free ligand), there is good indication that the ancillary substituted phosphine and arsines and anion X ligands appear to influence the $\nu(\mathrm{N_2})$ and $\nu(\mathrm{CO})$ to the same extent. Mössbauer[8] and IR intensity measurements[9] suggest that $\mathrm{N_2}$ is a weaker $\sigma$ donor and $\pi$ acceptor than CO, but the $\pi$-acceptor capacity is more important than the $\sigma$-donor propensity for $\mathrm{N_2}$. It is interesting to note that cis and trans ancillary ligands appear to have the same effect on $\mathrm{N_2}$ and CO bonded to Ir.

**Isolation of Iridium–Dinitrogen Complexes.** The IR spectral studies of solutions of $[\mathrm{Ir(PR_3)_2(CO)Cl}]$ and furoyl azide in $\mathrm{CHCl_3}$ gave indication of the relative stabilities of dinitrogen complexes. This information was used to direct our efforts to isolate *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)F}]$, *trans*-$[\mathrm{Ir}[(p\text{-}\mathrm{CH_3C_6H_4})_3\mathrm{P}]_2(\mathrm{N_2})\mathrm{Cl}]$, *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)(NCO)}]$, and *trans*-$\mathrm{Ir}[(\mathrm{AsPh_3})_2(\mathrm{N_2})(\mathrm{NCO})]$. While only dinitrogen complexes of Ir with organophosphine ligands had been previously reported, we found that organoarsine–carbonyl–iridium(I) complexes react with acyl azides to form dinitrogen complexes. Solid *trans*-$[\mathrm{Ir(AsPh_3)_2(N_2)Cl}]$ and $\mathrm{Ir(AsPh_3)_2(N_2)(NCO)}]$ were isolated, but satisfactory microanalytical data were obtained only for the latter complex. The lower stability of arsine compared to phosphine derivatized dinitrogen complexes has been previously noted for Re(I) and Mo(0) complexes.[10] It is of interest to note that the cyanate anion appeared to give the most stable dinitrogen complexes.

The lower stabilities of dinitrogen–iridium complexes which have lower values of $\nu(\mathrm{N_2})$ indicative of stronger $\mathrm{Ir{-}N_2}$ bonds were previously ascribed to the need for satisfaction of the electron donor rather than $\pi$-acceptor function of the dinitrogen ligand.[3] We conclude from the present study that whether a dinitrogen complex can be formed from reaction 1 and isolated does not depend solely on the effect of ancillary ligands on the stability of the $\mathrm{Ir{-}N_2}$ bond. The additional significant factors are, first, the favorable kinetics[2c] of reaction 1 leading to formation of the dinitrogen complex and, second, the kinetics of substitution and oxidative addition reactions of the dinitrogen complex. The short lifetimes of the $[\mathrm{Ir(PR_3)_2(N_2)X}]$ complexes with low $\nu(\mathrm{N_2})$ (hence stronger $\mathrm{Ir{-}N_2}$ bonds) observed for complexes with more basic and sterically less hindered $\mathrm{PR_3}$ can be attributed to their greater reactivity with the reactant acyl azide or byproduct acyl isocyanate or intramolecular insertion of Ir into C–H bonds of coordinated phosphine.[7]

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. T.G.C. and S.P.P. were National Science Foundation Undergraduate Research Participants.

