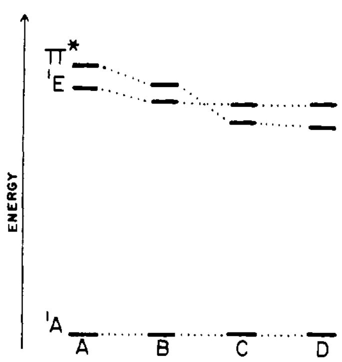

Figure 4. Relative energies (as inferred from the spectra of Figure 3) of the ligand field (^1E) and charge-transfer (π^*) excited states in the compounds (A) $[W(CO)_5]_2BPA$, (B) $W(CO)_5BPY$, (C) $[W(CO)_5]_2BPY$, and (D) $[W(CO)_5]_2BPE$.

moved to lower energy than that for $[W(CO)_5]_2BPA$, and in fact, it is observable only as a shoulder (more discernable in acetone) on the high-energy side of the LF band. In the compound $[W(CO)_5]_2BPY$ (Figure 3C), the CT band is lower in energy than the LF band and lower still for $[W(CO)_5]_2BPE$ (Figure 3D). The relative energies of these transitions (as inferred from the data of Table IV) are diagrammed in Figure 4. As can be seen in this figure, the more π conjugation present in the system $(CO)_5W-L-W(CO)_5$, the lower the energy of the π^* orbital of the heterocyclic ligand. This is as it should be. Accordingly, the compounds $[W(CO)_5]_2BPY$ and $[W(CO)_5]_2BPE$ should be placed into Zink's[4b] class 3(2).

We have synthesized and are characterizing other compounds of this class. We have good evidence that we will be able to separte the LF and CT transitions of these types of compounds by as much as 100 nm. It is then our hope to be able to study the photochemistries of such compounds as a function of the irradiation wavelength.

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Registry No. $W(CO)_5py$, 14586-49-3; $W(CO)_5BPY$, 81178-09-8; $[W(CO)_5]_2BPY$, 81178-10-1; $[W(CO)_5]_2BPA$, 81178-11-2; $[W(CO)_5]_2BPE$, 81178-12-3; BPY, 553-26-4; BPA, 4916-57-8; BPE, 1135-32-6; $W(CO)_6$, 14040-11-0.

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Synthesis of Chelating Bidentate Isocyano and Cyano Ligands and Their Metal Complexes

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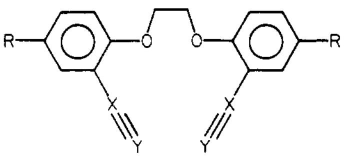
Three air-stable, odorless, solid, bidentate isocyano and cyano ligands of the following structure have been prepared:



DiCN, R = H, -X≡Y = -C≡N:
DiNC, R = H, -X≡Y = -N≡C:
t-BuDiNC, *t*-Bu, -X≡Y = -N≡C:

Molecular models indicate that they should chelate to metals with the donor groups at 90° with respect to each other. From reactions of the diisocyano ligand DiNC, the following complexes with chelating DiNC ligands have been isolated: $Cr(CO)_4(DiNC)$, $Mo(CO)_4(DiNC)$, $W(CO)_4(DiNC)$, $Mn(CO)_3(DiNC)Br$, $CpFe(CO)(DiNC)^+$, and $CpFe(CS)(DiNC)^+$. The characterization of these complexes demonstrates that DiNC can function as a chelating ligand despite its formation of a 13-member chelate ring. The *t*-BuDiNC ligand, which is much more soluble in organic solvents than DiNC, also gives complexes $Cr(CO)_4$(*t*-BuDiNC), $Mo(CO)_4$(*t*-BuDiNC), and $CpFe(CS)$(*t*-BuDiNC)$^+$, which are more soluble than their DiNC analogues. When only one ligand in a reacting complex such as $Cr(CO)_5[(CH_3)_2CO]$, $W(CO)_5[(CH_3)_2CO]$, or $W(CO)_4(piperidine)_2$ is substitution labile, DiNC reacts to give complexes in which the isocyano donors are coordinated to separate metal atoms; the resulting bridging DiNC complexes $[Cr(CO)_5]_2(\mu\text{-DiNC})$, $[W(CO)_5]_2(\mu\text{-DiNC})$, and [*cis*-$W(CO)_4(pip)]_2(\mu\text{-DiNC})$ have been isolated. The dicyano ligand DiCN reacts to form the following complexes: $Mn(CO)_3(DiCN)Br$, $CpFe(CS)(DiCN)^+$, and $PtCl_2(DiCN)$. These are the first examples of complexes containing a bidentate cyano ligand that chelates to a metal through the nitrogen lone pairs. The formation of $PtCl_2(DiCN)$ from equimolar $PtCl_2(NCPh)_2$ and DiCN indicates that the chelating DiCN binds more favorably to the metal than do the monodentate benzonitrile ligands. The ligands and complexes described above have been characterized by their IR, ^1H and ^{13}C NMR, and mass spectra.

Introduction

Potentially chelating multidentate cyano and isocyano ligands have received relatively little attention, despite the fact that multidentate ligands often have unique properties with respect to those of their monodentate analogues. We know of no previous $AlCl_3/CH_3CN/N(CH_3)_4Cl$ of bidentate cyano ligands capable of chelating to a single metal center through the nitrogen lone pairs. The coordination of polymethylene–diisocyano ligands, $CN-(CH_2)_n-NC$ (n = 3–8), to Rh(I)[1-3] has been investigated. Ligands possessing six or fewer methylene units are sterically incapable of chelation and therefore bridge two metal centers to give the cationic dimers,

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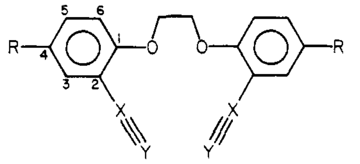
$[Rh_2(CN-(CH_2)_n-NC)_4]^{2+}$. Those with seven or eight methylenes chelate, giving rise to square-planar $\{Rh[CN-(CH_2)_{7,8}-NC]_2\}^+$ complexes and their oligomers.[2,3]

We report here the syntheses of a series of $AlCl_3/CH_3CN/L'$, rigid ligands bearing isocyano and cyano donor groups. Their structures are as follows:



DiCN, R = H, X≡Y = $-C\equiv N$:
DiNC, R = H, X≡Y = $-N\equiv C$:
t-BuDiNC, R = *t*-Bu, X≡Y = $-N\equiv C$:

Molecular models indicate that they are ideally suited to chelate with the donor groups at 90° to each other, as occurs in square-planar and octahedral complexes. A major goal of this research was to demonstrate that these ligands do in fact form chelate complexes, rather than oligomers, despite the large 13-membered chelate rings that would be formed. It was also hoped that such chelates would have greater stability than the corresponding monodentate phenyl isocyanide and benzonitrile complexes.

