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Synthesis and Characterization of Homoleptic Complexes of the Chelating Bidentate Isocyano Ligand *t*-BuDiNC

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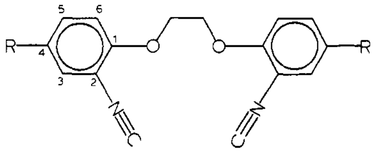
The six-coordinate homoleptic complexes $[\mathrm{M}(t\text{-BuDiNC})_3](\mathrm{PF}_6)_z$ (M = Cr, z = 0, 1, 2; M = Mn, z = 1, 2; M = Fe, z = 2; M = Co, z = 3) (t-BuDiNC = 1,2-bis(4-*tert*-butyl-2-isocyanophenoxy)ethane) have been prepared. The Co(III) complex of this series represents the first example of a hexakis(isocyanide) derivative of trivalent cobalt. Infrared spectra of the complexes show $\nu(\mathrm{C{\equiv}N})$ to increase with increasing charge on the complex or, for complexes of the same charge, with increasing atomic number. A comparison of the integrated intensities of the infrared $\nu(\mathrm{C{\equiv}N})$ bands of the 18-electron d^6 members of this series (M = Cr(0), Mn(I), Fe(II), Co(III)) shows the band intensity to decrease in a near-linear fashion in the order Cr(0) > Mn(I) > Fe(II). This trend is interpreted to indicate decreasing $d\pi-\pi^*_{\mathrm{CN}}$ back-bonding from the metal to the ligands in the same order. The very low intensity of the $\nu(\mathrm{C{\equiv}N})$ band of the Co(III) complex suggests that such back-bonding is of little or no importance in this case. Cyclic voltammetric studies show quasi-reversible interconversions among the species $[\mathrm{Cr}(t\text{-BuDiNC})_3]^{z+}$ (z = 0, 1, 2, 3) and $[\mathrm{Mn}(t\text{-BuDiNC})_3]^{z+}$ (z = 1, 2, 3); they also indicate a slight thermodynamic destabilization of the trivalent complexes relative to analogues containing para-substituted phenyl isocyanides or phenyl isocyanide itself. Electronic spectra of these homoleptic six-coordinate complexes are interpreted as arising from $d\pi \rightarrow \pi^*_{\mathrm{CN}}$ transitions; their energies are affected by both charge and atomic number. Syntheses of the pseudotetrahedral complexes $\mathrm{Ni(CO)_2}(t\text{-BuDiNC})$, $\mathrm{Ni}(t\text{-BuDiNC})_2$, and $[\mathrm{Cu}(t\text{-BuDiNC})_2]\mathrm{BF_4}$ are also reported. The existence of these complexes as mononuclear species (verified for $\mathrm{Ni(CO)_2}(t\text{-BuDiNC})$ by vapor-pressure osmometry) demonstrates that the t-BuDiNC ligand is capable of chelating to a metal center in which the preferred C–M–C angles are considerably greater than 90°.

Introduction

We recently described the synthesis of two bidentate isocyano ligands, DiNC (for R = H) and t-BuDiNC (for R = t-Bu)[1,2]



which were shown to form chelate complexes with a variety of low-valent metals possessing pseudooctahedral[1-3] or square-planar[4] coordination geometries. Because of recent interest in the spectroscopic[5-9] and chemical[9-16] properties of homoleptic isocyanide complexes, we sought to synthesize a series of homoleptic complexes containing the t-BuDiNC ligand. The properties of these derivatives, especially those of Fe(II) and Co(III), would be of special interest. Only one complex of the type $[\mathrm{Fe(CNAr)_6}]^{2+}$[17] and none of the composition $[\mathrm{Co(CNR)_6}]^{3+}$ (R = alkyl or aryl) are presently known.

Also reported herein are the syntheses of several complexes in which the t-BuDiNC ligand is coordinated to a pseudotetrahedral metal center. Space-filling molecular models suggest that chelation to such metals would be much less favored than would chelation to pseudooctahedral metals. The results presented here represent part of a more general investigation into the synthesis and coordination behavior of polydentate isocyano,[1-4,18,19] cyano,[1,2,20] and diazonium[21] ligands.

Experimental Section

General Information. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. Dichloromethane was distilled from $\mathrm{CaH_2}$. Acetone, EtOH, $\mathrm{CHCl_3}$, pentane, and hexane were dried over molecular sieves (4A) and purged with $\mathrm{N_2}$ before use. Unless stated otherwise, all other solvents were used as received after purging with $\mathrm{N_2}$. The reagents $\mathrm{Mn(CO)_5Cl}$[22] and $[\mathrm{Cu(CH_3CN)_4}]\mathrm{BF_4}$[23] were prepared by the cited procedures. The DiNC and t-BuDiNC ligands were prepared as described previously.[1] Anhydrous $\mathrm{FeCl_2}$ and $\mathrm{Ni(CO)_4}$ were obtained from commerical sources. Zinc dust was activated by washing for 30 s with 3 M HCl, then with $\mathrm{H_2O}$, and finally with EtOH. All other chemicals were used as received.

All complexes were prepared in Schlenk-ware or similar apparatus under $\mathrm{N_2}$ dried over 4A molecular sieves, by using standard inert-atmosphere techniques.[24] Routine infrared spectra were determined with Perkin-Elmer 281 or 681 spectrophotometers calibrated against CO gas. JEOL FX90Q and Bruker WM-300 spectrometers were used to record NMR spectra. Chemical shifts are reported in ppm downfield from tetramethylsilane. Electronic (UV–vis) spectra were recorded on a Perkin-Elmer 320 instrument. Conductivity measurements were made in spectral grade $\mathrm{MeNO_2}$ by using a Markson

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4402 conductivity meter and dip cell. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were observed on a Thomas hot-stage apparatus and are uncorrected. Electrochemical measurements were carried out by using a Princeton Applied Research Model 173 potentiostat/galvanostat, Model 175 Universal Programmer, and Houston Instruments Model 2000 X–Y recorder. A three-electrode configuration was employed, consisting of a stationary Pt-disk working electrode of area 0.45 cm^2, Pt-wire counterelectrode, and saturated calomel (aqueous KCl) reference electrode. Dry CH_2Cl_2 (see above) was used as solvent and contained 0.1 M Bu_4NPF_6[25] as supporting electrolyte. Analyte concentrations were ca. 5×10^{-3} M, and all experiments were carried out under an atmosphere of Ar gas.

Infrared integrated intensity measurements were carried out on an IBM IR 98 Fourier transform spectrometer at a resolution of 2 cm^{-1}. The cell path length, l (0.102 ± 0.001 cm^{-1}), was determined by the interference-fringe method.[26] Spectra in the ν(C≡N) region were plotted as absorbance scans for which the reference files were obtained by scanning the pure solvent in the cell. Solutions were prepared with dry, degassed CH_2Cl_2. Samples (typically 1–3 mg) were weighted onto Al-foil boats with the aid of a Perkin-Elmer AD-2Z Autobalance. The boats were inserted into small vials and the desired weight of solvent was introduced. Areas under absorption bands were measured with a polar planimeter, and apparent integrated intensities, B, were then calculated as $B = (2.303c^{-1}l^{-1})\int \log (T_0/T)\, d\nu$, where c represents concentration (M), l the cell path, and $\log (T_0/T)$ the apparent absorbance. Because of the large half-height widths of the bands, wing corrections were applied according to Ramsay (method II).[27] Absolute integrated intensities, A, were then determined by extrapolation of a plot of B vs. absorbance to zero absorbance,[28] though such plots deviated only slightly from zero slope. Integrated intensities of the ν(C≡N) band of $[Co(t\text{-BuDiNC})_3](PF_6)_3$ could only be estimated (by Ramsay's method I),[27] due to sample decomposition (vide infra) and the presence of an interfering solvent band at 2305 cm^{-1}.