**Registry No.** *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)F}]$, 71700-02-2; *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)Cl}]$, 21414-18-6; *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)Br}]$, 25036-66-2; *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)I}]$, 38255-33-3; *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)N_3}]$, 25036-67-3; *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)NCO}]$, 71700-03-3; *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)NCS}]$, 71700-04-4; *trans*-$[\mathrm{Ir(PPh_3)_2(N_2)CF_3CO_2}]$, 71700-05-5; *trans*-$[\mathrm{Ir}(\mathrm{P}(p\text{-}\mathrm{CH_3C_6H_4})_3)_2(\mathrm{N_2})\mathrm{Cl}]$, 71700-06-6; *trans*-$[\mathrm{Ir(PPh_2Me)_2(N_2)Cl}]$, 71700-07-7; *trans*-$[\mathrm{Ir(PPh_2Me)_2(N_2)Br}]$, 71700-08-8; *trans*-$[\mathrm{Ir(PPhMe_2)_2(N_2)Cl}]$, 28667-94-9; *trans*-$[\mathrm{Ir(PEt_3)_2(N_2)Cl}]$, 71700-09-9; *trans*-$[\mathrm{Ir(AsPh_3)_2(N_2)Cl}]$, 71700-10-2; *trans*-$[\mathrm{Ir(AsPh_3)_2(N_2)Br}]$, 71700-11-3; *trans*-$[\mathrm{Ir(AsPh_3)_2(N_2)N_3}]$, 71700-12-4; *trans*-$[\mathrm{Ir(AsPh_3)_2(N_2)NCO}]$, 71700-13-5; *trans*-$[\mathrm{Ir(P(OPh)_3)_2(N_2)Cl}]$, 71700-14-6; $\mathrm{Ir(CO)_2(PPh_3)_2H}$, 17250-59-8; $\mathrm{Ir(CO)(PPh_3)_3H}$, 17250-25-8; $[\mathrm{Ir(PPh_3)_2(CO)(CH_3CN)}]\mathrm{BF_4}$, 49745-75-7; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)F}]$, 32356-62-0; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)Cl}]$, 15318-31-7; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)Br}]$, 15842-08-7; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)I}]$, 19472-16-3; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)N_3}]$, 21414-23-3; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)NCO}]$, 28195-62-2; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)NCS}]$, 28195-61-1; *trans*-$[\mathrm{Ir(PPh_3)_2(CO)CF_3CO_2}]$, 50442-04-1; *trans*-$[\mathrm{Ir}(\mathrm{P}(p\text{-}\mathrm{CH_3C_6H_4})_3)_2(\mathrm{CO})\mathrm{Cl}]$, 28195-56-4; *trans*-$[\mathrm{Ir(PPh_2Me)_2(CO)Cl}]$, 15318-32-8; *trans*-$[\mathrm{Ir(PPh_2Me)_2(CO)Br}]$, 19354-07-5; *trans*-$[\mathrm{Ir(PPhMe_2)_2(CO)Cl}]$, 21209-82-5; *trans*-$[\mathrm{Ir(PEt_3)_2(CO)Cl}]$, 21209-85-8; *trans*-$[\mathrm{Ir(AsPh_3)_2(CO)Cl}]$, 23954-42-9; *trans*-$[\mathrm{Ir(AsPh_3)_2(CO)Br}]$, 14040-53-0; *trans*-$[\mathrm{Ir(AsPh_3)_2(CO)N_3}]$, 42482-39-3; *trans*-$[\mathrm{Ir(AsPh_3)_2(CO)NCO}]$, 42556-35-4; *trans*-$[\mathrm{Ir(P(OPh)_3)_2(CO)Cl}]$, 42482-37-1.

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## Meridional Tris(pyridine)tris(thiocyanato-*N*)chromium(III) and Its Conversion to the Cyanato-*N* Analogue by a Novel Method

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*Received April 9, 1979*

Chromium(III) normally shows a strong affinity for oxygen donors,[1] while the ambidentate cyanate ion is known to be predominantly nitrogen bonded.[2] We, therefore, expected a potential for linkage isomerism in the chromium(III)–cyanate system. The absence of stable linkage isomers of chromium(III) with simple ligands in the solid state and the existence of only a single cyanato linkage isomer[3] provided additional incentive for this work. We report here a new method for the synthesis of a (cyanato-*N*)chromium(III) complex in the solid crystalline state.

The only chromium(III)–cyanato complex reported before, tetraphenylarsonium hexakis(cyanato-*N*)chromate(III),[4] was obtained as a green oil, which solidified under vacuum. The material gave unsatisfactory analyses for chromium and carbon. All of our attempts for direct synthesis of any chromium(III)–cyanato complex in the pure state starting from other chromium(II) or chromium(III) compounds were unsuccessful. It was found that tris(pyridine)tris(thiocyanato-*N*)chromium(III) in pyridine reacts with potassium bromate to form the corresponding cyanato-*N* compound. The basic reaction appears to be

$$[\mathrm{Cr(py)_3(NCS)_3}] + 4\mathrm{BrO_3^-} \rightarrow [\mathrm{Cr(py)_3(NCO)_3}] + 4\mathrm{Br^-} + 3\mathrm{SO_3}$$

There have been several studies[5] on the oxidation of free and captive thiocyanates since 1900. The products of these reactions depend on both the nature and concentrations of the thiocyanate-containing moiety and the oxidizing agent, as well as the pH of the reactions. Sulfur is generally oxidized to sulfate, and various nitrogen-containing species including cyanide, cyanate, and ammonia are formed.