We report in detail the formation of a number of complexes of these ligands with low-valent transition metals. This work represents part of a more general investigation into the synthesis and reactivity of polydentate cyano, isocyano,[4,5] diazonium,[6] and acetylide ligands. A preliminary account of some of the results reported herein has already been published.[7]

Experimental Section

General Information. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl or $NaK_{2.8}$ under N_2 before use. All other solvents were reagent grade products and were dried over molecular sieves (4A) and purged with N_2 before use. The following compounds were prepared according to literature methods: acetic formic anhydride,[8] *cis*-$M(CO)_4(pip)_2$ (M = Mo,W),[9] $M(CO)_4(nor)$ (M = Cr,Mo),[10] $(Et_4N)[M(CO)_5I]$ (M = Cr,W),[11] $Mn(CO)_5Br$[12] (pip = piperidine, nor = norbornadiene), $[CpFe(CO)_2(CX)]PF_6$ (X = O,[13] S[14]), and $PtCl_2(PhCN)_2$.[15] All other chemicals were used as received.

All complexes were prepared in Schlenkware or similar apparatus under N_2 with use of standard inert-atmosphere techniques.[16] Infrared spectra were recorded on a Perkin-Elmer 281 infrared spectrophotometer calibrated against CO gas. Low-frequency infrared spectra were recorded on an IBM IR-98 Fourier transform instrument. Proton (89.55 MHz) and ^{13}C NMR spectra were obtained on a JEOL FX-90Q NMR spectrometer. Samples for ^{13}C NMR analysis contained $Cr(acac)_3$ (~0.1 M, acac = acetylacetonate) to reduce data collection time. Mass spectra were recorded on Finnigan 4000 or AEI MS902 mass spectrometers. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were measured on a Thomas hot-stage apparatus and are uncorrected.

Preparation of Ligands. 1,2-Bis(2-nitrophenoxy)ethane, $DiNO_2$. A solution of 2-nitrophenol (27.8 g, 0.20 mol) in dry dimethylformamide (DMF) (100 mL) was added over 45 min to a vigorously stirred suspension of NaH (4.8 g, 0.20 mol) in dry DMF (100 mL) under N_2. The deep red-orange mixture was stirred for 4 h to ensure complete reaction, after which 1,2-dichloroethane (7.9 mL, 0.10 mol) was added, and the mixture was refluxed for 6 h. The reaction mixture was cooled to room temperature and poured into 1 L of ice-cold water. The precipitated product was filtered off and washed successively with 2 M NaOH (3 × 50 mL), water (5 × 100 mL), 95% EtOH (5 × 100 mL) and Et_2O (3 × 100 mL). The yield of off-white $DiNO_2$ was 17.5 g (58%); mp 165–168 °C (lit.[17] 169–170 °C).

1,2-Bis(2-aminophenoxy)ethane, $DiNH_2$. Zinc dust (164 g, 2.5 mol) was added to a stirred (paddle-type stirrer) suspension of $DiNO_2$ (13.0 g, 42.7 mmol) in 78% $EtOH/H_2O$ (600 mL). (*Note*: Best results were obtained when the purity of the Zn was 95% or higher.) A solution of $CaCl_2$ (6.0 g) in 10 mL of water was then added, and the mixture was refluxed for 3 h. The hot mixture was filtered (a 350-mL coarse-frit funnel, packed with a 3-cm layer of Celite topped with a layer of glass wool, was very convenient for this operation), and the metal sludge was washed with 100 mL of boiling 78% EtOH. The filtrate was cooled to room temperature and then poured into 2 L of water; the pearly white product was filtered off, washed twice with 50 mL of water, and suction-dried overnight. The yield was 9.44 g (90%); mp 127–130 °C (lit.[18] mp 130–132 °C).

1,2-Bis(2-formamidophenoxy)ethane, DiFor. Acetic formic anhydride (2.0 mL, 22.7 mmol) was added to a solution of $DiNH_2$ (2.44 g, 10.0 mmol) in THF (50 mL) under N_2. The product began to precipitate within 1 min. After 30 min, 50 mL of hexane was added, and the mixture was filtered. The white DiFor was washed five times with 20 mL of Et_2O and vacuum-dried. The yield was 2.97 g (99%); mp 177–179 °C.

1,2-Bis(2-isocyanophenoxy)ethane, DiNC. A mixture of DiFor (3.00 g, 10.0 mmol), PPh_3 (5.50 g, 21.0 mmol), CCl_4 (2.00 mL, 20.7 mmol), Et_3N (2.80 mL, 20.0 mmol), and 1,2-dichloroethane (70 mL) was heated at 70–75 °C under N_2 for 8 h. The reaction mixture was cooled and filtered to remove Et_3NHCl, and the filtrate was evaporated under reduced pressure. The residue was dissolved in 80 mL of CH_2Cl_2, an equal volume of hexane was added, and the mixture was filtered to remove the precipitated Ph_3PO. The filtrate was evaporated, and the brown residue was stirred with 35 mL of EtOH for 30 min. Filtration, washing (twice with 10 mL of ice-cold EtOH, then three times with 25 mL of hexane) and vacuum drying gave DiNC (1.72 g, 65%) as an off-white powder sufficiently pure for most purposes. An analytical sample was recrystallized from CH_2Cl_2/hexane at −20 °C to give small, off-white needles of the isocyano compound, mp 150 °C.

4-*tert*-Butyl-2-nitrophenol. In a flask equipped with a thermometer, overhead stirrer, and dropping funnel, a solution of 45.0 g (0.300 mol) of 4-*tert*-butylphenol dissolved in 350 mL of benzene was cooled to 10 °C. With vigorous stirring, 100 mL of 6 M HNO_3 was added dropwise (during a 3-h period) such that the temperature stayed below 15 °C. The solution was stirred at 15 °C for 1 h after the addition and was subsequently poured into 500 mL of H_2O. The mixture was separated in a separatory funnel, and the aqueous layer was extracted with 100 mL of Et_2O. This ether extract was added to the benzene layer, and the resulting solution was washed three times with 100 mL of 5% aqueous NaCl. The solution was dried over $CaSO_4$ overnight. Ether and benzene were removed on a rotary evaporator, and the crude product was distilled [bp 81 °C (~0.1 torr)] (the product was usually collected as the second fraction, the first being an orange liquid). The product is a bright yellow oil: mp 10–15 °C; yield 39–47 g (67–80%).

1,2-Bis(4-*tert*-butyl-2-nitrophenoxy)ethane, *t*-$BuDiNO_2$. A solution of 4-*tert*-butyl-2-nitrophenol (19.5 g, 0.10 mol) in 40 mL of dry DMF was added dropwise to a stirred suspension of NaH (2.4 g, 0.10 mol) in dry DMF (50 mL) under N_2. After an additional 3 h of stirring, 1,2-dichloroethane (4.0 mL, 0.050 mol) was added, and the solution was refluxed for 7 h. The cooled (25 °C) reaction mixture was added to 1 L of cold (0 °C) H_2O and shaken, whereupon the crude product separated as an oil. The majority of the solution was decanted from the oil into a separatory funnel and extracted twice with 100 mL of Et_2O. The crude, oily product was stirred with 350 mL of Et_2O; the resulting solution was combined in a separatory funnel with the previous ether extracts. This solution was washed by successive

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extractions with 300-mL portions of H_2O until the aqueous extracts were only light yellow or orange. Any remaining phenol was extracted with 200-mL portions of 5% NaOH (usually three extractions). The Et_2O layer was finally washed with five 200-mL portions of H_2O and dried over $CaSO_4$. Diethyl ether was removed by rotary evaporation, and pale yellow needles of *t*-$BuDiNO_2$ were obtained by cooling a saturated, boiling hexane solution of the residue to 0 °C. A second batch of crystals was obtained by boiling solvent from the supernatant to one-third the original volume, followed by cooling to 0 °C and filtration: total yield 6.5–10.4 g (31–50%); mp 116–119 °C.