Preparation of Complexes. Cr(*t*-BuDiNC)$_3$ (1). A solution of $CrCl_3(THF)_3$ was prepared by stirring 0.023 g (0.145 mmol) of finely ground anhydrous $CrCl_3$ with 5 mg of Zn dust in 4 mL of THF until a homogeneous purple solution resulted. To this solution was added a solution of *t*-BuDiNC (0.167 g, 0.444 mmol) in 4 mL of THF, causing an immediate change in color to red-brown. The red-brown solution was transferred via a cannula tube to freshly prepared Na/Hg (0.045 g of Na/2 mL of Hg). After stirring for 30 min, the resulting blood red solution was transferred to a 15-mL centrifuge tube capped with a rubber septum, and the suspended NaCl was concentrated by centrifugation. The resulting solution was filtered and evaporated at reduced pressure, and the residue was dried in vacuo overnight. The product is a deep red air-sensitive, glassy solid: yield 0.112 g (65%); mp 175 °C.

[Cr(*t*-BuDiNC)$_3$]PF$_6$ (2). Acetone (3 mL) was added to a mixture of $Cr(t\text{-BuDiNC})_3$ (0.050 g, 0.042 mmol) and $AgPF_6$ (0.012 g, 0.047 mmol). A deep red-black solution formed rapidly, and a silver mirror was deposited on the walls of the flask. After being stirred for 1 h, the solution was filtered to remove suspended silver. The reaction flask and frit were rinsed with acetone, and the volume of the red-orange solution was reduced to 3 mL. Rapid addition of 10 mL of hexane gave an orange precipitate of the crude product, which was isolated by filtration, washed with ether, and dried; yield 0.052 g (83%). The product was recrystallized from CH_2Cl_2/hexane and obtained as an air-stable orange powder (0.038 g, 62%), mp 222 °C dec.

[Cr(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (3). In a reaction similar to the one just described, $Cr(t\text{-BuDiNC})_3$ (0.0538 g, 0.0455 mmol) and $AgPF_6$ (0.0225 g, 0.089 mmol) were allowed to react in 3 mL of acetone for 1.5 h. Workup of the reaction as before gave the crude product as a red powder (0.059 g, 90%). Recrystallization from acetone/hexane gave the product as an air-stable microcrystalline red solid (0.042 g, 64%), mp 260–280 °C dec.

[Mn(*t*-BuDiNC)$_3$]PF$_6$ (4). A solution of $Mn(CO)_5Cl$ (0.091 g, 0.39 mmol) and *t*-BuDiNC (0.453 g, 1.20 mmol) in 11 mL of THF was heated to reflux. During the first few hours of reaction, a pale yellow precipitate of $[Mn(t\text{-BuDiNC})_3]Cl$ formed. After 26 h, the mixture was cooled and filtered. The solid was washed with ether and dried in vacuo, giving 0.250 g (35%) of pale yellow $[Mn(t\text{-BuDiNC})_3]Cl$. This salt was then metathesized to the PF_6^- salt as follows. The crude solid was dissolved in CH_2Cl_2, the mixture was filtered, and the solvent was evaporated. The residue was treated with 35 mL of EtOH and heated to boiling, whereupon all the solid dissolved. A filtered solution of 0.130 g of NH_4PF_6 in 7 mL of EtOH was added to the hot solution, causing the desired product to precipitate from solution. The mixture was cooled to room temperature and filtered, and the product was washed with Et_2O. The cream-colored product was then dried in vacuo; yield 0.255 g (49% from $Mn(CO)_5Cl$). The product turns yellow at ca. 200 °C but does not melt below 350 °C.

[Mn(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (5). Concentrated HNO_3 (2 mL) was added to a stirred suspension of $[Mn(t\text{-BuDiNC})_3]PF_6$ (0.0420 g, 0.032 mmol) in 4 mL of glacial acetic acid in air, yielding a deep blue solution. Having been stirred for 10 min, the mixture was poured into a stirred, filtered solution of KPF_6 (0.33 g, 1.8 mmol) in 4 mL of H_2O. The deep blue precipitate that formed was isolated by filtration in air, washed with H_2O, and dried in vacuo; yield 0.0434 g (93%). Infrared spectral analysis showed that some Mn(I) product was present. An analytical sample was obtained by hexane precipitation from a CH_2Cl_2 solution containing a small amount of concentrated HNO_3. The complex decomposes slowly in $CHCl_3$ or CH_2Cl_2 solution to $[Mn(t\text{-BuDiNC})_3]PF_6$, but as a solid, it is stable.

***cis*-FeCl$_2$(*t*-BuDiNC)$_2$ (6).** Anhydrous $FeCl_2$ (0.017 g, 0.13 mmol) was dissolved in 5 mL of CH_3OH and, with stirring, was treated with 0.102 g (0.271 mmol) of solid *t*-BuDiNC. The color of the solution changed from pale yellow to deep orange within 10 s. After several minutes, a small amount of fine orange precipitate formed. The mixture was stirred a total of 15 min, filtered, and reduced in volume until more precipitate of the product formed. This suspension was treated with 7 mL of Et_2O and allowed to stand for 20 h. The resulting orange powder was collected by filtration, washed with Et_2O, and dried in vacuo; yield 0.0842 g (73%). Orange microcrystals of $\mathbf{6}\cdot{}^1/_2CHCl_3$ were obtained by allowing a concentrated, filtered $CHCl_3$ solution of the complex to stand for 2 days at room temperature. These were isolated by decantation of the mother liquor and then vacuum dried for 2 days. The lattice $CHCl_3$ was identified by its mass spectrum. Upon being heated from 200 °C, the compound turns black at 215 °C and melts from ca. 245 to 255 °C.

***trans*-FeCl$_2$(*t*-BuDiNC)$_2$ (7).** A solution of unrecrystallized **6** (0.101 g, 0.115 mmol) in 10 mL of CH_2Cl_2 was treated with $AlCl_3$ (0.005 g, 0.037 mmol). The solution was stirred for 15 min and then filtered to remove insoluble $AlCl_3$ hydrolysis products. After the solution stood for 15 days, the resulting lavender needles of the trans complex were collected by filtration, washed with CH_2Cl_2, and then dried, yielding 0.0765 g (77%). The compound appears to be insoluble in all common solvents, including $(CH_3)_2SO$. Upon being heated, the complex turns light brown at 235 °C and melts with decomposition at ca. 255 °C.

[Fe(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (8). A solution of **6** (0.153 g, 0.174 mmol) in 6.0 mL of CH_2Cl_2 was treated with 0.0885 g (0.350 mmol) of $AgPF_6$ dissolved in 4 mL of CH_2Cl_2. This led to immediate precipitation of AgCl. The solution was stirred for 25 min and then filtered to remove the AgCl. To the resulting orange solution was added 0.0670 g of *t*-BuDiNC (0.178 mmol) in 4 mL of CH_2Cl_2, causing a gradual color change to brown. This solution was stirred for 20 min and evaporated in vacuo. The resulting residue was dissolved in 3 mL of CH_2Cl_2 and then treated with 9 mL of Et_2O to give a tarry yellow residue. The solvent was decanted off, and the residue was triturated to a yellow powder with Et_2O. The product was filtered, washed with ether, and dried; yield 0.128 g (50%). Careful recrystallization from CH_2Cl_2/Et_2O gave the analytically pure compound as an off-white powder. The compound decomposed without melting from 335 to 350 °C.

[Co$_2$(*t*-BuDiNC)$_5$](PF$_6$)$_2$ (9). The reagents *t*-BuDiNC (0.153 g, 0.406 mmol) and $CoCl_2\cdot 6H_2O$ (0.036 g, 0.15 mmol) were dissolved in 5 mL of EtOH to give a brown-red solution. The addition of 0.015 g (0.23 mmol) of Zn dust caused a gradual color change to deep yellow. The mixture was stirred for 5.5 h, after which solid KPF_6 (0.050 g, 0.27 mmol) was added. After being stirred an additional 1 h, the solution was filtered. Reduction of the volume at reduced pressure and ambient temperature was carried out until the product began to crystallize. The solution was cooled to −80 °C and filtered. The resulting crude green-yellow product was washed with ether and dried;

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yield 0.062 g (36%). An analytically pure sample was obtained as yellow microcrystals by recrystallization from EtOH at −20 °C; mp 206–213 °C.