Werner[6] used the formation of coordinated ammonia by the oxidation of thiocyanate on a variety of bis(ethylenediamine)(thiocyanato)cobalt(III) complexes as evidence of co-

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balt–nitrogen bonding. Norris and Wilson[7] showed that the oxidation of *trans*-$[Co(en)_2(NH_3)(NCS)]^{2+}$ by $H_2O_2$ in acid media leads to *trans*-$[Co(en)_2(NH_3)(CN)]^{2+}$ and *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ as the only products. There is no earlier report of isolation of any cyanato-*N* complex by the oxidation of the corresponding thiocyanato compound. We found that *trans*-$[Cr(en)_2(NCS)_2]^+$ and *trans*-$[Cr(pn)_2(NCS)_2]^+$ react the same way as *mer*-$[Cr(py)_3(NCS)_3]$ to yield the cyanato-*N* complexes. Bromate–thiocyanate reactions are highly exothermic and potentially explosive, especially if carried out in large quantity. In a small batch the reactions can be controlled with high yield (~70%). The corresponding cis and *fac* isomers of Cr(III) react with bromate only at higher temperatures and yield mixtures of several products not yet fully characterized. Oxidation by bromate also appears to have some specificity, since oxidation with a number of other oxidizing agents failed to yield pure cyanato complexes. Palladium(II)–thiocyanate complexes[8] were shown to give identical palladium(II)–cyanide products, independent of the thiocyanate linkage isomers oxidized by $H_2O_2$. Preliminary investigation indicated that some thiocyanato-*S* complexes behave quite differently from thiocyanato-*N* complexes toward bromate. Further work on the apparent trans effect and linkage isomerism of coordinated thiocyanates during bromate oxidation is in progress. It is possible that bromate oxidation may be utilized to distinguish between *N*CX and NC*X* linkage isomers.

The following abbreviations have been used: en, ethylenediamine; pn, propylenediamine; py, pyridine; *N*CX, chalcocyanato-*N*; NC*X*, chalcocyanato-*X*.

## Experimental Section

**Materials.** *mer*-$[Cr(py)_3Cl_3]$ was prepared according to Taft and Jones.[9] Reinecke salt, $NH_4[Cr(NH_3)_2(NCS)_4]\cdot H_2O$, was synthesized by the method described by Brauer.[10] $[C(py)_3(NCS)_3]$ was obtained by following the procedure of Patel.[11] These compounds gave satisfactory analyses for chromium analyzed as $Cr_2O_3$ after controlled ignition with oxalic acid dihydrate in a platinum crucible. Silver cyanate was made by boiling a solution of silver nitrate with urea.[12] Reagent quality potassium bromate, pyridine, and solvents were used.

***mer*-Tris(pyridine)tris(thiocyanato-*N*)chromium(III).** An 8.4-g (0.025-mol) sample of Reinecke salt was boiled with 50 mL of pyridine under reflux for 8 h. The crystals that separated on cooling were filtered and washed under suction first with water and then with ethanol followed by ether. The product was then ground to a fine powder, washed several times with ethanol and then with ether, and dried under vacuum at 80 °C. It is soluble in acetone and nitromethane but insoluble in water, ethanol, chloroform, and ether; yield 6.2 g. Anal. Calcd for $CrC_{18}H_{15}N_6S_3$: Cr, 11.23; C, 46.65; H, 3.24; N, 18.14. Found: Cr, 11.09; C, 46.25; H, 3.17; N, 18.29.