1,2-Bis(2-amino-4-*tert*-butylphenoxy)ethane, *t*-BuDiNH$_2$. A mixture of *t*-$BuDiNO_2$ (4.33 g, 10.4 mmol), Zn dust (41 g, 627 mmol), $CaCl_2$ (1.4 g in 4 mL of H_2O), absolute EtOH (97 mL), and H_2O (28 mL) was heated to reflux under N_2 with overhead stirring. After 2.5 h of refluxing, the hot solution was filtered as described for $DiNH_2$. The gray sludge was washed with three portions of boiling 78% EtOH. The filtrate was heated to boiling to dissolve the crystallizing product, and H_2O was added until crystallization commenced. After slowly cooling, to 30 °C, the solution was chilled to 8 °C in an ice bath, and the white to pale brown crystals were filtered and dried in vacuo: yield 3.0–3.4 g (81–92%); mp 120–122 °C.

1,2-Bis(4-*tert*-butyl-2-formamidophenoxy)ethane, *t*-BuDiFor. Acetic formic anhydride (1.8 mL, 20.4 mmol) was added via syringe to a stirred solution of *t*-$BuDiNH_2$ (3.33 g, 9.35 mmol) in 300 mL of 1:1 Et_2O/hexane under N_2. Precipitation of the product began after 20 min, and stirring was continued for a total of 3 h. The product, *t*-BuDiFor, was filtered off, washed with three 20-mL portions of hexane, and dried in vacuo: yield 3.37 g (87%); mp 135–138 °C.

1,2-Bis(4-*tert*-butyl-2-isocyanophenoxy)ethane, *t*-BuDiNC. A mixture of *t*-BuDiFor (3.37 g, 8.18 mmol), PPh_3 (4.5 g, 17.2 mmol), Et_3N (2.3 mL, 16.5 mmol), CCl_4 (1.6 mL, 16.6 mmol), and 1,2-dichloroethane (50 mL) was heated to 70 °C under N_2 for 7 h. After cooling to 25 °C, the solution was filtered and the solvent evaporated on a rotary evaporator in a fume hood. The tan residue was stirred with 75 mL of hexane for 30 min to extract the product. Extractions were repeated until the infrared spectrum of the extract showed only a very weak $\nu(N{\equiv}C)$ peak (2125 cm^{-1} in hexane). The hexane extracts were combined, and the solvent was removed to give a yellow oil. Beautiful white needles of the product were obtained by scratching or seeding a cold, very concentrated hexane solution ($\sim$1:1 by volume) of this oil. An analytical sample was obtained by chromatography on silica gel, through eluting with $CHCl_3$/hexane (6:1): total yield 1.70 g (55%); mp 95 °C.

1,2-Bis(2-cyanophenoxy)ethane, DiCN. Sodium hydride (0.81 g, 33.5 mmol) was added to a stirred solution of 2-cyanophenol (4.00 g, 33.2 mmol) in dry DMF (30 mL) under N_2. The mixture was heated to 80–85 °C and stirred until all the NaH had reacted and all the phenoxide had dissolved to give a clear yellow solution. Dichloroethane (1.35 mL, 17.0 mmol) was then added, and the mixture was refluxed for 6 h. The cooled reaction mixture was poured into 100 mL of ice-cold water; the product was filtered off and washed, first with six 30-mL portions of water and then with three 10-mL portions of ice-cold MeOH. Recrystallization from hot $CHCl_3$ (or MeOH) gave small white needles of DiCN (2.33 g, 52%), mp 175–177 °C.

Preparation of Isocyano Complexes. *cis*-Cr(CO)$_4$(DiNC) (I). A THF solution (50 mL) of DiNC (0.264 g, 1.00 mmol) and $Cr(CO)_4(nor)$ (0.254 g, 0.99 mmol) was refluxed for 6 h. The solvent was removed in vacuo, and the residue was washed with three 5-mL portions of hexane. Recrystallization of the residue from $CHCl_3$/hexane at −20 °C gave the product as yellow crystals (0.306 g, 72%); the mass spectrum showed a parent ion (M^+) at *m*/*e* 428 and the $[M - n(CO)]^+$ ions (where n = 2–4) and the $[Cr(C_6H_4NCO)_n]^+$ ions for n = 1, 2 at *m*/*e* 170 and 288, respectively.

***cis*-Cr(CO)$_4$(*t*-BuDiNC) (II).** A solution of *t*-BuDiNC (0.0743 g, 0.197 mmol) and $Cr(CO)_4(nor)$ (0.0493 g, 0.193 mmol) in 5 mL of THF was refluxed for 5 h. Evaporation of the solution, drying in vacuo, and recrystallization of the residue from $CHCl_3$/hexane at −20 °C gave the product as opaque, pale yellow crystals (0.048 g, 46%); the mass spectrum showed M^+ at *m*/*e* 540 and $[M - n(CO)]^+$ ions for n = 3, 4.

***cis*-Mo(CO)$_4$(*t*-BuDiNC) (III).** A solution of *t*-BuDiNC (0.0715 g, 0.190 mmol) in 2 mL of Et_2O was added to a solution of $Mo(CO)_4(nor)$ (0.057 g, 0.190 mmol) in 2 mL of Et_2O. After 10 min, needles of the product began to form, and the odor of norbornadiene could be detected. Solvent was removed under a slow N_2 stream until the volume was 0.5 mL. The remaining solution was decanted off, and the resulting pale yellow crystals were washed with two 1-mL portions of cold hexane and dried in vacuo (0.075 g, 68%; the mass spectrum showed M^+ at *m*/*e* 586 (for ^{98}Mo) and peaks for $[M - n(CO)]^+$, n = 2–4.

***cis*-Mo(CO)$_4$(DiNC) (IV).** Solid DiNC (0.270 g, 1.02 mmol) was added to a solution of *cis*-$Mo(CO)_4(pip)_2$ (0.378 g, 1.00 mmol) in acetone (100 mL), and the mixture was stirred for 6 h. The solvent was removed under reduced pressure, and the residue was washed three times with 20 mL of hexane and recrystallized twice from CH_2Cl_2/hexane at −20 °C to give pale yellow needles of the complex (0.303 g, 64%); the mass spectrum showed M^+ at *m*/*e* 474 (for ^{98}Mo) and peaks for $[M - n(CO)]^+$, n = 1–4.