***trans*-$CoBr_2$(*t*-BuDiNC)$_2$ (10).** A solution of 0.500 g of *t*-BuDiNC (1.33 mmol) in 125 mL of acetone was treated with a solution of $CoBr_2 \cdot 6H_2O$ (0.210 g, 0.643 mmol) in 10 mL of acetone in air. A fine green precipitate of the product began to form after about 30 s. The reaction mixture was stirred for a total of 5 min, after which the product was filtered in air and washed with two 25-mL portions of acetone. The product was dried in vacuo to a very fluffy green powder: 0.486 g (78%); mp 254–263 °C dec.

***trans*-[$CoBr_2$(*t*-BuDiNC)$_2$]Br_3 (11).** A stirred suspension of **10** (0.102 g, 0.105 mmol) in 4.5 mL of CH_2Cl_2 was treated slowly with Br_2 (8 μL, 0.025 g, 0.157 mmol). Initially, a clear brown solution was formed. As the addition proceeded, a precipitate of small orange-brown needles formed. The solvent was removed at reduced pressure, and the solid was dried in vacuo. The product was isolated without purification, yielding 0.113 g (89%); mp 248–258 °C dec. The complex is stable in the solid state but is reduced by wet solvents to a deep brown compound with a ν(C≡N) value identical with that of *trans*-$CoBr_2$(*t*-BuDiNC)$_2$.

[Co(*t*-BuDiNC)$_3$](PF_6)$_3$ (12). A suspension of **10** (0.198 g, 0.204 mmol) in 10 mL of CH_2Cl_2 was treated with Br_2 (5.4 μL, 0.106 mmol), and the resulting clear brown solution was stirred for 20 min. Addition of $AgPF_6$ (0.158 g, 0.125 mmol) in 10 mL of CH_2Cl_2 caused precipitation of AgBr (91% of theoretical). The reaction mixture was stirred for 45 min and then filtered. A solution of *t*-BuDiNC (0.0775 g, 0.206 mmol) in 4 mL of CH_2Cl_2 was added, and after the solution was stirred an additional 30 min, its volume was reduced to 5 mL. The crude yellow-brown product was precipitated by rapid addition of 6 mL of Et_2O and was isolated by filtration. The final product was obtained by recrystallization from CH_2Cl_2/Et_2O (4 mL:6 mL) at −20 °C, followed by filtration, washing with Et_2O, and vacuum drying; yield 0.0736 g (22%). The yellow product is quite sensitive to atmospheric moisture and slowly decomposes even after brief exposure to air in the solid state. Upon being heated, the product melts with decomposition at 240–245 °C.

Ni(CO)$_2$(*t*-BuDiNC) (13). *Caution! Ni(CO)$_4$ is extremely toxic. This and similar reactions should be carried out in an efficient fume hood.* Approximately 0.1 mL (0.13 g, 0.76 mmol) of Ni(CO)$_4$ was condensed into a frozen solution of *t*-BuDiNC (0.240 g, 0.638 mmol) in 5 mL of CH_2Cl_2. After warming to room temperature, the reaction mixture was stirred for 1 h during which time CO evolution took place. The mixture was taken to near dryness, and 3 mL of hexane was added to precipitate the product as pale yellow microcrystals, which were filtered off, washed with hexane, and dried; yield 0.190 g, 61%. Upon being heated, the complex turns brown at ca. 140 °C. A vapor-pressure osmometric study (Knauer vapor-pressure osmometer) of the complex in 1,2-$C_2H_4Cl_2$ solution (0.01–0.02 M) showed the complex to be mononuclear, with an experimentally determined molecular weight of 475 (491 theoretical).

Ni(CO)$_2$(DiNC) (14). In a procedure similar to that described above, approximately 0.12 mL (0.16 g, 0.93 mmol) of Ni(CO)$_4$ was condensed into a frozen (−196 °C) solution of DiNC (0.336 g, 1.27 mmol) in 11 mL of CH_2Cl_2. Upon warming to room temperature, the solution began turning yellow as CO evolution commenced. After 15 min, a yellow precipitate began to form. The reaction was stirred for 1 h more, and the solid was filtered off, washed with 5 mL of CH_2Cl_2 at 0 °C, and vacuum dried. The product is a light yellow microcrystalline solid: yield 0.213 g (44% based on DiNC); mp 140 °C dec.

Ni(*t*-BuDiNC)$_2$ (15). Approximately 0.08 mL (0.10 g, 0.6 mmol) of Ni(CO)$_4$ was condensed into a frozen solution of *t*-BuDiNC (0.377 g, 1.00 mmol) in 10 mL of Et_2O, and the mixture was warmed to 20 °C. The yellow product began to precipitate from solution soon after the onset of CO evolution. When gas evolution had ceased, the volume of the solution was reduced to 2 mL, and 5 mL of pentane was added with stirring. The yellow residue was filtered off, washed with pentane, and dried in vacuo; yield 0.406 g (90%). Air-exposed samples are decomposed either as solids or in solution. Even under N_2, samples appear to darken noticeably at ambient temperatures in the laboratory. The complex decomposes quickly at ca. 120 °C.

[Cu(*t*-BuDiNC)$_2$]BF_4 (16). A solution of [Cu(CH_3CN)$_4$]BF_4 (0.041 g, 0.130 mmol) and *t*-BuDiNC (0.102 g, 0.271 mmol) in 10 mL of CH_2Cl_2 was stirred for 50 min. Evaporation of the solvent gave a clear oil. This was washed twice with 10 mL of Et_2O to remove excess ligand and CH_3CN. Drying in vacuo gave an off-white solid, which was scraped out of the reaction vessel: yield 0.080 g (68%); mp 190–200 °C.

Results and Discussion

Metal Halide *t*-BuDiNC Complexes. These complexes were investigated primarily as precursors to homoleptic six-coordinate complexes (vide infra). Anhydrous $FeCl_2$ and *t*-BuDiNC react in methanol solution to afford *cis*-$FeCl_2$(*t*-BuDiNC)$_2$ (**6**) as the only product. Recrystallization from $CHCl_3$ yields orange microcrystals of **6**$\cdot {}^1/_2CHCl_3$, whose infrared spectrum is very similar to those of *cis*-$FeCl_2$(CN-*p*-anisyl)$_4$[29] and *cis*-$FeCl_2$(DiNC)$_2$.[3] Because of the presence of two chelate rings, this complex has C_2 symmetry and is chiral. The CH_2CH_2 unit, which is defined as an ABCD spin system, yields a broad singlet resonance in the ^1H NMR spectrum, and the two pairs of inequivalent *tert*-butyl groups give rise to two singlet resonances. Pure, lavender *trans*-$FeCl_2$(*t*-BuDiNC)$_2$ (**7**) crystals are obtained by addition of a catalytic amount of $AlCl_3$ to a CH_2Cl_2 solution of the unrecrystallized cis isomer **6**. Solutions of recrystallized **6**, however, precipitated needles of the trans isomer **7** over a period of several days even without added $AlCl_3$. Complex **7**, which is virtually insoluble in all common solvents, exhibits only a single sharp ν(C≡N) band as expected for the assigned trans stereochemistry.[3]

Dilute acetone solutions of *t*-BuDiNC (0.01 M) react with added $CoBr_2 \cdot 6H_2O$ to yield a fine, green precipitate of the 19-electron complex *trans*-$CoBr_2$(*t*-BuDiNC)$_2$ (**10**). More concentrated *t*-BuDiNC solutions (0.1 M) yield only an intractable brown sludge. Addition of $^1/_2$ mol of Br_2 to a suspension of 1 mol of **10** in CH_2Cl_2 yields a deep brown solution, presumably of the 18-electron Co(III) complex *trans*-[$CoBr_2$(*t*-BuDiNC)$_2$]Br. The cation was obtained as its pure, Br_3^- salt (**11**) by introducing an additional 1 mol of Br_2 into the solution. Similar oxidations of monodentate isocyanide complexes, $CoX_2(CNR)_4$, have been reported.[9,30]

An interesting homoleptic dinuclear complex, {[Co(*t*-BuDiNC)$_2$]$_2$(μ-*t*-BuDiNC)}(PF_6)$_2$ (**9**) is obtained via the Zn reduction of $CoCl_2 \cdot 6H_2O$ in the presence of 2.5 mol of *t*-BuDiNC in EtOH solution. This complex should have a local coordination geometry similar to those of the many known D_{3h} complexes of the type [Co(CNR)$_5$]X.[9,31]