**Tris(pyridine)tris(cyanato-*N*)chromium(III).** A 1-g (0.002-mol) sample of *mer*-$[Cr(py)_3(NCS)_3]$ dissolved in 50 mL of pyridine was stirred magnetically with 4 g of finely powdered potassium bromate in a tall, narrow 300-mL beaker. Depending on the ambient temperature and stirring, a vigorous exothermic reaction ensued in 15–45 min, and the color of the solution turned deep brown. The reaction mixture was cooled in an ice bath to prevent the temperature from going over 80 °C and to reduce the formation of polymeric species formed at higher temperatures. The reaction was complete within a few minutes after the onset. The mixture was stirred for 15 min and poured slowly into 500 mL of cold water. The light pink crystals formed were collected by filtration, washed with water, and dried by suction at room temperature. The product was dissolved in chloroform, filtered, and reprecipitated by addition of ether. This was purified by recrystallization from warm nitromethane and dried under vacuum at 80 °C. It is soluble in acetone, nitromethane, and chloroform but insoluble in water, ethanol, and ether; yield 0.62 g. Anal. Calcd for $CrC_{18}H_{15}N_6O_3$: Cr, 12.53; C, 52.05; H, 3.61; N, 20.24. Found: Cr, 12.45; C, 52.58; H, 3.64; N, 20.44.

## Results and Discussion

Infrared spectra were taken in KBr disks on a Perkin-Elmer Model 283 IR spectrometer. Almost identical spectra in Nujol mull indicated that there was no interaction in the bromide matrix. The spectra are reproduced in Figure 1 and summarized in Table I.

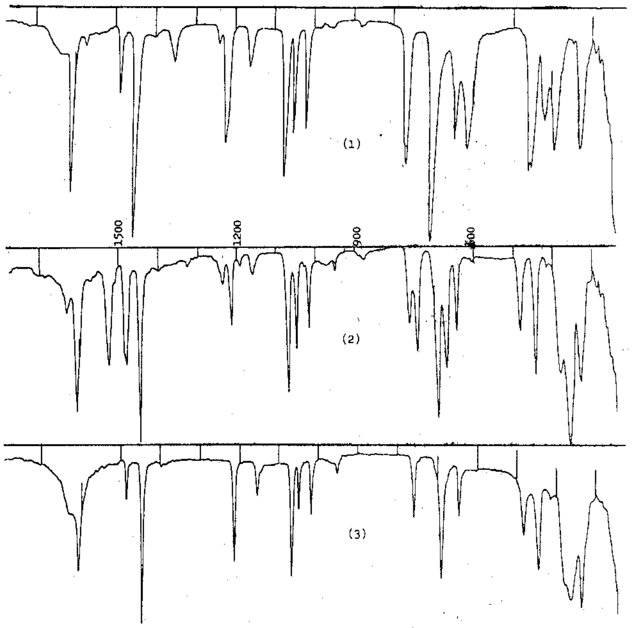

**Figure 1.** Infrared spectra (0.5% in KBr disks): (1) $[Cr(py)_3(NCO)_3]$, (2) *mer*-$[Cr(py)_3(NCS)_3]$, (3) *fac*-$[Cr(py)_3(NCS)_3]$.

**Table I.** Infrared Spectra in KBr Disks

| | $[Rh(py)_3Cl_3]$[a] | | $[Cr(py)_3(NCS)_3]$ | | $[Cr(py)_3(NCO)_3]$[c] |
|---|---|---|---|---|---|
| | *fac* | *mer* | *mer*[c] | *fac*[b] | |
| CN str | | | 2050 vs | 2082 vs | 2212 vs |
| CO str | | | | | 1351 w |
| $\delta_{NCX}$ | | | 476 s | 478 s | 609 s |
| M–N(NCX) | | | 374 s | 384 s | 416 s |
| | | | 351 s | 359 s | 398 s |
| | | | 322 s | 332 s | 325 s |
| out of plane | | 781 m | 755 s | 757 s | 765 sh |
| py ring | 760 s | 762 s | 737 s | | 760 s |
| def | 752 sh | 754 m | 685 s | 694 s | 695 s |
| | | 699 sh | | | |
| | 692 s | 692 s | 663 s | | |
| | 684 w | 686 s | 636 s | 645 m | 640 s |
| in plane | 1604 s | 1610 m | 1604 s | 1605 s | 1609 s |
| py ring | | | 1523 s | | 1572 w |
| def | 1481 w | 1485 w | 1480 s | 1484 m | 1486 m |
| | 1472 w | 1478 w | 1475 s | | |
| | 1446 s | 1450 s | 1442 s | 1445 s | 1447 s |

[a] Reference 16. [b] Compound prepared according to ref 11. [c] This work.