Reaction of *cis*-W(CO)$_4$(pip)$_2$ with DiNC. A solution of *cis*-$W(CO)_4(pip)_2$ (0.233 g, 0.500 mmol) and DiNC (0.140 g, 0.530 mmol) in 60 mL of acetone was refluxed for 6 h. The solvent was evaporated, and the residue was washed with hexane. Extraction with CS_2 (40 mL) and filtration gave a yellow solution, which was evaporated, and the residue was recrystallized from CH_2Cl_2/hexane at −20 °C to give light yellow needles of *cis*-$W(CO)_4$(DiNC) (V) (0.051 g, 18%). The CS_2-insoluble solid was recrystallized twice from CH_2Cl_2/hexane at −20 °C to give golden yellow crystals (0.202 g, 78%) of *cis*-$[W(CO)_4(pip)]_2(\mu\text{-DiNC})$ (VI), which were washed with Et_2O and dried in vacuo.

[Cr(CO)$_5$]$_2$(μ-DiNC) (VII). A solution of $AgPF_6$ (0.230 g, 0.909 mmol) in 5 mL of acetone was added over a period of 10 min to a rapidly stirred solution of $(Et_4N)[Cr(CO)_5I]$ (0.402 g, 0.895 mmol) in 35 mL of THF at 25 °C. After an additional 20 min of stirring, the orange solution was filtered to remove precipitated AgI. A CH_2Cl_2 solution (6 mL) of DiNC (0.120 g, 0.455 mmol) was then added; the solution was stirred for 20 min and evaporated to dryness. The resulting yellow residue was taken up in 8 mL of $CHCl_3$ and eluted with 20 mL of $CHCl_3$ from a short column (1 × 7 cm) of silica gel to remove $(Et_4N)(PF_6)$. Evaporation of the $CHCl_3$ gave the product as a pale yellow powder, which was recrystallized from $CHCl_3$/hexane at −20 °C to give pale yellow needles (0.201 g, 69%). The mass spectrum showed M^+ at *m*/*e* 648 as well as peaks for $[M - n(CO)]^+$ (n = 5–10), $Cr(DiNC)^+$, And $[Cr(C_6H_4NCO)]^+$.

[W(CO)$_5$]$_2$(μ-DiNC) (VIII). A procedure analogous to that above using 0.520 g (0.895 mmol) of $(Et_4N)[W(CO)_5I]$, 0.230 g (0.909 mmol) of $AgPF_6$, and 0.118 g (0.447 mmol) of DiNC gave the product (0.169 g, 41%) as colorless to pale yellow needles.

***fac*-Mn(CO)$_3$(DiNC)Br (IX).** The diisocyanide (0.264 g, 1.00 mmol) and $Mn(CO)_5Br$ (0.280 g, 1.02 mmol) were stirred at room temperature in 70 mL of $CHCl_3$ for 30 h. The solution was filtered and evaporated under reduced pressure. The residue was washed three times with 20 mL of Et_2O and then recrystallized from CH_2Cl_2/hexane at −20 °C to give yellow microcrystals of the product (0.415 g, 86%).

[CpFe(CS)(DiNC)]PF$_6$ (X). A solution of $[CpFe(CO)_2(CS)]PF_6$ (0.366 g, 1.00 mmol) and DiNC (0.270 g, 1.02 mmol) in 60 mL of CH_3CN was stirred overnight. Evaporation of the solution under reduced pressure, extraction of the residue with CH_2Cl_2, filtration, and evaporation gave the brown product, which was recrystallized twice from acetone/Et_2O at −20 °C (0.490 g, 85%); molar conductivity in CH_3NO_2 79.8 $cm^2\ \Omega^{-1}\ mol^{-1}$.

[CpFe(CO)(DiNC)]PF$_6$ (XI). The same procedure as above with $[CpFe(CO)_3]PF_6$ (0.350 g, 1.00 mmol) and DiNC (0.264 g, 1.00 mmol) gave yellow $[CpFe(CO)(DiNC)]PF_6$ (0.465 g, 83%).

[CpFe(CS)(*t*-BuDiNC)]PF$_6$ (XII). A solution of $[CpFe(CO)_2(CS)]PF_6$ (0.0577 g, 0.158 mmol) and *t*-BuDiNC (0.0589 g, 0.157 mmol) in 12 mL of CH_3CN was stirred overnight. Evaporation gave a brown oil, which was washed with 5 mL of Et_2O and recrystallized twice from CH_2Cl_2/Et_2O at −20 °C to give 0.0571 g (54%) of the product as brown crystals.

Preparation of Cyano Complexes. *fac*-Mn(CO)$_3$(DiCN)Br (XIII). A solution of DiCN (0.396 g, 1.50 mmol) and $Mn(CO)_5Br$ (0.420 g, 1.53 mmol) in $CHCl_3$ (80 mL) was refluxed for 3 h. Workup as for the DiNC analogue (IX) gave yellow-orange *fac*-$Mn(CO)_3$(DiCN)Br (0.590 g, 82%).

***cis*-PtCl$_2$(DiCN) (XIV).** The dicyano ligand (0.270 g, 1.02 mmol) was refluxed with $PtCl_2(PhCN)_2$ (0.472 g, 1.00 mmol) in 1,2-dichloroethane (80 mL) for 5 h, after which the solvent was removed under reduced pressure. The gummy residue was stirred with 100 mL of Et_2O for 30 min. The solid product was then filtered off, washed five times with 20 mL of Et_2O, and recrystallized from CH_2Cl_2 at −20 °C to give small yellow crystals (0.420 g, 79%).

Table I. Analytical Data

compd	%C calcd	%C found	%H calcd	%H found	%N calcd	%N found
DiNC	72.72	72.80	4.58	4.40	10.60	10.51
t-BuDiNC	76.55	76.64	7.50	7.57	7.45	7.38
DiCN	72.72	72.73	4.58	4.43	10.60	10.49
$Cr(CO)_4$(DiNC) (I)	56.08	56.21	2.82	2.91		
$Cr(CO)_4$(*t*-BuDiNC) (II)	62.22	61.78	5.22	5.39	5.18	5.09
$Mo(CO)_4$(*t*-BuDiNC) (III)	57.54	58.07	4.83	4.47	4.79	4.85
$Mo(CO)_4$(DiNC) (IV)	50.85	50.69	2.56	2.63	5.93	5.95
$[W(CO)_4(pip)]_2$(DiNC) (VI)	39.79	39.94	3.34	3.17		
$[Cr(CO)_5]_2$(DiNC) (VII)	48.16	47.60	1.87	1.83	4.32	4.15
$[W(CO)_5]_2$(DiNC) (VIII)	34.24	34.06	1.33	1.34	3.07	3.14
$Mn(CO)_3$(DiNC)Br (IX)	47.23	47.27	2.50	2.56		
[CpFe(CS)(DiNC)]PF_6 (X)	46.01	45.75	2.98	2.96		
[CpFe(CO)(DiNC)]PF_6 (XI)	47.34	46.42	3.07	3.20	5.02	4.77
$Mn(CO)_3$(DiCN)Br (XIII)	47.23	47.46	2.50	2.42		
$PtCl_2$(DiCN) (XIV)	46.01	45.89	2.98	2.74	4.89	4.90
[CpFe(CS)(DiCN)]PF_6 (XV)	36.24	36.08	2.28	2.46	5.28	5.17