Six-Coordinate Homoleptic Complexes, [M(*t*-BuDiNC)$_3$]$^{z+}$. The most highly reduced member of this series, Cr(*t*-BuDiNC)$_3$ (**1**), is prepared in 65% yield by Na/Hg reduction of $CrCl_3(THF)_3$ in the presence of *t*-BuDiNC, which represents a new route to Cr(CNAr)$_6$ complexes (eq 1). In the solid

$$CrCl_3 + 3t\text{-BuDiNC} \xrightarrow{Na/Hg} \underset{\mathbf{1}}{Cr(t\text{-BuDiNC})_3} + 3NaCl \qquad (1)$$

state, **1** (ν(C≡N) 1940 cm^{-1}) reacts slowly with air to yield [Cr(*t*-BuDiNC)$_3$]$^+$, identified by its IR spectrum (vide infra). This oxidation is much more rapid in solution, requiring several hours, or in the presence of Al_2O_3, requiring only a few minutes to reach completion. The 17-electron complex [Cr(*t*-BuDiNC)$_3$]PF_6 (**2**) is prepared independently in 62% yield by the method of Treichel and Essenmacher,[32] through the reaction of **1** with $AgPF_6$. Upon reaction of **1** with 2 equiv of $AgPF_6$, [Cr(*t*-BuDiNC)$_3$](PF_6)$_2$ (**3**) is formed in high yield.

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Table I. Analytical Data for *t*-BuDiNC Complexes

compd	% calcd			% found		
	C	H	N	C	H	N
Cr(*t*-BuDiNC)$_3$ (1)	73.19	7.17	7.11	72.69	7.31	6.92
[Cr(*t*-BuDiNC)$_3$]PF$_6$ (2)	65.20	6.38	6.34	65.18	6.52	6.10
[Cr(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (3)	58.77	5.75	5.71	59.45	6.26	5.44
[Mn(*t*-BuDiNC)$_3$]PF$_6$ (4)	65.05	6.37	6.32	64.51	6.33	6.28
[Mn(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (5)	58.66	5.74	5.70	58.03	5.78	5.64
cis-FeCl$_2$(*t*-BuDiNC)$_2$ (6·$^1/_2$CHCl$_3$)	62.01	6.06	5.96	62.40	6.59	5.92
trans-FeCl$_2$(*t*-BuDiNC)$_2$ (7)	65.53	6.42	6.37	65.21	6.18	6.31
[Fe(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (8)	58.62	5.74	5.70	58.93	5.90	5.70
[Co$_2$(*t*-BuDiNC)$_5$](PF$_6$)$_2$ (9)	62.93	6.16	6.12	62.87	6.59	6.17
trans-CoBr$_2$(*t*-BuDiNC)$_2$ (10)	59.33	5.81		58.88	5.78	
trans-[CoBr$_2$(*t*-BuDiNC)$_2$]Br$_3$ (11)	47.59	4.66	4.62	47.91	4.89	4.65
[Co(*t*-BuDiNC)$_3$](PF$_6$)$_3$ (12)	54.23	5.88	5.44	53.27	5.22	5.18
Ni(CO)$_2$(*t*-BuDiNC) (13)	63.57	5.75		63.42	5.78	
Ni(CO)$_2$DiNC (14)	57.02	3.19	7.39	56.74	3.05	7.24
Ni(*t*-BuDiNC)$_2$ (15)	71.03	6.95	6.90	69.91	7.20	6.83
[Cu(*t*-BuDiNC)$_2$]BF$_4$ (16)	63.82	6.25	6.20	63.96	6.44	6.21

Both reactions are well-documented for a large number of Cr(CNAr)$_6$ complexes.[32] A species with ν(CN) at 2206 cm^{-1} (CH$_2$Cl$_2$) presumed to be the 15-electron trication, [Cr(*t*-BuDiNC)$_3$]$^{3+}$, is generated chemically by the addition of SbCl$_5$ to a CH$_2$Cl$_2$ solution of **1** at −20 °C; this reaction is similar to that described by Bohling and Mann for the oxidation of Cr(CNC$_6$H$_5$)$_6$.[33]

The 18-electron d^6 complex [Mn(*t*-BuDiNC)$_3$]Cl is obtained by refluxing Mn(CO)$_5$Cl with 3 equiv of *t*-BuDiNC in THF solution. Metathesis of the Cl$^-$ salt with NH$_4$PF$_6$ in EtOH gives the cream-colored product [Mn(*t*-BuDiNC)$_3$]PF$_6$ (**4**) in 49% yield (eq 2). Like its monodentate analogues, **4** undergoes an oxidation reaction with HNO$_3$[6,34] to afford the deep blue product, [Mn(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (**5**). Over a period of 36 h in either CHCl$_3$ or CH$_2$Cl$_2$ solution, **5** undergoes an apparent autoreduction back to **4**. The complex [Mn(CN-*p*-anisyl)$_6$](PF$_6$)$_2$ also decomposes in this fashion, but over a time period of only ca. 15 min.[6]

$$\mathrm{Mn(CO)_5Cl} + 3t\text{-BuDiNC} \rightarrow 5\mathrm{CO} + [\mathrm{Mn}(t\text{-BuDiNC})_3]\mathrm{Cl} \xrightarrow{\mathrm{NH_4PF_6}} \mathbf{4} \quad (2)$$

The d^6 complex [Fe(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (**8**) is obtained by addition of 2 equiv of AgPF$_6$ to *cis*-FeCl$_2$(*t*-BuDiNC)$_2$ (**6**) in CH$_2$Cl$_2$, which precipitates 2 equiv of AgCl quantitatively, followed by addition of *t*-BuDiNC to the filtered solution (eq 3). Crude **8** (50% yield) after recrystallization is obtained as an off-white solid. The presumed intermediate in this reaction, [Fe(*t*-BuDiNC)$_2$]$^{2+}$, appears to be quite acidic, since only one Cl$^-$ ion is removed from **6** when the reaction is carried out in CH$_3$CN solution. Solvation of Ag$^+$ by CH$_3$CN may render Ag$^+$ too weakly acidic to remove the second chloride ion. In 1955, Padoa claimed to have isolated unreactive compounds of the type [Fe(CNAr)$_4$](ClO$_4$)$_2$ by reaction of Fe(ClO$_4$)$_2$ with aromatic isocyanides.[9,35] A repetition of that work by Bonati and Minghetti failed to support those results but did lead to the isolation of [Fe(CN-*p*-tol)$_6$](ClO$_4$)$_2$, the only reported monodentate aromatic isocyanide analogue of **8**, in 2% yield.[17] The two compounds have similar infrared spectra (Table III) and colors.

$$cis\text{-}\mathrm{FeCl_2}(t\text{-BuDiNC})_2 \xrightarrow[-2\mathrm{AgCl}]{+2\mathrm{AgPF_6}} \xrightarrow{t\text{-BuDiNC}} [\mathrm{Fe}(t\text{-BuDiNC})_3](\mathrm{PF_6})_2 \quad (3)$$

Table II. Conductivity Data for Ionic *t*-BuDiNC Complexes[a]

compd	10^3 × concn, M	Λ_M, Ω^{-1} cm^2 mol^{-1}	compd	10^3 × concn, M	Λ_M, Ω^{-1} cm^2 mol^{-1}
2	1.01	83.1	**9**	1.03	148
3	0.99	157	**11**	1.03	79.7
4	1.00	84.8	**12**	1.10	229
8	1.02	156	**16**	0.97	84

[a] Expected ranges for Λ_M in CH$_3$NO$_2$: (1:1), 75–95; (2:1), 150–180; (3:1), 220–260 (Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81).

