

Bonding through the terminal nitrogen would not be expected to greatly alter the change in dipole moment of the PN absorption.²³⁻²⁵ The observed decrease in area of the PN mode in the adduct and the tentative assignment of a PB stretch²¹ indicate that the best representation of the adduct is attachment of the borane group to the phosphorus atom and not to one of the nitrogens; however, until a ¹¹B nmr can be obtained showing ³¹P-¹¹B coupling the bonding site of the adduct is uncertain.

Experimental Section

Materials and General Techniques.—The PF₂Br, PF₂I,²⁹ and B₂H₆³⁰ were prepared by literature methods. NaN₃ and LiN₃ were obtained from Matheson Coleman and Bell and Eastman Organics.

High-vacuum techniques were used throughout.³¹ Although no explosions occurred with PF₂N₃, secondary products are highly explosive (HN₃, P(N₃)₃, etc.).^{7,32,33} and proper precautions should be followed. Several explosions have occurred in this laboratory during transfer and disposal of side products and a violent explosion occurred during transfer of PF₂N₃·BH₃.

Infrared spectra were recorded at a sample pressure of 10 mm on a Perkin-Elmer 137 NaCl spectrophotometer and a Perkin-Elmer 421 grating spectrophotometer using a 10-cm gas cell with KBr windows. The mass spectrum was obtained on a Varian M60-6 (70 eV), while nmr spectra for ¹⁹F were recorded on a Jeolco JNM-C-60 HL operating at 56.4 MHz. Chemical shifts refer to CF₃COOH by tube interchange.

Synthesis of PF₂N₃.—After allowing a 15.0-mmol sample of LiN₃ to sit at ambient temperature in moist air, we placed it in a 500-cm³ reaction bulb and evacuated the bulb for several minutes. A slight excess of PF₂Br (16.0 mmol) was condensed on the LiN₃ at -196°. The reactants then were alternately warmed to room temperature and refrozen at -196°; this procedure was repeated several times. We cooled the reaction mixture to -78° in a Dry Ice-acetone slush and allowed it to sit 18 hr. The material was then distilled through traps held at -110, -135, and -196°. The material at -110°, a mixture of PF₂HO³⁴ and several explosive azides (HN₃, etc.),^{7,32,33} was identified by ir and then carefully discarded. Small amounts of PF₃ at -196° were also discarded. The trap at -135° contained PF₂N₃, very small amounts of F₂POPF₂,³⁵ and unreacted PF₂Br. This material was condensed on an excess of ZnF₂ and warmed and refrozen several times. The latter procedure converted the PF₂Br to PF₃ which could be removed by distillation. The products from this reaction were led through traps held at -110, -135, and -196°. Again the material at -110 and -196° was discarded with care, while the -135° trap contained 9.0 mmol of PF₂N₃, contaminated by very small amounts of F₂POPF₂. Separation of these two compounds was extremely difficult, but samples of PF₂N₃ could be obtained fairly pure by careful distillation through traps held at -112 and -196° (see mass spectra). PF₂N₃ was trapped in the -112° trap.

If the LiN₃ was very carefully dried, no reaction occurred. PF₂I could be substituted for PF₂Br and NaN₃ could be substituted for LiN₃.

Properties of PF₂N₃.—Difluorophosphine azide is a colorless

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spontaneously flammable gas at room temperature. No detonations were observed with the pure compound.

Difluorophosphine azide was characterized by its gas molecular weight at 23° (found, 111.6; calcd for PF₂N₃, 111.0) and the mass spectrum splitting pattern. Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of PF₂N₃: 154 (PF₂OPF₂⁺), 2.2; 111 (PF₂N₃⁺), 72.3; 92 (FPN₃⁺), 8.2; 88 (PF₃⁺), 1.6; 85 (PF₂O⁺), 1.1; 83 (PF₂N⁺), 30.4; 69 (PF₂⁺), 100; 64 (PFN⁺), 16.9; 50 (PF⁺), 15.8; 47 (PO⁺), 1.6; 45 (PN⁺), 3.8; 43 (HN₃⁺), 2.7; 42 (N₃⁺), 6.0; 32 (PH⁺), 2.7; 31 (P⁺), 3.8; 28 (N₂⁺), 11.4.

