**). After some experimentation, we discovered a simple procedure—subsequently named "inverse recrystallization"—for the separation of the mixture and purification of the desired isomer **1a**. The crude product did not dissolve in CH₃CN at room temperature, forming merely a blue suspension. However, cooling of this suspension to -30 °C effected dissolution of the solid and formation of a yellow-green homogeneous solution. Upon rewarming of the solution to room temperature, a blue solid crystallized, which proved to be significantly enriched in **1a**. After two repetitions of this procedure isomerically pure Tp''CoI was obtained in 20% overall yield and in the form of big blue cubes.

The structure of Tp''CoI has been determined by X-ray diffraction, and the result is shown in Figure 1. Selected interatomic distances and angles are listed in the figure caption. The geometry of the four-coordinate Co is roughly tetrahedral, with N-Co-N angles and N-Co-I angles averaging 93.9 and 122.5°, respectively. The iodide lies essentially on the pseudo-3-fold axis defined by B1 and Co1, and the Co-I distance (2.538-(2) Å) falls within the range of previously determined bond lengths

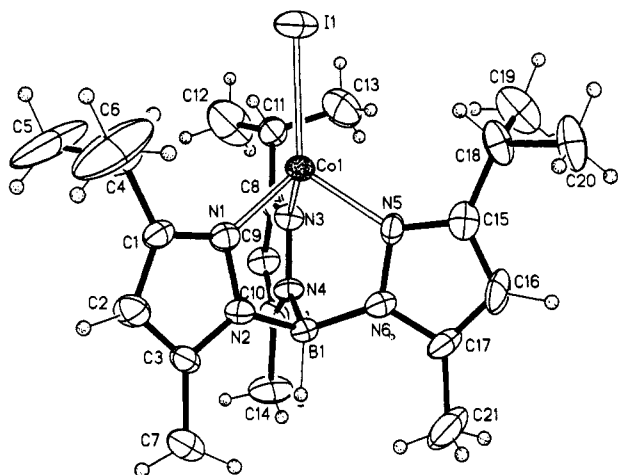


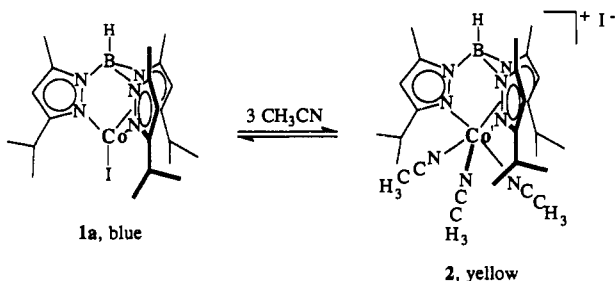
Figure 1. Molecular structure of $\text{Tp}''\text{CoI}$ (**1a**). Selected interatomic distances (Å) and angles (deg): Co1-I1 , 2.538(2); Co1-N1 , 2.030(8); Co1-N3 , 2.010(8); Co1-N5 , 2.013(8); I1-Co1-N1 , 121.5(2); I1-Co1-N3 , 123.0(2); I1-Co1-N5 , 122.6(3); N1-Co-N3 , 94.1(3); N1-Co-N5 , 95.3(3); N3-Co-N5 , 92.7(3). Only one of the two crystallographically independent molecules is shown.

Table 1. Crystallographic Data for $\text{Tp}''\text{CoI}$

$\text{C}_{21}\text{H}_{34}\text{BCoIN}_6$	$fw = 567.2$
$a = 16.077(3)$ Å	$P2_1/c$
$b = 18.013(4)$ Å	$\lambda = 0.71073$ Å
$c = 19.880(4)$ Å	$\rho_{\text{calc}} = 1.404$ g cm^{-3}
$\beta = 111.19(3)^\circ$	$\mu = 1.793$ mm^{-1}
$V = 5368(2)$ Å ³	transm coeff = 1.10
$Z = 8$	$R(F)^a = 5.50\%$
$T = 25$ °C	$R_w(F)^a = 5.89\%$

^a $R(F) = \sum |F_o - F_c| / \sum (F_o)$ and $R_w(F) = \sum [|F_o - F_c| w^{0.5}] / \sum [F_o w^{0.5}]$ with $w^{-1} = \sigma^2(F_o) + gF_o$.

