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Iron(II) Complexes with the Chelating Bidentate Isonitrile Ligand DiNC

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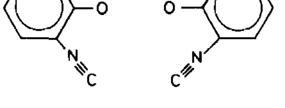
A series of Fe(II) complexes containing the chelating bidentate isonitrile ligand DiNC have been prepared and characterized. Both cis *and* trans *isomers of* $FeCl_2(DiNC)_2$ *are obtained from the reaction of* $FeCl_2 \cdot 4H_2O$ *with DiNC. One* Cl^- *in* cis-$FeCl_2(DiNC)_2$ *is readily substituted by various ligands L to yield the* $FeCl(L)(DiNC)_2^+$ *complexes, where* $L = CO, PPh_3, AsPh_3, P(OPh)_3$, *or* C_5H_5N. *Mercuric chloride reacts with* cis-$FeCl_2(DiNC)_2$ *to give the adduct* cis-$Fe(DiNC)_2Cl_2 \cdot HgCl_2$, *which is converted to the* $[FeCl(L)(DiNC)_2]HgCl_3$, $L = CO$ *or CDMe, salts upon reaction with CO and CNMe. Combination of* cis-$FeCl_2(DiNC)_2$ *with the proper stoichiometry of* $SnCl_2 \cdot 2H_2O$ *yields the* $-SnCl_3$ *complexes,* cis-$FeCl(DiNC)_2(SnCl_3)$ *and* cis-$Fe(DiNC)_2(SnCl_3)_2$. *A comparison of these results with previously known chemistry of related Fe(II) monodentate arylisonitrile complexes indicates that, except for the required* cis *isonitrile donor geometry of DiNC, the ligand properties of DiNC are very similar to those of related monodentate aryl isonitrile ligands.*

Introduction

The bidentate diisonitrile ligand DiNC,



has been shown to form chelate complexes of the type $M(CO)_4(DiNC)$ (where M = Cr, Mo, W), $Mn(CO)_3(DiNC)Br$, $CpFe(CO)(DiNC)^+$, $CpFe(CS)(DiNC)^+$ and $Rh(DiNC)_2^+$ [1–3]. In the work described herein, these studies have been extended to a series of Fe(II)–DiNC coordination compounds in order to determine if the chelating nature of the DiNC ligand appreciably alters the chemistry from that already known for Fe(II)–monodentate isonitrile complexes.

Experimental Section

Chemicals and solvents were of reagent grade and used as received from commercial sources. All reactions were performed in an air atmosphere. The bidentate isonitrile ligand DiNC was prepared as described previously [1, 2]. Infrared band positions were measured on a Perkin-Elmer 281 or 337B spectrophotometer and referenced to bands of gaseous CO. ^1H NMR spectra were recorded on a Perkin-Elmer R-20B or Varian HA-100 spectrometer using tetramethylsilane as the internal reference. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Compounds

cis- *and* trans-$FeCl_2(DiNC)_2$

To $FeCl_2 \cdot 4H_2O$ (0.093 g, 0.46 mmol) in 30 ml of MeOH was added a solution of DiNC (0.24 g, 0.92 mmol) in a minimum volume of CH_2Cl_2. The pale yellow solution darkened immediately to give a reddish solution and a suspended precipitate. The solution was stirred at room temperature for 30 min, then filtered to remove a blue solid. This solid appears to be primarily *trans*-$FeCl_2(DiNC)_2$ (ν(CN): 2144 cm^{-1}; 28% yield). The *cis* isomer was obtained by evaporating the orange filtrate to ¼ its volume under vacuum and adding Et_2O. The resulting precipitate was recrystallized by dissolving in MeOH; concentration of the solution under vacuum gave pure orange *cis*-$FeCl_2(DiNC)_2$ in 34% yield. *Anal.* Calcd. for $C_{32}H_{24}N_4O_4Cl_2Fe$: C, 58.65; H, 3.69. Found: C, 58.18; H, 3.62. The yield of *cis*-$FeCl_2(DiNC)_2$ varied in each preparation, apparently depending upon the relative amounts of the MeOH and CH_2Cl_2 solvents that were used.