Synthesis of PF₂N₃·BH₃.—PF₂N₃ (6.53 mmol) was condensed with 14.0 mmol of B₂H₆ at -196° in a 500-cm³ reaction bulb. The mixture was allowed to warm and then sit for 6 hr at room temperature. The reaction mixture was distilled through traps held at -67, -110, -140, and 196°. The material at -67° (small amounts of unidentified solids) and -140° (0.1 mmol of PF₂N₃) was discarded. The -196° trap held 10.9 mmol of unreacted B₂H₆, while the -110° trap contained 6.02 mmol of PF₂N₃·BH₃. The yield of the adduct was 95% and PF₂N₃ and BH₃ combined in the ratio 0.99:1.0.

Properties of PF₂N₃·BH₃.—Difluorophosphine azide-borane is a colorless liquid at room temperature. A violent explosion was experienced on transferring this compound.

The borane was characterized by its infrared spectrum given earlier; mass spectrum, and its molecular weight at 20° and 175 mm (found, 125.3; calcd for PF₂N₃·BH₃, 124.8). The following are the mass numbers (species) and relative abundances of the major ions in the mass spectrum of PF₂N₃·BH₃: 125 (PF₂N₃¹¹BH₃⁺), 2.81; 124 (PF₂N₃¹⁰BH₃⁺), 17.5; 123 (PF₂N₃-¹¹BH), 8.5; 112 (PF₂N₃H⁺), 3.1; 111 (PF₂N₃), 48.3; 95 (PF₂N-¹¹BH⁺), 2.44; 94 (PF₂N¹¹B⁺), 20.8; 93 (PF₂N¹⁰B⁺), 5.3; 92 (PFN₃⁺), 8.3; 83 (PF₂N⁺), 12.2; 76 (PFN¹¹BH⁺), 3.9; 64 (PF₂N⁺), 72.1; 51 (PFH⁺), 5.7; 50 (PF⁺), 10.0; 49 (PNH₁⁺), 7.8; 46 (PNH⁺), 12.8; 33 (NF⁺), 3.0; 32 (PH⁺), 5.3; 31 (P⁺), 8.6; 30 (¹¹BH⁺), 2.8; 28 (N₂⁺), 9.8; 18 (H₂O⁺), 6.7; 13 (¹¹BH₂⁺), 4.9.³⁶

Acknowledgment.—The authors are grateful for the assistance of John Gray with the nmr and Roy Jones with the mass spectrometer. We also thank the Air Force for the use of a Jeolco 60-MHz nmr at Robins Air Force Base and gratefully acknowledge the Petroleum Research Fund administered by the American Chemical Society for support of this work.

(36) NOTE ADDED IN PROOF.—Since acceptance of this note a paper has appeared by S. R. O'Neill and J. M. Shreeve [*Inorg. Chem.*, **11**, 1629 (1972)] describing the preparation of PF₂N₃ by a similar route. Although we did not experience any explosions with PF₂N₃ their work suggests caution.

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A Novel and Improved Synthesis of [IrCl(NO)(P(C₆H₅)₃)₂]⁺. A Nitrosyl Analog of Vaska's Compound

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There has been a great deal of interest lately, by ourselves¹ and others,² in the synthesis and properties of the complex [IrCl(NO)(P(C₆H₅)₃)₂]⁺.

We report here a novel and greatly improved preparation for the complexes [IrX(NO)(P(C₆H₅)₃)₂]⁺ (X = Cl, Br) beginning with the readily available com-

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plexes $[\text{IrX}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$). This synthesis involves only two steps, in contrast to the usual six-step process,¹ and results in substantially improved yields.

A preliminary report of the chemical reactivity of this complex with several Lewis acids is also presented. The complex shows decreased chemical reactivity in comparison to its carbonyl analog³ in agreement with previous reports.^{2c}

Experimental Section

Apparatus and Techniques.—All of the infrared spectra of compounds were recorded on a Perkin-Elmer 257 grating infrared spectrophotometer using Nujol mulls and calibrated with polystyrene. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and M-H-W Laboratories, Garden City, Mich. All reactions were carried out under a nitrogen atmosphere.