Table II. IR Spectral Data

compd	solvent	ν(N≡C), cm^{-1}	ν(C≡O), cm^{-1}	other, cm^{-1}
DiNC	$CHCl_3$	2128 s		
$Cr(CO)_4$(DiNC) (I)	$CHCl_3$	2142 w, 2091 w	2009 s, 1932 vs, br	
	hexane	2135 w, 2076 w	2008 m, 1955 s, 1942 vs, 1936 sh	
$Mo(CO)_4$(DiNC) (IV)	$CHCl_3$	2143 w, 2094 m	2014 s, 1935 vs, br	
	hexane	2133 w, 2075 w	2010 m, 1954 s, 1945 vs, br	
$W(CO)_4$(DiNC)	$CHCl_3$	2143 w, 2087 w	2007 m, 1934 s, 1926 s, br	
$[W(CO)_4(pip)]_2$DiNC (VI)	$CHCl_3$	2112 w	1999 m, 1945 m, sh, 1902 s, br, 1858 m, sh	
$[Cr(CO)_5]_2$DiNC (VII)	$CHCl_3$	2146 w	2059 s, 1998 m, sh, 1952 vs, br	
$[W(CO)_5]_2$DiNC (VIII)	$CHCl_3$	2146 w	2060 s, 1992 w, sh, 1950 vs, br	
$Mn(CO)_3$(DiNC)Br (IX)	$CHCl_3$	2180 w, 2152 w	2045 vs, 2005 s, 1955 s	
[CpFe(CS)(DiNC)]PF_6 (X)	CH_2Cl_2	2173 s, 2150 s		ν(CS) 1315[a]
[CpFe(CO)(DiNC)]PF_6 (XI)	CH_2Cl_2	2183 s, 2154 s	2034 s	
t-BuDiNC	$CHCl_3$	2126 s		
$Cr(CO)_4$(*t*-BuDiNC) (II)	$CHCl_3$	2143 w, 2089 w	2010 s, 1934 vs, br	
$Mo(CO)_4$(*t*-BuDiNC) (III)	$CHCl_3$	2143 w, 2092 w	2014 s, 1935 vs, br	
[CpFe(CS)(*t*-BuDiNC)]PF_6 (XII)	CH_2Cl_2	2179 sh, 2159 m		ν(CS) 1310[f]
cis-$Cr(CO)_4$(CN-*p*-tol)$_2$[b]	hexane	2136, 2081	2011, 1955, 1944	
$Cr(CO)_5$(CN-*p*-tol)[b]	hexane	2140	2058, 1966	
$Mo(CO)_5$(CN-*p*-anis)[c]	$CHCl_3$	2145	2062, 1953	
$Mn(CO)_3$(CN-Ph)$_2$Br[d]	KCl	2198, 2174	2053, 2004, 1954	
[CpFe(CS)(CN-Ph)$_2$]PF_6[e]	CH_2Cl_2	2180, 2140		ν(CS) 1310[f]
DiCN	$CHCl_3$	2230		
$Mn(CO)_3$(DiCN)Br (XIII)	$CHCl_3$	2269 vw, 2230 vw	2044 s, 1968, 1938 s	
$PtCl_2$(DiCN) (XIV)	*f*	2284 s		ν(Pt–Cl) 362.1, 352.5
[CpFe(CS)(DiCN)]PF_6 (XV)	CH_2Cl_2	2268 vw		ν(CS) 1310[a]
$PtCl_2(PhCN)_2$[g]	*f*	2290 sh, 2285 s		ν(Pt–Cl) 356.0, 345.5

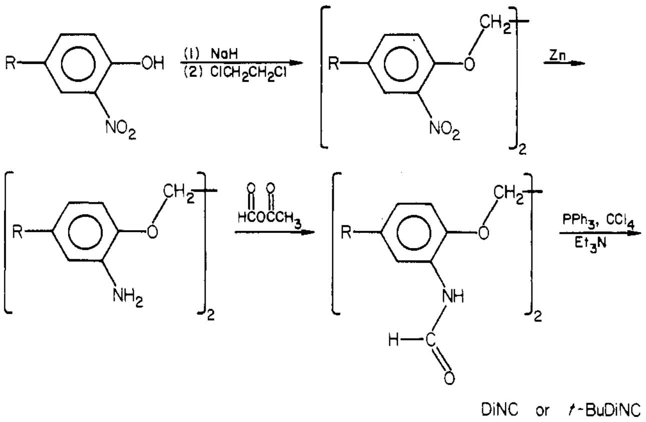
[a] In a KBr pellet. [b] Reference 22. [c] Reference 23, anis = anisyl. [d] Reference 24. [e] Reference 25. [f] Nujol mull. [g] Reference 31.

[CpFe(CS)(DiCN)]PF_6 (XV). A solution of $[CpFe(CO)_2(CS)]PF_6$ (0.366 g, 1.00 mmol) and DiCN (0.270 g, 1.02 mmol) in 40 mL of CH_3CN was ultraviolet irradiated for 10 h at 254 nm in a quartz Schlenk tube (photolysis apparatus from Bradford Scientific Co.). Filtration of the solution and evaporation under reduced pressure, followed by recrystallization of the residue from acetone/Et_2O at −20 °C gave brown crystals of the complex (0.502 g, 87%); molar conductivity in CH_3NO_2 82.4 $cm^2\ \Omega^{-1}\ mol^{-1}$.

Results and Discussion

Synthesis of the Ligands. The dicyano ligand DiCN is prepared in 52% yield simply by refluxing 2-cyanophenoxide with 1,2-dichloroethane in dimethylformamide (DMF). The product is an air-stable, colorless solid that is moderately soluble in $CHCl_3$, CH_2Cl_2, and acetonitrile, very slightly pairwise in Et_2O, and even less soluble in saturated hydrocarbons.