Oxidation of *trans*-CoBr$_2$(*t*-BuDiNC)$_2$ with $^1/_2$ equiv of Br$_2$, bromide abstraction with 3 equiv of AgPF$_6$, and addition of *t*-BuDiNC give the d^6 Co(III) complex [Co(*t*-BuDiNC)$_3$](PF$_6$)$_3$ (**12**) in 22% isolated yield (eq 4). As with **6**, halide abstraction from [CoBr$_2$(*t*-BuDiNC)$_2$]$^+$ is incomplete in the presence of CH$_3$CN, showing the presumed intermediate, [Co(*t*-BuDiNC)$_2$]$^{3+}$, to have a very high affinity for halide ion. It is probably this acidity that thwarted earlier attempts to obtain homoleptic cobalt(III) isocyanide complexes.[9,30] Complex **12** is quite moisture sensitive, not unlike the tricationic Cr(III) complexes of the type [Cr(CNAr)$_6$]$^{3+}$ described recently by Bohling and Mann.[33] Decomposition takes place over a period of several hours when solid **12** is exposed to air, and is accompanied by a color change from yellow to brown. As observed by IR, the initially weak ν(C≡N) band of **12** at 2259 cm^{-1} is replaced by a broad, more intense band at ca. 2225 cm^{-1}.

$$\mathrm{CoBr_2}(t\text{-BuDiNC})_2 \xrightarrow{{}^1/_2\mathrm{Br_2}} [\mathrm{CoBr_2}(t\text{-BuDiNC})_2]\mathrm{Br} \xrightarrow[-3\mathrm{AgBr}]{3\mathrm{AgPF_6}} \mathbf{12} \quad (4)$$

The six-coordinate homoleptic complexes have been characterized by various methods, including elemental analyses (Table I), molar conductances (Table II), infrared spectra (Table III and Figure 1), ν(C≡N) integrated intensities (Table IV and Figure 2), ^{1}H NMR spectra (Table V), ^{13}C NMR spectra (Table VI), cyclic voltammetry (Table VII and Figure 3), and UV–visible spectra (Table VIII and Figure 4). The infrared spectrum of each complex in the region 2300–1900 cm^{-1} shows a single, symmetrical ν(C≡N) band (Table III). The energy of this band (CH$_2$Cl$_2$ solution) ranges from 1958 cm^{-1} for the Cr(0) complex **1** to 2258 cm^{-1} for the Co(III) complex **12**. These extreme values represent shifts in ν(C≡N) of −170 and +130 cm^{-1}, respectively, with respect to the free *t*-BuDiNC frequency of 2128 cm^{-1}. The ν(C≡N) value found for **12** appears to be the highest recorded for an aromatic isocyanide complex to date. The closest are those

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Table III. Infrared Spectral Data

compd	medium	ν(C≡N), cm^{-1}	other freq, cm^{-1}
Cr(*t*-BuDiNC)$_3$ (1)	CH_2Cl_2	1958 vs, br	
	Nujol	1940 vs, br	
[Cr(*t*-BuDiNC)$_3$]PF$_6$ (2)	CH_2Cl_2	2056 vs	
	Nujol	2050 vs	ν(P–F) 848 s
[Cr(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (3)	CH_2Cl_2	2153 s	
	Nujol	2155 s	ν(P–F) 844 vs
[Cr(*t*-BuDiNC)$_3$](SbCl$_6$)$_3$[a]	CH_2Cl_2	2206 m	
[Mn(*t*-BuDiNC)$_3$]PF$_6$ (4)	CH_2Cl_2	2082 vs	
	Nujol	2071 vs	ν(P–F) 848 s
[Mn(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (5)	CH_2Cl_2	2162 s	
	Nujol	2162 s	ν(P–F) 847 vs
cis-FeCl$_2$(*t*-BuDiNC)$_2$ (6)	CH_2Cl_2	2200 w, sh, 2154 vs, br, 2126 s, sh	
	Nujol	2190 w, sh, 2147 vs, 2131 s, sh	
trans-FeCl$_2$(*t*-BuDiNC)$_2$ (7)	Nujol	2146 vs	
[Fe(*t*-BuDiNC)$_3$](PF$_6$)$_2$ (8)	CH_2Cl_2	2194 s	
	Nujol	2195 s	ν(P–F) 847 vs
[Co$_2$(*t*-BuDiNC)$_5$](PF$_6$)$_2$ (9)	Nujol	2150 s, sh, 2108 vs	ν(P–F) 846 s
trans-CoBr$_2$(*t*-BuDiNC)$_2$ (10)	Nujol	2188 s, 2109 w, sh	ν(CoBr) 158 s
trans-[CoBr$_2$(*t*-BuDiNC)$_2$]Br$_3$ (11)	Nujol	2227 m	
[Co(*t*-BuDiNC)$_3$](PF$_6$)$_3$ (12)	CH_2Cl_2	2258 w	
	Nujol	2259 w	ν(P–F) 845 vs
Ni(CO)$_2$(*t*-BuDiNC) (13)	$CHCl_3$	2145 s, 2094 s	ν(C≡O) 2014 s, 1975 s
Ni(CO)$_2$(DiNC) (14)	$CHCl_3$	2146 s, 2092 s	ν(C≡O) 2014 s, 1972 s
Ni(*t*-BuDiNC)$_2$ (15)	$CHCl_3$	2040 vs, br	
	Nujol	2160 w, sh, 2020 vs, br	
[Cu(*t*-BuDiNC)$_2$]BF$_4$ (16)	$CHCl_3$	2169 vs	
	Nujol	2165 vs	ν(B–F) 1047 s, br

[a] See text.

Table IV. Linear Intensities (ϵ) and Specific Integrated Intensities of the ν(C≡N) Bands of *t*-BuDiNC and Homoleptic *t*-BuDiNC d^6 Complexes in CH_2Cl_2

compd	$\Delta\nu_{1/2}$[a]	ϵ[b]	A_{sp}[c,d]
t-BuDiNC	12	603	1.11×10^4
Cr(*t*-BuDiNC)$_3$	91	7.77×10^3	33.8×10^4
[Mn(*t*-BuDiNC)$_3$]PF$_6$	42	9.05×10^3	19.7×10^4
[Fe(*t*-BuDiNC)$_3$](PF$_6$)$_2$	24	3.58×10^3	4.61×10^4
[Co(*t*-BuDiNC)$_3$](PF$_6$)$_3$[e]	18	3.6×10^2	0.5×10^4

[a] Half-height bandwidth; units of cm^{-1}. [b] Units of M^{-1} cm^{-1}. [c] Units of M^{-1} cm^{-2}. [d] Specific intensity as defined by Noack.[48] [e] All values are estimates–see Experimental Section.

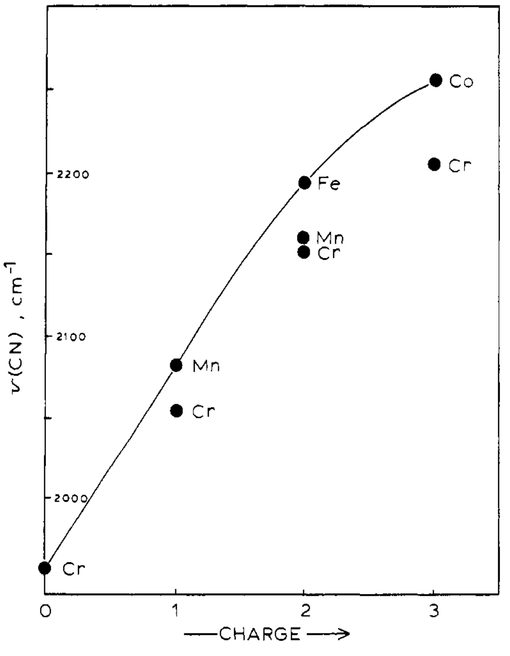

Figure 1. Plot of ν(C≡N) vs. charge for homoleptic complexes [M(*t*-BuDiNC)$_3$]$^{z+}$.