Pure *trans*-$FeCl_2(DiNC)_2$ was obtained by dissolving the *cis* isomer in $CHCl_3$ and stirring the solution for several days at room temperature (heating causes some decomposition) until all of the orange *cis* isomer had been converted to the blue *trans*

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form. *Anal.* Calcd for $C_{32}H_{24}N_4O_4Cl_2Fe$: C, 58.65; H, 3.69. Found: C, 58.37; H, 4.09.

cis-*Fe(DiNC)$_2$Cl$_2$·HgCl$_2$*

Solid $HgCl_2$ (0.021 g, 0.076 mmol) was added to a solution of *cis*-$FeCl_2(DiNC)_2$ (0.050 g, 0.076 mmol) in 50 ml of $CHCl_3$. While the suspension was stirred for 3 h, the orange solution gradually darkened and a red-orange precipitate of *cis*-$Fe(DiNC)_2Cl_2 \cdot HgCl_2$ (77% yield) formed. *Anal.* Calcd. for $C_{32}H_{24}N_4O_4Cl_4FeHg$: C, 41.47; H, 2.61; Found: C, 40.86; H, 2.59.

cis-*FeCl(DiNC)$_2$(SnCl$_3$)*

To *cis*-$FeCl_2(DiNC)_2$ (0.050 g, 0.076 mmol) in 40 ml of $CHCl_3$ was added solid $SnCl_2 \cdot 2H_2O$ (0.017 g, 0.076 mmol). After the solution was stirred for 3 h, its volume was reduced under vacuum causing precipitation of yellow-orange *cis*-$FeCl(DiNC)_2(SnCl_3)$ in 70% yield. *Anal.* Calcd. for $C_{32}H_{24}N_4O_4Cl_4FeSn$: C, 45.49; H, 2.86. Found: C, 45.90; H, 3.06.

cis-*Fe(SnCl$_3$)$_2$(DiNC)$_2$*

A large excess of solid $SnCl_2 \cdot 2H_2O$ (0.17 g, 0.76 mmol) was added to a solution of *cis*-$FeCl_2(DiNC)_2$ (0.050 g, 0.076 mmol) in 50 ml of $CHCl_3$. After stirring the mixture for at least 12 h, the excess $SnCl_2 \cdot 2H_2O$ was removed by filtration, and the solution was evaporated to 1/5 its volume. The addition of Et_2O precipitated yellow microcrystalline needles of *cis*-$Fe(SnCl_3)_2(DiNC)_2$, which were removed by filtration and were then recrystallized from MeOH in 60% yield. *Anal.* Calcd. for $C_{32}H_{24}N_4O_4Cl_6FeSn_2$: C, 37.15; H, 2.34. Found: C, 36.84; H, 2.62.

*[*cis-*FeCl(CNMe)(DiNC)$_2$]HgCl$_3$*

To $Fe(DiNC)_2Cl_2 \cdot HgCl_2$ (0.10 g, 0.11 mmol) in 20 ml of acetone was added 0.44 mmol of MeNC *via* syringe. The mixture was stirred for 12 h during which time the starting complex dissolved to give a yellow solution. The volume of this solution was reduced under vacuum and Et_2O addition precipitated the yellow product. Reprecipitation from MeOH/EtOH with Et_2O gave $[FeCl(CNMe)(DiNC)_2]HgCl_3$ in 85% yield. *Anal.* Calcd. for $C_{34}H_{27}N_5O_4Cl_4FeHg$: C, 42.19; H, 2.81. Found: C, 41.74; H, 2.73.

[FeCl(CO)(DiNC)$_2$]BPh$_4$

Carbon monoxide was bubbled through a solution of *cis*-$FeCl_2(DiNC)_2$ (0.10 g, 0.15 mmol) in 50 ml of MeOH for 12 h or until most of the complex had dissolved. The yellow solution was filtered to remove any insoluble material and then concentrated under vacuum. Addition of a solution of $NaBPh_4$ (0.050 g, 0.15 mmol) in 15 ml of MeOH precipitated pale yellow $[FeCl(CO)(DiNC)_2]BPh_4$ in 60% yield. *Anal.* Calcd. for $C_{57}H_{44}N_4O_5BFeCl$: C, 70.79; H, 4.59. Found: C, 70.99; H, 4.56.

[FeCl(L)(DiNC)$_2$]BPh$_4$, where L = PPh$_3$, AsPh$_3$, P(OPh)$_3$, C$_5$H$_5$N

The desired ligand L was added in 10% excess, either as a solid or neat liquid, to *cis*-$FeCl_2(DiNC)_2$ (0.10 g, 0.15 mmol) in 50 ml of MeOH. While the solution was stirred for 3–4 h, most of the complex dissolved and the solution changed from orange to yellow (except for $AsPh_3$ which remained orange). After the solution was filtered, a solution of $NaBPh_4$ (0.050 g, 0.15 mmol) in 15 ml of MeOH was added to precipitate the product in 40–60% yield. All of the compounds were yellow except for that of $AsPh_3$, which was orange.

Anal. Calcd. for $[FeCl(PPh_3)(DiNC)_2]BPh_4$: C, 73.98; H, 4.95. Found: C, 72.94; H, 5.04.