As may be argued from symmetry, and shown for other *fac* isomers,[13] *fac*-$[Cr(py)_3(NCS)_3]$ has a less complex spectrum than the *mer* isomer. The number of pyridine ring deformation bands in $[Cr(py)_3(NCO)_3]$ is more than the number in *fac*-$[Cr(py)_3(NCS)_3]$ but less than that in *mer*-$[Cr(py)_3(NCS)_3]$. The geometrical configuration of the cyanato compound thus could not be indicated on this criterion. The *fac* isomer is more polar than its *mer* isomer and is expected to absorb at a higher energy. The frequency of each of the bands in Table I is higher for the *fac* isomer.

The integrated intensities for the CN stretching band for *mer*-$[Cr(py)_3(NCS)_3]$ and $[Cr(py)_3(NCO)_3]$ according to the method of Ramsay[14] were found to be 13 × $10^4$ and 17 × $10^4$ $cm^{-2}$ (mol of CN)$^{-1}$ $L^{-1}$, respectively, indicating the compounds to be nitrogen bonded.

The high value of CO stretching frequency[15] at 1351 $cm^{-1}$ in $[Cr(py)_3(NCO)_3]$ also indicated N bonding. The CS stretching region was masked by pyridine bands, and the

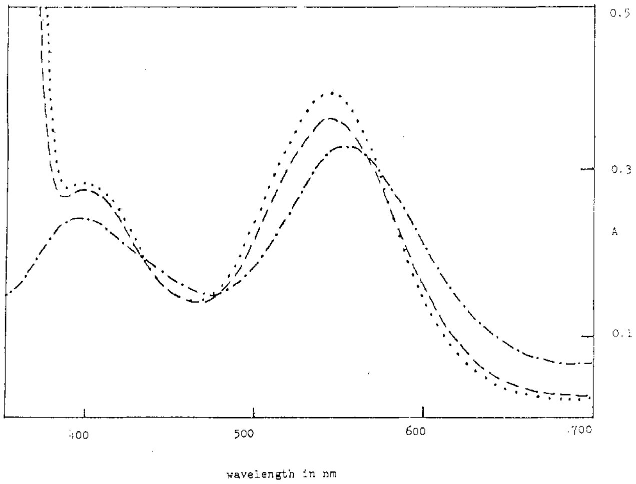

**Figure 2.** Spectra in acetone solution (0.003 M): -··-, [Cr(py)$_3$(NCO)$_3$]; - - -, *mer*-[Cr(py)$_3$(NCS)$_3$]; ···, *fac*-[Cr(py)$_3$(NCS)$_3$].

**Table II.** Spectra in Acetone Solution[a]

*mer*-[Cr(py)$_3$(NCS)$_3$]: $\lambda_{max}$ 546 nm, $\epsilon$ 121; $\lambda_{max}$ 399 nm, $\epsilon$ 93
*fac*-[Cr(py)$_3$(NCS)$_3$]: $\lambda_{max}$ 545 nm, $\epsilon$ 133; $\lambda_{max}$ 398 nm, $\epsilon$ 97
[Cr(py)$_3$(NCO)$_3$]: $\lambda_{max}$ 556 nm, $\epsilon$ 110; $\lambda_{max}$ 393 nm, $\epsilon$ 83

[a] $\epsilon$ is the molar absorptivity in L mol$^{-1}$ cm$^{-1}$.

200–300 cm$^{-1}$ region was not well-defined to assign characteristic Cr–py vibrations.

Visible spectra in acetone solutions recorded on a 118 Cary spectrophotometer are given in Figure 2. The results are summarized in Table II. While the spectra are practically identical, higher molar absorptivitiy of the facial isomer is in keeping with the higher dipole moment of the isomer. N-Bonded cyanates have been found to produce a weaker crystal field in complexes[17] compared to the corresponding *N*CS compounds.

The lowest energy d–d transition band in the *N*CS compounds has shifted by 10 nm in the *N*CO compound. This red shift is of a magnitude expected for a transition from *N*CS to *N*CO.