Scheme 1



of this type.³ As might be expected, all three isopropyl substituents have their methyl groups turned away from the bulky iodo ligand. The resulting pocket is significantly larger than that of the $\text{Tp}''\text{Co}$ moiety, and the reactivity of $\text{Tp}''\text{Co}$ complexes bears witness to this difference.

The unusual temperature effect on the solubility and the thermochromism of **1a-c** in acetonitrile piqued our curiosity, and we have investigated this phenomenon with a combination of variable-temperature NMR and UV/vis/near-IR experiments. Specifically, Figure 2 shows the effect of adding CH_3CN to a CD_2Cl_2 solution of $\text{Tp}''\text{CoI}$ at low temperature. At 192 K, the five original resonance of $\text{Tp}''\text{CoI}$ are replaced by a wholly different set of six isotropically shifted resonances along with the signal of free CH_3CN . Upon an increase of the temperature, the resonances of $\text{Tp}''\text{CoI}$ gradually and reversibly reappeared. On the basis of these observations and integral intensities, we assign the formula $[\text{Tp}''\text{Co}(\text{NCCCH}_3)_3]\text{I}$ (**2**) to the new complex, which is in equilibrium with $\text{Tp}''\text{CoI}$ (see Scheme 1).

The structural assignments of **1a** and **2** are supported by electronic spectroscopy. In a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixture (9:1) at

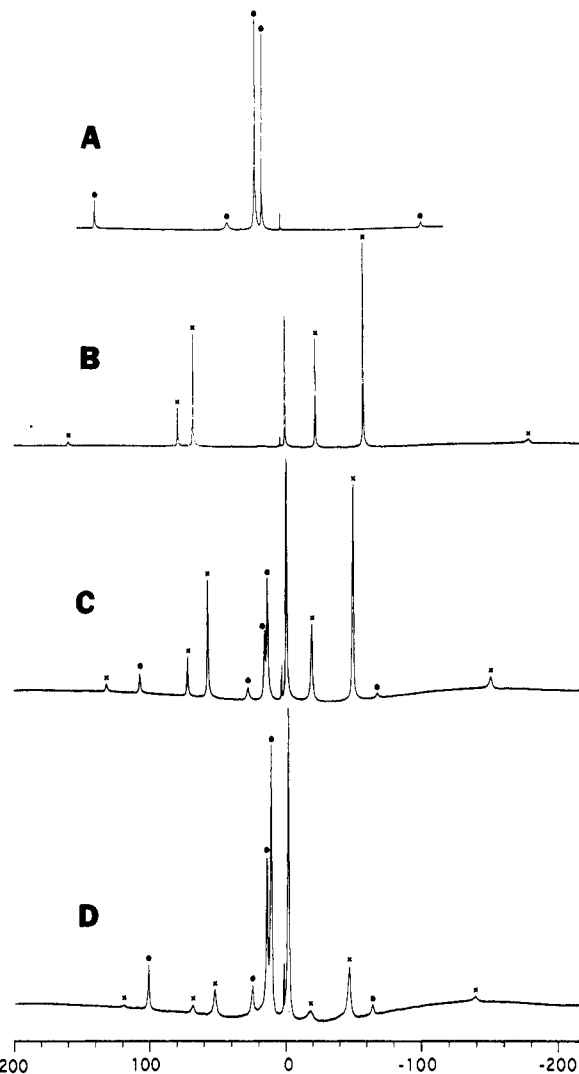


Figure 2. Variable-temperature $^1\text{H-NMR}$ spectra of the equilibrium mixture of $\text{Tp}''\text{CoI}$ (\bullet), $[\text{Tp}''\text{Co}(\text{NCCCH}_3)_3]^+\text{I}^-$ (\times), and free acetonitrile in CD_2Cl_2 ($[\text{Co}]_{\text{tot}} = 0.155$ M). Key: (A) $T = 191.5$ K, in the absence of acetonitrile; (B) $T = 191.5$ K; (C) $T = 229$ K; (D) $T = 234.5$ K, in the presence of 5.7 equiv of CH_3CN with respect to Co.