Reactions and Solutions.—*trans*- $[\text{IrX}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were purchased from Strem Chemicals Inc., Danvers, Mass., and were used without further purification. Tetracyanoethylene and fumaronitrile were purchased from Aldrich Chemical Inc. and sublimed prior to use. *p*-Nitrobenzoyl azide was purchased from Eastman Organic Chemical Distillation Products Inc. and was recrystallized prior to use. Nitrosyl tetrafluoroborate (95% pure) was purchased from Alfa Inorganics Ventron and was used without further purification. All solvents, methanol, chloroform, absolute ethanol, and *n*-hexane, were dried over 4A molecular sieves and were degassed by passing a stream of nitrogen through the solvent with a filtered bubbling tube for 0.5 hr and then cooling to 0° before use.

Preparation of the Complexes. Preparation of $\text{IrCl}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$.—This complex was prepared from $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and *p*-nitrobenzoyl azide using a previously reported procedure.⁴

Preparation of $\text{IrBr}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$.—A magnetic stirring bar and 0.31 g (0.37 mmol) of $\text{IrBr}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ were placed in a Schlenk apparatus which was flushed with nitrogen by alternately applying a vacuum and refilling with nitrogen in a drybag filled with nitrogen gas. The apparatus was cooled in a ice bath and 5 ml of ice-cold chloroform was injected through the stopcock by means of a hypodermic syringe. After the magnetic stirrer was turned on, a precooled solution of (0.081 g, 0.42 mmol) *p*-nitrobenzoyl azide in 2 ml of chloroform was injected.

Within 2–3 min, the yellow suspension became a clear yellow solution. After a total reaction time of 10 min, 30 ml of cold methanol was immediately injected to precipitate the nitrogen complex. At least 10 min should be allowed to complete the precipitation. The yellow, crystalline complex was collected on the filter and washed with a 20-ml portion of cold methanol. The product was dried *in vacuo* for 1 hr.

The infrared band at 1960 cm^{-1} (carbonyl stretching frequency) disappeared completely and a new band at 2095 cm^{-1} attributed to the nitrogen stretching frequency appeared. This band was identical with that previously reported⁴ for the chloro analog, $\text{IrCl}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$. The yellow, microcrystalline solid gave 0.22 g (70% yield).

Attempted Preparation of $\text{IrI}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$.—This complex was prepared from $\text{IrI}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ in a manner analogous to that used to prepare the bromo complex, except that the reaction time was limited to 3 min. The product was a mixture of $\text{IrI}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and a trace of $\text{IrI}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$. The infrared spectrum exhibited an intense absorption at 2095 cm^{-1} attributed to the nitrogen stretching frequency in $\text{IrI}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and a very weak band at 1960 cm^{-1} attributed to the carbonyl stretching frequency in $\text{IrI}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$. Due to the air sensitivity of $\text{IrI}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and $\text{IrI}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$, which is unstable even in the solid state at room temperature, we found it impossible satisfactorily to separate the products of this mixture.

Preparation of $[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$.—Solid 95% NOBF_4 (0.0016 g, 0.0132 mmol) was added to an ice-cold solution of 0.1 g (0.0129 mmol) of $\text{IrCl}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ in 10 ml of chloroform. The color of the solution changed from yellow to red in 10 min and was filtered to remove any remaining solid. The red solution was evaporated in a vacuum desiccator and the product

was recrystallized from a chloroform-*n*-hexane mixture. The red crystals gave 0.10 g (90% yield). *Anal.* Calcd for $\text{IrNOClP}_2\text{BF}_4\text{C}_{36}\text{H}_{30}$: C, 49.74; H, 3.45; N, 1.61. Found: C, 49.09; H, 3.83; N, 1.39. The infrared spectrum is identical with that previously reported^{1, 2b, c} for $[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ prepared by other methods with $\nu(\text{NO})$ at 1902 cm^{-1} .

Preparation of $[\text{IrBr}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$.—This complex was prepared in a manner analogous to that used for the chloro complex, *vide supra*, except that $\text{IrBr}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ was used as a starting material. *Anal.* Calcd for $\text{IrNOBrP}_2\text{BF}_4\text{C}_{36}\text{H}_{30}$: C, 47.32; H, 3.28; N, 1.53. Found: C, 46.95; H, 3.53; N, 1.25. The infrared spectrum yielded an intense band attributed to $\nu(\text{NO})$ at 1902 cm^{-1} .