The polar cis octahedral compounds of the type MA$_4$B$_2$ are found to have a lower $R_f$ value in thin-layer chromatograms compared to the corresponding trans compounds. The same effect was reported for *fac* isomers.[13] The three Cr(III) complexes are soluble in acetone, *fac*-[Cr(py)$_3$(NCS)$_3$] being the most and [Cr(py)$_3$(NCO)$_3$] the least of the three. On silica gel all the three compounds ran with the solvent front in acetone. Ethanol effected a separation, but nitromethane was found to be the most suitable solvent. Sample sizes of 2–5 $\mu$L in acetone solutions of the compounds were applied, and chromatograms developed in nitromethane. The compounds are highly colored and can be spotted directly on the chromatograms. The $R_f$ values were fairly reproducible. Table III summarizes the results.

On the basis of infrared and visible spectra we have designated the ethanol-soluble [Cr(py)$_3$(NCS)$_3$] prepared by Patel as the facial isomer. The ethanol-insoluble [Cr(py)$_3$(NCS)$_3$] was prepared from *trans*-[Cr(NCS)$_4$(NH$_3$)$_2$]$^-$ and pyridine. It is reasonable to assume that the two trans NH$_3$ groups were first displaced by pyridine, forming the *mer* isomer. This is supported by infrared and visible spectra, as well as its higher $R_f$ value in TLC. Very high $R_f$ for the [Cr(py)$_3$(NCO)$_3$] may indicate its *mer* or low-polarity character.

So far our attempts to isolate any cyanato-*O* isomer in the pure state have been unsuccessful. It was, however, found that a cold acetone solution of *mer*-[Cr(py)$_3$Cl$_3$] reacts with solid silver cyanate, AgNCO, which is known to be N bridged[18] to yield a blue-violet solution with absorption bands at 572 and 447 nm, with a shoulder at 430 nm. The shift of d–d band from 556–572 nm may indicate formation of cyanato-*O* coordination. Even though the infrared spectra of solids isolated from such reaction products indicated a possible Cr–OCN coordination, the purity was unsatisfactory and indicated that cyanato-*O* initially formed led to OCN bridging by eliminating pyridine and resulting in polymeric forms.

Table III[a]

| | $R_f$ | $R_f/R_f$(*fac*-[Cr(py)$_3$(NCS)$_3$]) |
|---|---|---|
| *fac*-[Cr(py)$_3$(NCS)$_3$] | 0.41 | 1.00 |
| *mer*-[Cr(py)$_3$(NCS)$_3$] | 0.49 | 1.20 ± 0.02 |
| *mer*(?)-[Cr(py)$_3$(NCO)$_3$] | 0.86 | 2.10 ± 0.03 |

[a] Solvent nitromethane; TLC Eastman Chromagram Sheet 6061; silica gel without fluorescent indicator; room temperature 24 °C.

**Acknowledgment.** The authors gratefully acknowledge the services extended by Union Carbide Corp. Technical Center at South Charleston, W.Va., especially to Mr. J. T. Hildebrand for running C, H, N analysis and to Dr. L. Cosby and to Mrs. L. K. Scholl for spectral analysis facilities.

**Registry No.** *mer*-[Cr(py)$_3$(NCS)$_3$], 71629-72-6; *mer*-[Cr(py)$_3$(NCO)$_3$], 71606-77-4; *fac*-[Cr(py)$_3$(NCS)$_3$], 71629-73-7; NH$_4$[Cr(NH$_3$)$_2$(NCS)$_4$], 13573-16-5.

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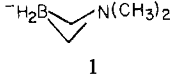
# 1,1-Dimethyl-1,3-azoniaboratacyclobutane

Garry F. Warnock and Norman E. Miller*

*Received March 9, 1979*

The title four-membered heterocycle, **1**, with two coterminus



**1**

BCN sequences, has been isolated and characterized among the products from the reaction of *tert*-butyllithium and the BCN-sequenced salt[1] (CH$_3$)$_3$NBH$_2$CH$_2$N(CH$_3$)$_3$$^+$Cl$^-$. The heterocycle is named as a cyclobutane replacement derivative

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