Scheme I



The isocyano ligands, DiNC and *t*-BuDiNC, are prepared as shown in Scheme I in maximum overall yields of 30% and 18%, respectively. The first step in this scheme employs a phenoxy coupling reaction[19] to give the dinitro compound. Reduction of the nitro groups,[20] formylation of the resulting diamine with acetic formic anhydride,[8] and dehydration of the formamide[21] give the diisocyano ligands. Both DiNC and

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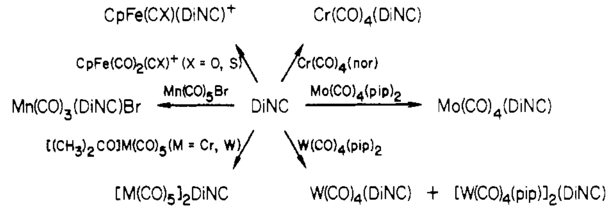
Table III. ^1H NMR Spectral Data

compd	chemical shifts, ppm[a] Ar-H[b]	CH$_2$[c]	*t*-Bu
DiNC[d]	7.5-6.9	4.51	
DiNC[e]	7.5-6.9	4.62	
I[d]	7.4-6.9	4.42	
IV[d]	7.4-6.9	4.43	
V[d]	7.4-6.9	4.43	
VI[d,f]	7.4-6.9	4.56	
VII[d]	7.4-6.9	4.50	
VIII[d]	7.4-6.9	4.51	
IX[d]	7.4-6.9	4.44 br	
X[e,g]	7.6-7.0	4.62	
XI[e,g]	7.6-7.0	4.59	
t-BuDiNC[d]	7.4-7.0	4.47	1.28
t-BuDiNC[e]	7.6-7.2	4.58	1.30
II[d]	7.4-6.9	4.37	1.29
III[d]	7.4-6.9	4.38	1.30
XII[e,h]	7.6-7.2	4.53	1.30
DiCN[d]	7.7-7.0	4.54	
DiCN[e]	7.7-7.0	4.64	
XIII[e]	7.7-7.1	4.63 br	
XIV[e]	8.0-7.2	4.71	
XV[e,i]	8.0-7.1	4.64	

[a] For spectra in CDCl$_3$, chemical shifts are referenced to internal Me$_4$Si. Spectra in acetone-d_6 are referenced to acetone-d_5 (2.04 ppm). [b] Multiplet. [c] Observed as a sharp singlet unless otherwise noted. [d] CDCl$_3$ solvent. [e] Acetone-d_6 solvent. [f] $C_5H_{11}N$ (3.28 m, 2.62 m, 1.50 m ppm). [g] Cp (5.64 s ppm). [h] Cp (5.58 s ppm). [i] Cp (5.38 s ppm).

Scheme II



t-BuDiNC are crystalline, colorless solids that become slightly yellow upon exposure to light over a period of months. They have been fully characterized by their elemental analyses and infrared and ^1H and ^{13}C NMR spectra (see Tables I-IV). DiNC is moderately soluble in CHCl$_3$ but only very slightly soluble in Et$_2$O and hexane. The solubilities of *t*-BuDiNC and its metal complexes are substantially greater than those of DiNC and its complexes. In CHCl$_3$, *t*-BuDiNC is extremely soluble; even in Et$_2$O it is very soluble, while in hexane it is only slightly soluble. As compared with many other isocyano ligands, DiNC and *t*-BuDiNC are particularly pleasant to work with because of their air stability and lack of odor.

Metal Complexes of the Bidentate Isocyano Ligands. So that the coordinating ability of DiNC might be explored, a series of reactions with metal complexes that are known to form complexes with monodentate isocyano ligands was performed. These are summarized in Scheme II.

The reaction of DiNC or *t*-BuDiNC with Cr(CO)$_4$(nor) in refluxing THF for 6 h gives Cr(CO)$_4$(DiNC) and Cr(CO)$_4$(*t*-BuDiNC) in 72 and 46% yields, respectively. The analogous reaction of Mo(CO)$_4$(nor) with *t*-BuDiNC occurs within minutes at room temperature to give Mo(CO)$_4$(*t*-BuDiNC) in 68% yield. In a somewhat slower reaction at room temperature, Mo(CO)$_4$(pip)$_2$[9] combines with DiNC to give Mo(CO)$_4$(DiNC) in 64% yield.

The corresponding reaction of W(CO)$_4$(pip)$_2$ yields two products. The minor product isolated in 18% yield is W(CO)$_4$(DiNC); the major product (78%) [*cis*-W(CO)$_4$(pip)]$_2$(μ-DiNC) results from the substitution of only one piperidine ligand and contains a bridging DiNC, in which the isocyano groups coordinate to different tungsten atoms. It is possible that replacement of the first piperidine occurs faster than that of the second,[9] which favors coordination of DiNC to another tungsten atom rather than chelate formation. By the use of M(CO)$_5$[(CH$_3$)$_2$CO], where M is Cr or W, in which the acetone ligand is very labile, the DiNC ligand can also be induced to form DiNC-bridging complexes [M(CO)$_5$]$_2$(μ-DiNC) in 69 and 41% yields for the Cr and W complexes, respectively. Related bis(diazenato) ligands, DiN$_2^{2+}$, were also observed[6] to form bridged complexes, but no chelated compounds were obtained in those systems.

An 86% yield of *fac*-Mn(CO)$_3$(DiNC)Br is isolated from the room-temperature reaction of Mn(CO)$_5$Br with DiNC. Likewise, CpFe(CO)$_3^+$ reacts at room temperature in acetonitrile solvent with DiNC to give CpFe(CO)(DiNC)$^+$ in 83% yield. The corresponding thiocarbonyl complex CpFe(CO)$_2$(CS)$^+$ reacts under the same conditions with DiNC and *t*-BuDiNC to give only the CO-substituted products CpFe(CS)(DiNC)$^+$ and CpFe(CS)(*t*-BuDiNC)$^+$ in 85 and 54% yields, respectively.

The complexes of DiNC and *t*-BuDiNC were characterized by their elemental analyses (Table I), infrared (Table II), ^1H (Table III) and ^{13}C (Table IV) NMR spectra, and mass spectra (see Experimental Section). The infrared spectrum of Cr(CO)$_4$(DiNC) in the ν(NC) and ν(CO) regions is very similar to that reported[22] for *cis*-Cr(CO)$_4$(CN-*p*-tol)$_2$ (see Table II, tol = tolyl). Spectra of the other M(CO)$_4$(L-L) complexes, where M is Cr, Mo, or W, and L-L is DiNC or *t*-BuDiNC, are also very similar; generally they exhibit fewer than the four allowed ν(CO) absorptions, but the broadness of the low-frequency bands suggests that they include several absorptions, as is found in the monodentate systems.[22] Four ν(CO) bands are observed in [*cis*-W(CO)$_4$(pip)]$_2$(μ-DiNC), which supports a structure in which the pip and isocyano groups are coordinated cis to each other.

In contrast to the M(CO)$_4$(L-L) complexes, which exhibit two ν(NC) absorptions, only one band is observed in spectra of [M(CO)$_5$]$_2$(μ-DiNC), where M = Cr or W. In the ν(CO) region, the [M(CO)$_5$]$_2$(μ-DiNC) spectra are very similar to those of the related M(CO)$_5$(CN-*p*-tol) complexes[22,23] (Table II). Spectra of the other complexes are very similar to those of comparable complexes with monodentate isocyano ligands given in the literature; such comparisons may be seen (Table II) for Mn(CO)$_3$(DiNC)Br and Mn(CO)$_3$(CNPh)$_2$Br[24] and for CpFe(CS)(DiNC)$^+$ and CpFe(CS)(CNPh)$_2^+$.[25]

To ensure that the proposed chelated complexes are indeed mononuclear, we determined mass spectra on the M(CO)$_4$(L-L) complexes, I-IV. In all cases a +1 parent ion of weak to medium intensity corresponding to the molecular weight of the mononuclear complex was obtained, and no ions at higher m/e values were observed. These results strongly support the chelated structures for these complexes and strengthen arguments favoring chelated structures for the other complexes. The detection of a parent ion in the mass spectrum of [Cr(CO)$_5$]$_2$(μ-DiNC) establishes it as the expected binuclear complex.