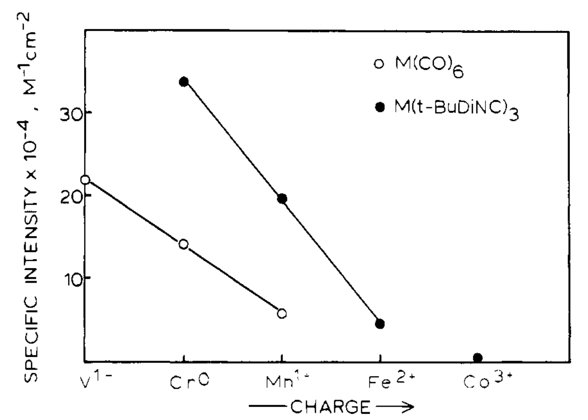

Figure 2. Plot of specific integrated intensities vs. charge for [M(CO)$_6$]$^{z+}$ (THF solution, ref 48) and [M(*t*-BuDiNC)$_3$]$^{z+}$ (CH_2Cl_2 solution).

of [Pt(NC-*p*-tol)$_4$]PtCl$_4$ (2248 cm^{-1})[36] and [Pt(DiNC)$_2$]PtCl$_4$ (2238 cm^{-1}).[4] The high value of ν(C≡N) for these complexes is attributed to a strong σ-bonding interaction between the isocyano carbon and the charged metal center.[37,38] Conversely, the low values of ν(CN) for complexes such as **1**, **2**, and **4** are determined by strong bonding interactions involving the occupied metal dπ and vacant isocyanide π^* orbitals.[37,38]

Figure 1 bears out this direct relationship between charge and ν(CN). It is also obvious from this plot that, for complexes of the same charge, the higher ν(CN) value rests with the metal of higher atomic number. This is undoubtedly due to the stabilization of the metal d orbitals with increasing atomic number (note the regular increase of nth ionization potentials across the series Cr–Co),[39] which would weaken the dπ →

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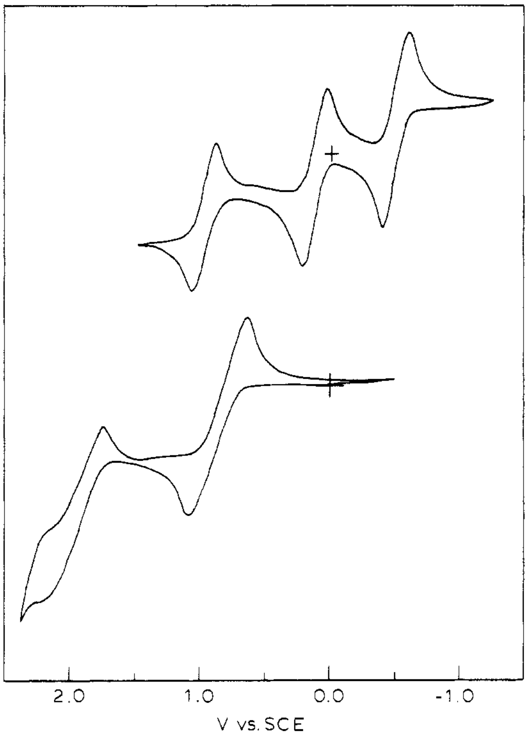


Figure 3. Cyclic voltammograms for (top) $[Cr(t\text{-BuDiNC})_3]PF_6$ and (bottom) $[Mn(t\text{-BuDiNC})_3]PF_6$ at a scan rate of 20 mV s^{-1}.

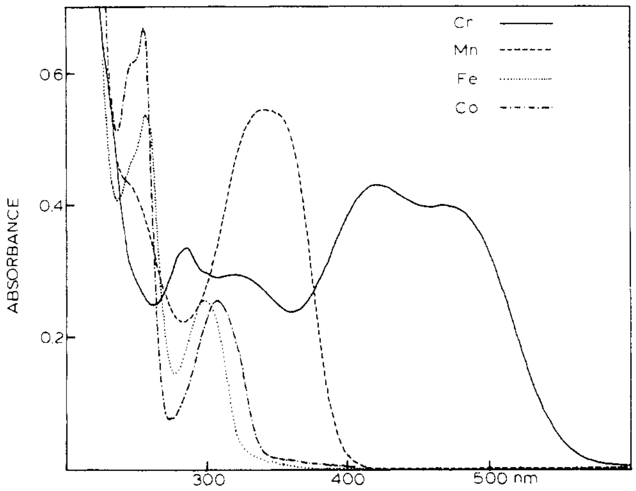


Figure 4. Electronic spectra of the d^6 complexes $[M(t\text{-BuDiNC})_3]^{z+}$, where $M^{z+} = Cr^0, Mn^+, Fe^{2+}$, and Co^{3+}. Concentrations are ca. 9×10^{-5} M; path length = 1 mm.

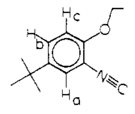
π^*_{CN} and strengthen the $\sigma_{CN} \rightarrow d\sigma$ bonding interactions. Both factors would be expected to increase the ν(CN) values, as observed.

Measurements of the absolute integrated intensities, A, of the ν(CN) bands of the d^6 complexes **1**, **4**, **8**, and **12**, and of t-BuDiNC itself, were carried out to demonstrate the widely varying importance of metal $d\pi-\pi^*_{CN}$ back-bonding across this series. Integrated intensities of ν(CO) bands of a large number of metal carbonyl complexes have been measured,[40] and it is now well accepted that these intensities are affected largely by the amount of $d\pi-\pi^*_{CO}$ bonding.[40,41] Intensities have also been measured for complexes containing coordinated N_2,[42] CS,[43] CN^-,[44] and benzonitrile[45] ligands, as well as for free isocyanides.[46,47] However, to our knowledge, no integrated intensities of isocyanide complexes have been reported.

Table V. ^{1}H NMR Data (90 MHz)[a]

compd	Ar	CH$_2$[b]	t-Bu[b]
t-BuDiNC	7.47–7.01 m	4.48	1.28
DiNC[c]	7.50–6.84 m	4.51	. . .
1[d]	7.17–6.57 m	3.78	1.04
4	7.41–7.29 m; 7.10–6.90 m	4.41	1.26
4[e]	7.36–7.33 m, H$_a$, H$_b$; 7.06–7.03 m, H$_c$	4.39	1.27
6[c]	7.71–6.85 m	4.39 br	1.31, 1.23 [1:1]
8	7.60–7.50 m; 7.23–7.13 m	4.50	1.30
8[e]	7.59–7.54 m, H$_a$, H$_b$; 7.18 d (8.8), H$_c$	4.50	1.30
9	7.50–6.94 m	4.51, 4.15 [4:1]	1.24, 1.16 [4:1]
11[f]	7.95 d (2.4), H$_a$; 7.67 dd (2.4, 8.8), H$_b$; 7.19 d (8.8), H$_c$	4.54	1.35
12	7.97 d (2.4), H$_a$; 7.68 dd (2.4, 8.8), H$_b$; 7.19 d (8.8), H$_c$	4.53	1.31
13	7.44–7.31 m, H$_a$, H$_b$; 7.08–6.97 m, H$_c$	4.36	1.30
14[c]	7.40–6.92 m	4.41	. . .
15[c,e]	7.32 d (2.4), H$_a$; 7.19 dd (2.4, 8.7), H$_b$; 6.91 d (8.7), H$_c$	4.35	1.25
16	7.61–7.15 m	4.50	1.30
t-BuDiNO$_2$[c,g]	7.82 d (2.3), H$_a$; 7.58 dd (2.3, 8.8), H$_b$; 7.16 d (8.8), H$_c$	4.50	1.33

[a] In ppm; CD$_2$Cl$_2$ solvent unless noted otherwise. Coupling constants (Hz) are given in parentheses. Aromatic protons are labeled as follows:



[b] Sharp singlet unless noted otherwise. Where more than one peak is observed, approximate intensity ratios are given in brackets. [c] CDCl$_3$ solvent. [d] C$_6$D$_6$ solvent. [e] 300-MHz spectrum. [f] CD$_3$CN solvent. [g] Reference 1.