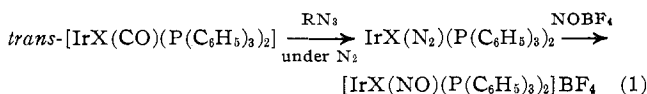
Attempted Preparation of $[\text{IrI}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$.—This complex was prepared in a manner analogous to that used for the chloro complex, *vide supra*, except that $\text{IrI}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ was used as a starting material. Since the starting material contained a trace of $\text{IrI}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$, the product obtained was probably a mixture of $[\text{IrI}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$ and $[\text{IrI}(\text{CO})(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$. The infrared spectrum yielded a strong band at 2040 cm^{-1} attributed to $\nu(\text{CO})$ in $[\text{IrI}(\text{CO})(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$.⁵

Preparation of $[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{TCNE}\cdot\text{C}_6\text{N}_4$.—The complex $[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ was dissolved in a small volume of absolute ethanol at room temperature and up to a fivefold excess of TCNE (C_6N_4) was added. The red color of the solution disappeared and a pale yellow solid precipitated. The solid was filtered, washed with absolute ethanol, and dried in a vacuum desiccator. *Anal.* Calcd for $\text{IrCl}_2\text{P}_2\text{O}_6\text{N}_5\text{C}_{42}\text{H}_{30}$: C, 49.94; H, 2.97. Found: C, 52.07; H, 3.88. The infrared spectrum exhibited a strong band at 1590 cm^{-1} attributed to $\nu(\text{NO})$.

Attempted Preparation of $[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{FUM}\text{BF}_4$.—This adduct was prepared in a manner analogous to that used to prepare the TCNE adduct, *vide supra*, except that fumaronitrile ($\text{C}_4\text{N}_2\text{H}_2$) was used as a Lewis acid and tetrafluoroborate was the counterion. There was no color change or precipitation after a reasonable period, indicating no reaction had occurred, and the infrared spectrum yielded a strong band at 1902 cm^{-1} attributed to $\nu(\text{NO})$ in the starting material.

Results and Discussion

The route for the synthesis of *trans*- $[\text{IrX}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) from *trans*- $[\text{IrX}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) is given by eq 1. The



results of our infrared studies and some properties of these complexes are presented in Table I. The syn-

TABLE I
PROPERTIES OF IRIUM COMPLEXES

Complex	Color	Ir bands, cm^{-1}
$\text{IrCl}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$	Bright yellow	$\nu(\text{NN})$ 2095
$\text{IrBr}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$	Yellow	$\nu(\text{NN})$ 2095
$\text{IrI}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$	Yellow	$\nu(\text{NN})$ 2095
$[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$	Red	$\nu(\text{NO})$ 1902
$[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$	Red	$\nu(\text{NO})$ 1902
$[\text{IrBr}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$	Red	$\nu(\text{NO})$ 1902
$[\text{IrI}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{BF}_4$	Pale red	$\nu(\text{NO})$ 1895
$[\text{IrCl}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{TCNE}\text{ClO}_4$	Pale yellow	$\nu(\text{NO})$ 1595, $\nu(\text{CN})$ 2131

thesis of the nitrosyl complexes by this method results in a substantial saving in time and labor and also produces a higher yield.

The infrared criteria for distinguishing between NO^+ and NO^- have been a matter of controversy for some years.⁶ Recently, Ibers and coworkers have deter-

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mined the structures of a number of complexes with coordinated nitric oxide.⁷ On the basis of their X-ray data and infrared stretching frequencies they^{7c} have proposed the following criteria: NO⁺ complexes have $\nu(\text{NO})$ in the range 1600–1845 cm⁻¹ and for NO⁻ complexes $\nu(\text{NO})$ is in the range 1525–1720 cm⁻¹. Therefore, it is inadequate to use $\nu(\text{NO})$ solely to determine the mode of coordination in the region 1600–1720 cm⁻¹. We may conclude, however, that NO is coordinated as NO⁺ in our nitrosyl complexes.

Reactions of tetracyanoethylene and fumaronitrile with IrX(CO)(P(C₆H₅)₃)₂ (X = Cl, Br, I) have been studied extensively.³ A number of new compounds have been isolated and characterized in these and similar reactions.