It was hoped that chelated and bridging DiNC ligands could also be distinguished by ^1H NMR studies of the CH$_2$ groups in the ligand. These CH$_2$ groups might be held in a signifi-

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Table IV. ^{13}C NMR Spectral Data for DiNC and *t*-BuDiNC Complexes

	chemical shifts, ppm[a]										
compd	NC	1	2	3	4	5	6	OCH_2	*C*-$(CH_3)_3$	C-$(\mathit{CH}_3)_3$	other
DiNC[b]		156.5	112.0	127.2	121.8	130.3	115.1				
DiNC	167.7	153.9	116.6	127.7	121.3	130.5	113.6	67.9			
DiNC[c]	169.7	155.1	116.7	128.5	122.0	131.6	114.6	68.8			
I	182.2	154.2	120.1	126.2	122.1	129.0	114.8	67.8			CO (220.1, 217.1)
IV	171.2	154.1	119.3	126.4	122.0	129.3	114.7	67.8			CO (209.7, 205.8)
VII	175.5	154.6	117.8	126.3	121.2	130.1	112.4	66.8			CO (216.8,[e] 214.6[f])
VIII	155.6	154.7	117.2	126.6	121.3	130.4	112.4	66.9			CO (196.4,[e] 194.0[f])
IX[d]	*g*	154.7	*g*	127.2	122.3	131.2	115.8	68.6			CO (212.9, 218.6)
X[c]	163.5	155.7	119.7	127.8	123.0	132.4	116.7	69.2			Cp (90.1), CS[g]
XI[d]	170.7	155.0	121.7	127.2	122.5	131.8	115.6	68.3			Cp (86.1), CO[g]
t-BuDiNC[b]		153.4	111.6	123.8	143.9	126.9	114.8				
t-BuDiNC	167.0	151.8	116.2	124.8	144.7	127.5	113.7	68.0	34.2	31.2	
t-BuDiNC[d]	168.0	152.2	116.4	125.3	145.1	127.9	113.8	68.5	34.6	31.4	
II	180.9	151.7	119.3	123.0	145.2	125.6	114.3	68.0	34.0	31.0	CO (220.1, 217.0)
III	170.4	152.1	119.0	123.8	145.7	126.4	114.7	68.3	34.4	31.3	CO (210.2, 206.0)
XII[c]	162.3	153.3	119.0	124.5	146.0	129.1	116.1	69.2	34.7	31.5	Cp (90.0), CS (322.6)

[a] Chemical shifts referenced to deuterated solvent multiplets ($CDCl_3$, 77.06; acetone-d_6, 29.80; CD_2Cl_2, 53.80 ppm). Spectra run in $CDCl_3$ solvent unless noted otherwise. [b] Values calculated according to procedure in ref 27. [c] Acetone-d_6 solvent. [d] CD_2Cl_2 solvent. [e] Trans CO. [f] Cis CO. [g] Resonance not observed.

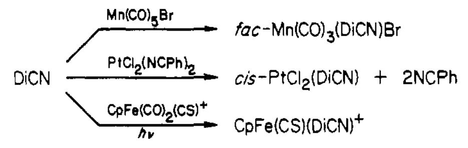
cantly different environment in the fairly rigid chelate than in the flexible bridging DiNC ligand. Among the Cr, Mo, W, and Mn complexes, it is observed (Table III) that the chemical shifts of the CH_2 in chelated DiNC complexes are all at slightly higher field (0.07–0.10 ppm) than in free DiNC. In contrast, the CH_2 chemical shifts in complexes with bridging DiNC ligands are at the same, or slightly lower, field relative to free DiNC. Thus, the CH_2 position may be useful in assigning bridging vs. chelated DiNC structures.

On the other hand, in the positively charged complexes $CpFe(CO)(DiNC)^+$ and $CpFe(CS)(DiNC)^+$, the CH_2 chemical shift is essentially the same as in the free ligand. The shift to lower field than that observed in other chelated DiNC complexes is reasonable in terms of the more positive metal center in these iron complexes; however, the charge on the metal is another parameter that must be considered when ^1H NMR is used to make chelated vs. bridging DiNC structural assignments.

Carbon-13 NMR spectra were obtained on several of the DiNC and *t*-BuDiNC complexes (Table IV). Assignments to the observed absorptions of the ligands were made by comparing them with expected chemical shifts calculated by a procedure given in ref 27. The carbon, C-2, to which the –NC group is attached was assigned to the broadest peak in the aromatic region; quadrupolar broadening is commonly observed for carbon atoms bonded to ^{14}N. The low solubility of the Mn and Fe complexes of DiNC made assignment of their CO and isocyano resonances difficult, even with the aid of the relaxation agent $Cr(acac)_3$.[26] Complexes containing *t*-BuDiNC are generally more soluble and give satisfactory spectra. The isocyano carbon resonance ranges from 155 to 182 ppm in the metal complexes, while the value for free DiNC and *t*-BuDiNC is 168.0 ppm in $CDCl_3$. This resonance is normally of low intensity and broadened by coupling to ^{14}N. The CO and CN resonances of the molybdenum complexes are approximately 10 ppm upfield of those in the analogous chromium complexes; those of the tungsten complex (VIII) are approximately 20 ppm upfield of the resonance in the chromium derivative (VII), a trend which has been noted previously.[28]

Although there are too few data to draw broad conclusions, it appears that the DiNC $^{13}CH_2$ chemical shift in chelated DiNC complexes is at the same, or lower, field than in the free ligand. On the other hand, this resonance occurs upfield (~1.0 ppm) of free DiNC in the binuclear complexes VII and VIII. These observations may also be useful in assigning structures to bridging and chelated DiNC complexes.

Scheme III



Metal Complexes of the Bidentate Cyano Ligand DiCN. Several complexes of the dicyano ligand DiCN are readily prepared as shown in Scheme III. The reaction of $Mn(CO)_5Br$ with DiCN in refluxing $CHCl_3$ gives an 82% yield of *fac*-$Mn(CO)_3(DiCN)Br$, whose infrared spectrum (Table II) exhibits three strong $\nu(CO)$ bands characteristic of the facial geometry; the spectrum is very similar to that of the related acetonitrile complex *fac*-$Mn(CO)_3(NCMe)_2Br$.[29] The $\nu(NC)$ absorptions in $Mn(CO)_3(DiCN)Br$ are very weak and at somewhat higher frequencies than in the free DiCN ligand; this shift is also observed in $Mn(CO)_3(NCMe)_2Br$ and $Re(CO)_3(NCPh)_2Br$.[30] The compound is not stable in solution and gives ^1H NMR spectra with broad peaks. Due to the low volatility of this and other DiCN complexes, it has not been possible to establish the mononuclear nature of these complexes by mass spectrometry. However, all other data are consistent with mononuclear chelated structures for the compounds.