Table IV contains specific integrated intensities, which are obtained by dividing the total integrated intensity by the number of isocyano groups.[48] Data for t-BuDiNC and its complexes, as well as for the homoleptic d^6 CO complexes $V(CO)_6^-$ through $Mn(CO)_6^+$,[48] are plotted in Figure 2. The t-BuDiNC specific intensity of 1.1×10^4 M^{-1} cm^{-2} compares well with the value of 1.29×10^4 M^{-1} cm^{-2} reported for C_6H_5NC in CHCl$_3$ solution,[46] especially since electron-releasing substituents are reported to lower the ν(CN) intensity somewhat.[47] As for the homoleptic $[M(CO)_6]^{z+}$ (M = V, Cr, Mn) series, the plot of specific intensities of $[M(t\text{-BuDiNC})_3]^{z+}$ vs. charge is linear for Cr(0), Mn(I), and Fe(II) (Figure 2), suggesting that $d\pi-\pi^*_{CN}$ back-bonding decreases regularly across the series. The greater sensitivity of the isocyano group intensities to changes in z, relative to CO group intensities, is probably due to a large number of factors including the ligands' different electronic structures and differences in the $d\pi-\pi^*_{1ig}$ energy gap for each CO and t-BuDiNC complex. The low integrated intensity of the ν(CN) band of the Co(III)

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Table VI. ^{13}C NMR Data[a]

compd	1	2	3	4	5	6	CN	OCH_2	*C*Me$_3$	$C(CH_3)_3$
t-BuDiNC	152.2	116.4	125.3	145.1	127.9	113.8	167.9	68.5	34.2	31.2
1[b]	152.0	*c*	124.6	144.4	127.2	113.6	170.2	67.8	38.8	30.9
4	152.6	120.1	123.4	145.8	126.7	115.3	*c*	68.6	34.6	31.4
8	152.8	117.1	124.1	146.0	126.7	115.0	153.4[d]	67.8	34.5	31.0
14[e]	152.1	119.5	123.4	146.0	126.7	115.5	166.4	69.4	34.4	31.2
15	151.6	121.1	122.5	145.4	124.4	115.3	158.8	69.4	34.0	30.9
16	152.9	116.4	124.1	146.1	129.5	115.8	*c*	69.1	34.6	31.2

[a] In ppm; in $CDCl_3$ solvent unless noted otherwise. [b] C_6D_6 solvent. [c] Resonance not observed. [d] Assignment is questionable, due to very low peak intensity. [e] CO at 197.8.

Table VII. Cyclic Voltammetric Data[a]

compd	scan rate, mV s^{-1}	$\frac{1}{2}[E_{p,a} + E_{p,c}]$, V[b]	$[E_{p,c} - E_{p,a}]$, V	couple
$[Cr(t\text{-BuDiNC})_3]PF_6$	20	−0.50	0.18	Cr/Cr^+
	20	+0.10	0.19	Cr^+/Cr^{2+}
	20	+0.99	0.19	Cr^{2+}/Cr^{3+}
	100	−0.54	0.61	Cr/Cr^+
	100	+0.16	0.61	Cr^+/Cr^{2+}
	100	+1.05	0.57	Cr^{2+}/Cr^{3+}
$[Mn(t\text{-BuDiNC})_3]PF_6$	20	+0.86	0.46	Mn^+/Mn^{2+}
	20	+2.00	0.51	Mn^{2+}/Mn^{3+}
	100	+0.85	0.60	Mn^+/Mn^{2+}
	100	+1.92	0.61	Mn^{2+}/Mn^{3+}

[a] In CH_2Cl_2 solution; 0.1 M Bu_4NPF_6 supporting electrolyte. Other experimental parameters are as defined in Experimental Section. [b] Vs. SCE.

Table VIII. Electronic Spectra of Homoleptic *t*-BuDiNC Complexes

compd	solvent	λ_{max}, nm (10^{-3} ϵ)	assignt[a]
1	THF	468 sh (44.1)	$d\pi \rightarrow \pi_v^*$
		420 (47.2)	$d\pi \rightarrow \pi_v^*$
		320 sh (32.3)	$d\pi \rightarrow \pi_h^*$
		300 (32.7)	$d\pi \rightarrow \pi_h^*$
		286 (37.1)	intraligand
2	CH_2Cl_2	443 sh (30.9)	$d\pi \rightarrow \pi_v^*$
		365 (49.6)	$d\pi \rightarrow \pi_v^*$
		276 (36.3)	intraligand
4	CH_2Cl_2	341 (60.9)	$d\pi \rightarrow \pi_v^*$
		249 sh (47.1)	intraligand
5	CH_2Cl_2	684 br (4.4)	*b*
		481 br (3.3)	*b*
		355 sh (8.9)	*b*
		303 (42.4)	$d\pi \rightarrow \pi_v^*$
		282 sh (37.3)	$d\pi \rightarrow \pi_v^*$
		246 sh (54.3)	intraligand
8	CH_2Cl_2	298 (30)	$d\pi \rightarrow \pi_v^*$
		258 (64)	$d\pi \rightarrow \pi_v^*$
		247 sh (56)	intraligand
12	CH_2Cl_2	307 (29)	$d\pi \rightarrow \pi_v^*$
		255 (77)	$d\pi \rightarrow \pi_v^*$
		248 sh (71)	intraligand

[a] Assignments made as in ref 5. [b] Possibly due to transitions from lower bonding levels into the $(d\pi)^5$ orbital.[5,6]

complex **12** is taken as evidence that $d\pi-\pi^*_{CN}$ back-bonding is of little or no importance in this case. A similar agreement has been put forth for CO adsorbed to metal oxide surfaces, where high ν(CO) values are associated with very low integrated intensities.[41]

^1H NMR spectra (Table V) of the d^6 complexes **1**, **4**, **8**, and **12** all show singlets assignable to the CH_2 and *t*-Bu groups and a multiplet for the three aromatic types of protons. The 90-MHz NMR spectrum of $[Co(t\text{-BuDiNC})_3]^{3+}$ is first order in the aromatic region; chemical shifts of aromatic protons a, b, and c are 7.97, 7.67, and 7.19 ppm. For the Fe(II) (**8**) and Mn(I) (**4**) complexes, the chemical shifts of the aromatic protons, especially H_a, drop rapidly and second-order spectra are observed at 90 MHz. The 300-MHz spectra of **8** and **4** are much better resolved. The low-field position of the Co(III) complex **12** resonances are thought to be due to the electron-withdrawing nature of the bound Co^{3+} ion. Interestingly, the ^1H NMR spectrum of the dinitro analogue of *t*-BuDiNC, 1,2-bis(4-*tert*-butyl-2-nitrophenoxy)ethane ("*t*-BuDiNO$_2$"),[1] is very similar to that of **12**. This is taken as further evidence that the $-N{\equiv}CCo^{3+}$ unit, like the nitro group, can be considered a strongly electron-withdrawing functional group.

Electrochemical data for $[Cr(t\text{-BuDiNC})_3]PF_6$ and $[Mn(t\text{-BuDiNC})_3]PF_6$ are presented in Table VII. Figure 3 shows the cyclic voltammogram of the chromium complex recorded at a scan rate of 20 mV s^{-1}. As seen in Figure 3, there are three distinct redox waves due to the interconversion of the four $[Cr(t\text{-BuDiNC})_3]^{z+}$ (z = 0–3) species. Half-wave potentials, $E_{1/2}$, for these processes are −0.50, +0.10, and +0.99 V vs. SCE. The chemical reversibility, not to be confused with electrochemical reversibility, of each process is indicated by an $i_{p,a}/i_{p,c}$ ratio of unity. The first two $E_{1/2}$ values are very close to those reported by Treichel and co-workers[32] for $Cr(CN\text{-}p\text{-anisyl})_6$ under similar conditions: −0.44, +0.11, and +0.84 V vs. SCE. The last process, $Cr^{2+} \rightleftarrows Cr^{3+}$, is seen to be about 0.15 V more positive for the *t*-BuDiNC complex than for the *p*-anisyl isocyanide complex, indicating a slight destabilization of $[Cr(t\text{-BuDiNC})_3]^{3+}$ relative to $[Cr(CN\text{-}p\text{-anisyl})_6]^{3+}$. Bohling, Evans, and Mann[14] have similarly observed an anodic shift of 0.15 V for $E^{\circ\prime}_{3+/2+}$ of $[Cr(CN\text{-}o\text{-tol})_6]^{2+,3+}$ vs. $[Cr(CN\text{-}p\text{-tol})_6]^{2+,3+}$, but the reasons for the destabilization of the Cr(III) complexes of these ortho-substituted isocyanides (i.e., *t*-BuDiNC and *o*-tolyl isocyanide) are not understood. As observed for many other $Cr(CNR)_6$ systems,[10,32] peak-to-peak separtions for each redox process of $[Cr(t\text{-BuDiNC})_3]^{z+}$ are found to vary with the scan rate (Table VII). This system is thus characterized as electrochemically quasi-reversible, where the rate of electron transfer is somewhat slow relative to the rate of potential change.[10,32,50]