TCNE will add to [IrCl(NO)(P(C₆H₅)₃)₂]⁺ to give [IrCl(NO)(P(C₆H₅)₃)₂TCNE]ClO₄. There is a change in the bonding of NO to iridium upon coordination as evidenced by the change in $\nu(\text{NO})$ from 1902 to 1595 cm⁻¹. It seems plausible that this structure would be similar to the bent coordinated NO as determined crystallographically in [IrCl(CO)(NO)(P(C₆H₅)₃)₂]BF₄⁵ and that NO is coordinated as NO⁻ here. However, such proposals must be vindicated by crystallographic study.

The addition of the weaker Lewis acid fumaronitrile to [IrCl(NO)(P(C₆H₅)₃)₂]⁺ produced no reaction, in contrast to [IrCl(CO)(P(C₆H₅)₃)₂] which forms a stable compound.³ This decrease in chemical reactivity is consistent with previous reports on this complex.^{2c} The decrease in apparent chemical reactivity is probably due to the positive charge on the complex and the resultant decrease in electron density on the metal. For example, this complex shows no tendency to combine with O₂,^{2c} whereas the uncharged complex RuCl(NO)(P(C₆H₅)₃)₂ forms an irreversible adduct with O₂.³

Acknowledgment.—We are indebted to Professor Abbas A. El-Awady for helpful discussions throughout the course of this research.

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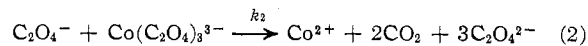
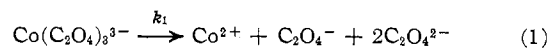
Free Radical Mechanism in the Acid-Catalyzed Redox Decomposition of Tris(oxalato)cobaltate(III) Ion in Aqueous Solution¹

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Although there has been some dispute concerning the detailed path by which the acid-catalyzed redox decomposition of Co(C₂O₄)₃³⁻ is initiated,² there has been general agreement up to now that the overall mech-

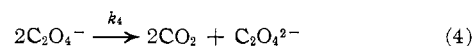
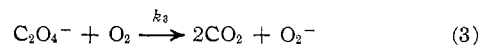
anism involves production of a free radical (C₂O₄⁻ or CO₂⁻) which reattacks the substrate to form additional Co²⁺.³⁻⁹ In simplest terms this process may be represented



where Co(C₂O₄)₃³⁻ may be taken here to include protonated and ring-opened forms, C₂O₄²⁻ includes HC₂O₄⁻ and H₂C₂O₄, and C₂O₄⁻ includes its protonated form (or CO₂⁻ and CO₂H). The basis for this free radical mechanism appears to have arisen largely by analogy to the photochemical decomposition^{3,4} and to other oxalate reactions¹⁰ in which free radicals have been implicated. Some additional support has been offered by the observation that the thermal decomposition leads to other processes which are accepted as involving free radicals, such as vinyl polymerization.³

Recently Hin-Fat and Higginson¹¹ have advanced the hypothesis that the thermal decomposition does not involve free radicals at all. The key observation, cited by these authors for both Co(C₂O₄)₃³⁻ and Co(C₂O₄)₂(H₂O)₂⁻, is a deviation from first-order behavior as seen by curvature in plots of log(A_t - A_∞) vs. time (where A = absorbance). The fact that wholly linear plots could be obtained by addition of a term inverse in complex concentration, together with the effect of changes in reaction conditions on the magnitude of this term, led these authors¹¹ to favor a mechanism involving a concerted three-center redox reaction between the substrate and a ring-opened species.

At appropriate relative concentrations of the reactive species, with O₂ as an added scavenger, reactions 3 and 4 can predominate over (2), where 2k₄ = 1 × 10⁹ M⁻¹



sec⁻¹¹² and (3) is assumed to be very efficient by analogy to the CO₂⁻-O₂ reaction.¹³ In highly acidic solution, the O₂⁻ radical will exist in its H₂O₂⁺ form¹⁴ which does not appear to be effective in reducing simple Co(III) complexes.¹⁵ Thus, the formation of Co²⁺ in the presence of O₂ from secondary radical reactions is of negligible contribution.¹⁶ Here, in the slow thermal

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