The reaction of equimolar $PtCl_2(NCPh)_2$ and DiCN in refluxing dichloroethane results in the displacement of benzonitrile to yield air-stable $PtCl_2(DiCN)$ in 79% yield. This displacement indicates that there is greater stability associated with the DiCN chelate relative to that of the complex with monodentate benzonitrile ligands. The expected cis geometry of the complex is supported by the observation of two $\nu(Pt–Cl)$ absorptions at 362.1 and 352.5 cm^{-1}, which are comparable to those seen in *cis*-$PtCl_2(NCPh)_2$[31] (Table II).

While substitution of the CO groups in $CpFe(CS)(CO)_2^+$ proceeds thermally with DiNC at room temperature, it is necessary to use ultraviolet photolysis to promote the formation of the DiCN complex $CpFe(CS)(DiCN)^+PF_6^-$ in 87% yield.

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Results of conductivity studies of this compound are consistent with its formulation as a 1:1 electrolyte.

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Registry No. I, 80890-32-0; II, 80890-33-1; III, 80890-34-2; IV, 74237-51-7; V, 74237-52-8; VI, 80951-31-1; VII, 80890-35-3; VIII, 80890-36-4; IX, 74237-58-4; X, 74237-57-3; XI, 74237-55-1; XII, 80890-38-6; XIII, 74252-09-8; XIV, 74237-61-9; XV, 74237-60-8; DiNC, 74255-20-2; *t*-BuDiNC, 80878-98-4; DiCN, 74255-19-9; $DiNO_2$, 51661-19-9; *t*-$BuDiNO_2$, 80878-99-5; $DiNH_2$, 52411-34-4; *t*-$BuDiNH_2$, 75030-59-0; DiFor, 74255-22-4; *t*-BuDiFor, 80879-00-1; 2-nitrophenol, 88-75-5; 1,2-dichloroethane, 107-06-2; acetic formic anhydride, 2258-42-6; 4-*tert*-butylphenol, 88-18-6; 4-*tert*-butyl-2-nitrophenol, 3279-07-0; 2-cyanophenol, 611-20-1; $Cr(CO)_4(nor)$, 12146-36-0; $Mo(CO)_4(nor)$, 12146-37-1; *cis*-$Mo(CO)_4(pip)_2$, 65337-26-0; *cis*-$W(CO)_4(pip)_2$, 56083-13-7; $(Et_4N)[Cr(CO)_5I]$, 14780-98-4; $(Et_4N)[W(CO)_5I]$, 14781-01-2; $Mn(CO)_5Br$, 14516-54-2; $[CpFe(CO)_2(CS)]PF_6$, 34738-61-9; $[CpFe(CO)_3]PF_6$, 38834-26-3; $PtCl_2(PhCN)_2$, 15617-19-3.

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Hydrogen-Evolving Systems. 5. Nitrogen Reduction in the $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2 \cdot H_2O$ Systems: Factors Influencing Selectivities and Yields of Hydrazine and Ammonia Production

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New observations are reported for the reduction of molecular nitrogen in the $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2 \cdot H_2O$ systems. The reduction of N_2 can be directed to yield predominantly hydrazine or ammonia by selecting appropriate reaction conditions. Hydrazine is formed preferentially if the reduction of N_2 is conducted at high dilution, at high N_2 pressures, at low $V(OH)_2/Mg(OH)_2$ ratios, and at high NaOH concentrations. Under these conditions only traces of ammonia are formed because the secondary reduction of product hydrazine to ammonia is effectively suppressed. Trapping experiments and the observed yields of hydrazine on $p_{N_2}^2$ are consistent with the previously proposed mechanism of hydrazine formation through the disproportionation of diazene and rule out a direct reduction of N_2 to N_2H_4. The formation of ammonia is favored at small reaction solution volumes, at high $V(OH)_2/Mg(OH)_2$ ratios, and at low NaOH concentrations. In the $V(OH)_2/ZrO_2 \cdot H_2O$ system, the yields of ammonia and of hydrazine are generally lower but depend qualitatively on the same variables. The ammonia is formed by the secondary reduction of product hydrazine by $V(OH)_2$.

Introduction

In 1970, Shilov and co-workers observed that coprecipitated alkaline suspensions of $V(OH)_2$ and $Mg(OH)_2$ reduce molecular nitrogen to hydrazine and ammonia.[1] The Russian workers subsequently suggested that N_2H_4 is formed from N_2 directly by way of a "collective 4-electron-transfer process".[2-4] Assuming that $V(OH)_2$ acts as a 1-electron reductant, they postulated the reduction to take place in clusters of four or more V^{2+} ions at the $Mg(OH)_2$ surface. An analogous mechanism was also proposed for the reduction of C_2H_2 to C_2H_6 by $V(OH)_2/Mg(OH)_2$.[4]

In contrast, our work[5-7] has demonstrated that $V(OH)_2$ acts as a 2-electron reductant. The reduction of N_2 to N_2H_4 in the $V(OH)_2/Mg(OH)_2$ system was shown to occur in a stepwise fashion via diazene, N_2H_2, as the intermediate, and no evidence for the participation of V^{2+} clusters was obtained. We also demonstrated that the reduction of C_2H_2 in the $V(OH)_2/Mg(OH)_2$ system proceeds via C_2H_4 rather than directly to C_2H_6.

Maintaining their initial mechanistic ideas, Shilov et al. have since suggested[8] that NH_3 is formed directly from N_2 if the pH of the reaction medium is kept below 12. They also reject diazene as a possible intermediate of N_2 reduction on inappropriate thermodynamic grounds and on equivocal interpretations[9] of observed ^{15}N-isotope effects.

In the present paper, we will show that the stepwise mechanism of N_2 reduction[10] is also valid in the $V(OH)_2/Mg(OH)_2$ system under conditions leading to NH_3 and will present arguments against alternative mechanisms that have been proposed. In addition, we will also discuss the mechanistic significance of the kinetic ^{15}N-isotope effects described in ref 9. The experimental variables which determine the yields of NH_3 and N_2H_4 in reductions of N_2 by $V(OH)_2/Mg(OH)_2$ will be delineated first. Mechanistic aspects of N_2 reduction to NH_3 will be discussed next with particular reference to the intermediate formation of N_2H_2 and N_2H_4. Finally, new information on the reduction of N_2 in the $V(OH)_2/ZrO_2 \cdot H_2O$ system will be reported.

Results

Nitrogen Reduction in the $V(OH)_2/Mg(OH)_2$ System. The reduction of N_2 to either N_2H_4 or NH_3 depends on the relative concentrations of $V(OH)_2$ in the $Mg(OH)_2$ gels, on p_{N_2}, on reaction temperature, on the concentration of aqueous base,

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