$[Mn(t\text{-BuDiNC})_3]PF_6$, like other $[Mn(CNR)_6]^+$ systems,[10,51] shows two quasi-reversible waves, corresponding to the processes $Mn^+ \rightleftarrows Mn^{2+}$ and $Mn^{2+} \rightleftarrows Mn^{3+}$, with $E_{1/2}$ values of +0.86 and ca. +2.0 V vs. SCE, respectively (Table V, Figure 3). Exact determination of the latter value is complicated by the onset of solvent decomposition. The difference between $E_{1/2}$ values for these two processes is ca. 1.1 V, significantly larger than analogous $E_{1/2}$ differences for homoleptic unsubstituted and para-substituted phenyl isocyanide complexes of Mn, which range from 0.86 to 0.94 V.[10,51] As for the Cr system, it appears that the *t*-BuDiNC ligand causes a slight thermodynamic destabilization of $[Mn(t\text{-BuDiNC})_3]^{3+}$ relative to the monodentate $[Mn(CNAr)_6]^{3+}$ systems.

Unlike its isoelectronic chromium and manganese analogues, $[Fe[t\text{-BuDiNC})_3](PF_6)_2$ undergoes no chemically reversible redox processes when examined by cyclic voltammetry. The most prominent feature in the voltammograms is a chemically

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and kinetically irreversible cathodic wave in the vicinity of −2 V vs. SCE.

Table VIII presents UV–vis data obtained for the homoleptic six-coordinate complexes; traces recorded for the d^6 complexes **1**, **4**, **8**, and **12** are shown in Figure 4. On the basis of assignments made by Mann et al. for $Cr(CNC_6H_5)_6$ and $[Mn(CNC_6H_5)_6]Cl$,[5] the two lowest energy bands for each complex are assigned as metal-to-ligand charge-transfer (MLCT) transitions of the type $d\pi \rightarrow \pi^*_v$, where π^*_v is the π^*_{CN} orbital which is lowered in energy by interaction with the phenyl-ring π^* orbitals.[52] Spectra of the Cr(0) and Mn(I) complexes are similar to their phenyl isocyanide analogues.[5] In Figure 4 and Table VIII, one can see that the $d\pi$–π^*_v bands for the d^6 compounds increase in energy in the following order: Cr(0) < Mn(I) < Fe(II) ~ Co(III). The spectra of the Fe(II) and Co(III) complexes are surprisingly similar, despite the difference in charge. For the Co(III) complex **12**, the $d\pi$–π^*_v energy gap is smaller than expected perhaps because of the absence of significant $d\pi$–π^*_{CN} back-bonding and/or lowering of the π^*_{CN} energies by σ-inductive effects caused by the strong electron-withdrawing ability of the Co^{3+}. The Cr(I) and Mn(II) complexes **2** and **5** afford blue-shifted spectra as compared with **1** and **4**, in accord with the MLCT nature of the transitions.[5]

Four-Coordinate Homoleptic Complexes. All the complexes of DiNC and *t*-BuDiNC prepared heretofore have employed the ligands either as chelating ligands at pseudooctahedral metal sites (i.e., with C–M–C angles of ca. 90°)[1-4] or as bridging ligands.[1] The following studies were carried out to determine if these ligands are able to chelate to pseudotetrahedral metal centers. If they did coordinate, a C–M–C angle in the chelate ring of 109° would require considerable distortion of the ligand from its normal geometry. However, if the ligand is not distorted, the C–M–C angle is likely to be close to 90°.

Reactions between $Ni(CO)_4$ and *t*-BuDiNC or DiNC afford the complexes $Ni(CO)_2(t\text{-BuDiNC})$ (**13**) and $Ni(CO)_2(DiNC)$ (**14**) in moderate yields (eq 5). The fully substituted complex $Ni(t\text{-BuDiNC})_2$ (**15**) is obtained from the reaction

$$Ni(CO)_4 + t\text{-BuDiNC} \rightarrow \underset{\mathbf{13}}{Ni(CO)_2(t\text{-BuDiNC})} + 2CO \qquad (5)$$

between $Ni(CO)_4$ and additional *t*-BuDiNC (eq 6) (or via the

$$Ni(CO)_4 + 2t\text{-BuDiNC} \rightarrow Ni(t\text{-BuDiNC})_2 + 4CO \qquad (6)$$

reaction of $Ni(CO)_2(t\text{-BuDiNC})$ with *t*-BuDiNC in $CHCl_3$ solution). Isoelectronic $[Cu(t\text{-BuDiNC})_2]BF_4$ (**16**) is synthesized by displacement of four CH_3CN ligands from $[Cu(CH_3CN)_4]BF_4$ by *t*-BuDiNC. The dicarbonyl derivatives **13** and **14** each exhibit two ν(CN) and two ν(CO) bands similar in energy to those of $Ni(CO)_2(CNC_6lH_5)_2$.[53] The mononuclearity of $Ni(CO)_2(t\text{-BuDiNC})$ was confirmed by an osmometric molecular weight determination, and $Ni(CO)_2(DiNC)$ is presumed to be mononuclear as well. The tetrasubstituted complexes $Ni(t\text{-BuDiNC})_2$ (**15**) and $[Cu(t\text{-BuDiNC})_2]BF_4$ (**16**) each exhibit a single, strong ν(CN) band at 2040 and 2169 cm^{-1}, respectively. Each complex is readily soluble in organic solvents such as $CHCl_3$. This observation, along with the known mononuclear structure of $Ni(CO)_2(t\text{-BuDiNC})$, suggests that **15** and **16** possess mononuclear, rather than polymeric, structures. It is clear that the *t*-BuDiNC ligand does chelate to normally tetrahedral metals. However, the exact structures of the complexes must await an X-ray diffraction investigation.

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Registry No. **1**, 87711-97-5; **2**, 87711-99-7; **3**, 87712-01-4; **4**, 87712-03-6; **5**, 87712-05-8; **6**, 87712-06-9; **7**, 87760-31-4; **8**, 87712-08-1; **9**, 87712-10-5; **10**, 87712-11-6; **11**, 87712-12-7; **12**, 87712-14-9; **13**, 87712-15-0; **14**, 87712-16-1; **15**, 87712-17-2; **16**, 87712-19-4; $CrCl_3(THF)_3$, 10170-68-0; $AgPF_6$, 26042-63-7; $Mn(CO)_5Cl$, 14100-30-2; $AlCl_3$, 7446-70-0; $CoCl_2$, 7646-79-9; $Ni(CO)_4$, 13463-39-3; $[Cu(CH_3CN)_4]BF_4$, 15418-29-8; Br_2, 7726-95-6.

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Synthesis and Structure of the Lithium Bromide–Pentamethyldiethylenetriamine 1:1 Adduct

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Reaction of BrBu-*n* with LiBu-*n*(PMDETA) affords in high yield (PMDETA)LiBr (**1**) (PMDETA = $Me_2N(CH_2)_2NMe(CH_2)_2NMe_2$), which forms dimeric aggregates in the solid. Crystals are triclinic, of space group $P\bar{1}$, with a = 14.887 (7) Å, b = 11.737 (6) Å, c = 8.631 (7) Å, α = 73.43 (6)°, β = 77.64 (5)°, γ = 80.93 (4)°, and Z = 2 dimers. The unit cell contains a pair of dimeric aggregates possessing "bridging" bromine atoms; the metal–halogen distances within each centrosymmetric aggregate are unsymmetric. Li–Br: 2.51 (1) and 3.20 (2) Å, aggregate **1**; 2.57 (1) and 2.87 (1) Å, aggregate **2**.

Introduction

Permethylated amines readily form metal N-chelate complexes with main group 1 halides, with a feature of high solubility of the derived complexes in organic solvents.[1] Although solution properties of these complexes have been studied in depth by using NMR techniques, there being postulated solvent–complex interactions in order to account for ^1H chemical shift variations of CH_3 and CH_2 resonances,[2] no detail of the nature of these compounds in the solid is

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