Table 2. Electronic Absorption Spectra of $\text{Tp}''\text{CoI}$ in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9/1)

λ , nm	ϵ , M^{-1}	E , cm^{-1}	transition	temp, K
273	3200	36 630	} $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$	295
310	2800	32 260		
605	620	16 530		
645	780	15 504		
905	180	11 050		
308	2000	32 470	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$	200
466	60	21 460		

25 °C, a group of intense absorptions between $\lambda = 645$ and 605 nm account for the blue color of $\text{Tp}''\text{CoI}$ and, together with a weaker absorption at $\lambda = 905$ nm, these are characteristic of a tetrahedral $\text{Co}(\text{II})$ (d^7) complex. At -70 °C, however, these absorptions were replaced by one weaker d-d transition at 466 nm, typical of octahedral coordination of $\text{Co}(\text{II})$.⁴ The spectroscopic data and assignments are listed in Table 2.

In the temperature range 218–251 K the equilibrium constant (see eq 1) for the reaction of Scheme 1 could be evaluated by ^1H NMR integration. Note that the concentration dependence of the equilibrium position indicates the formation of a tight ion

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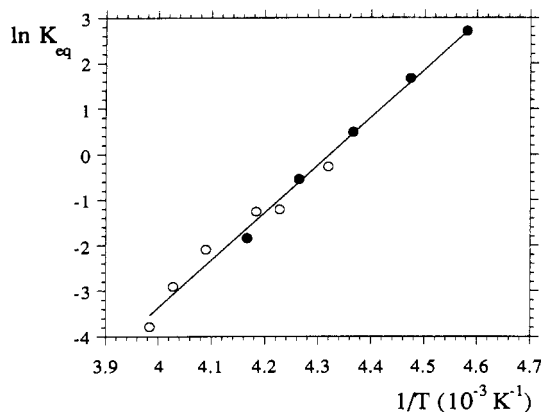


Figure 3. Temperature dependence of the equilibrium constant for the reaction of Scheme 1 (see eq 1): (O): 12.7 equiv of CH₃CN; (●) 5.7 equiv of CH₃CN. Results of van't Hoff analysis: $\Delta H = -20.9(7)$ kcal/mol; $\Delta S = -90(3)$ eu.

$$K_{\text{eq}} = \frac{[\text{Tp}''\text{Co}(\text{NCCH}_3)_3^+\text{I}^-]}{[\text{Tp}''\text{CoI}][\text{CH}_3\text{CN}]^3} \quad (1)$$

pair (i.e. [Tp''Co(NCCH₃)₃⁺I⁻]), rather than dissociation into free ions. The temperature dependence of K_{eq} in the form of a van't Hoff plot is shown in Figure 3. The derived thermochemical parameters were $\Delta H = -20.9(7)$ kcal/mol and $\Delta S = -90(3)$ eu.

Conclusions

"Inverse recrystallization" presumably works due to differences in the affinity of regioisomers **1a–c** for acetonitrile (and possibly

other donor solvents). While all three isomers can apparently be transformed from insoluble tetrahedral molecules into soluble octahedral salts, the most sterically protected isomer—i.e. Tp''CoI, **1a**—is least prone to do so and reverts back to its insoluble, tetrahedral form most easily. This phenomenon may well be of general use for the separation of other structurally closely related metal complexes with low coordination numbers.

The Tp'' ligand is a "tetrahedral enforcer", as seen in Figure 1. However, unlike its Tp' analog, it does not categorically prohibit association of a fifth and even sixth ligand. This flexibility and the participation in shifting equilibria may open new reaction pathways to complexes containing the Tp'' ligand. We have certainly found this to be true in Tp''Co/O₂ chemistry.⁵ It is becoming ever more apparent that the structural diversity of the tris(pyrazolyl)borate ligand family is a major advantage for the molecular engineer. We are continuing our quest for catalytically active [tris(pyrazolyl)borato]metal complexes.

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Supplementary Material Available: Tables of X-ray data for Tp''CoI (10 pages). Ordering information is given on any current masthead page.

(5) Reinaud, O. M.; Theopold, K. H. *J. Am. Chem. Soc.*, submitted for publication.