Anal. Calcd. for $[FeCl(AsPh_3)(DiNC)_2]BPh_4$: C, 71.37; H, 4.78. Found: C, 71.41; H, 4.73.

Anal. Calcd. for $[FeCl(P(OPh)_3)(DiNC)_2]BPh_4$: C, 71.14; H, 4.76. Found: C, 70.94; H, 4.82.

Anal. Calcd. for $[FeCl(C_5H_5N)(DiNC)_2]BPh_4$: C, 71.96; H, 4.85. Found: C, 72.13; H, 4.89.

All complexes are relatively air stable but decompose slowly when exposed to air for long periods (weeks). The CO-containing compounds are the least stable.

Results and Discussion

The reaction of $FeCl_2 \cdot 4H_2O$ with DiNC in MeOH leads to the precipitation of the insoluble blue *trans*-$FeCl_2(DiNC)_2$ complex. The orange *cis*-$FeCl_2(DiNC)_2$ isomer can be isolated from the solution. Structural assignments of these two isomers are based on the single ν(CN) absorption which is expected for the pseudo-D_{4h} symmetry of the *trans* isomer and the four expected absorptions of the *cis* form (Table I). Although only 3 ν(CN) bands are observed for *cis*-$FeCl_2(DiNC)_2$, their broadness may obscure the fourth band. These assignments are supported by the colors of several related $FeCl_2(CNR)_4$ complexes, which exist in blue-to-violet *trans* forms and yellow-to-orange *cis* forms [4–9]. Infrared spectra of the $FeCl_2(CNR)_4$ complexes are also very similar to those of *cis*- and *trans*-$FeCl_2(DiNC)_2$ [5–9].

When *trans*-$FeCl_2(DiNC)_2$ is suspended in MeOH, EtOH, dimethylformamide, or dimethylsulfoxide, the complex gradually dissolves as it isomerizes to the *cis* isomer. Conversely, *cis*-$FeCl_2(DiNC)_2$, when dissolved in $CHCl_3$ or CH_2Cl_2, slowly isomerizes to the *trans* isomer which precipitates from solution.

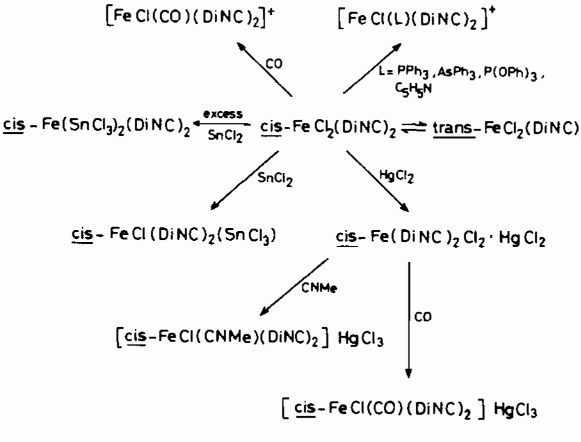
Reactions of *cis*-$FeCl_2(DiNC)_2$ are summarized in Scheme I. A few reactions were tried with the *trans* isomer, but these were all much slower than

TABLE I. Infrared and ^{1}H NMR Data.

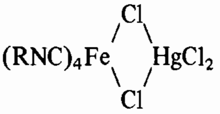
Compound	ν(CN)[a], cm^{-1}	^{1}H Chemical Shifts, δ ppm[b]	
		$-CH_2CH_2-$	C_6H_4
DiNC	2127s	4.48	6.78–7.50
cis-$FeCl_2(DiNC)_2$	2195w, 2156s,br, 2143s,br[c]	4.5br[d]	6.92–7.92[d,e]
trans-$FeCl_2(DiNC)_2$	2144		
cis-$Fe(DiNC)_2Cl_2 \cdot HgCl_2$	2208m, 2170s, 2159s		
cis-$FeCl(DiNC)_2(SnCl_3)$	2188m, 2157sh, 2144s		
cis-$Fe(SnCl_3)_2(DiNC)_2$	2193m, 2150s, 2140s		
[*cis*-$FeCl(CNMe)(DiNC)_2$]$HgCl_3$	2203m, 2188sh, 2178s, 2152s[f]	3.75, 4.46[g]	7.30–7.70[g]
[*cis*-$FeCl(CO)(DiNC)_2$]$HgCl_3$	2223w, 2195sh, 2185s[h]		
$[FeCl(CO)(DiNC)_2]BPh_4$	2225w, 2182s,br[i]	3.78–4.08br	6.6–7.1[j]
$[FeCl(PPh_3)(DiNC)_2]BPh_4$	2198m, 2150s	3.85br,[k] 4.11	6.61–7.20[l]
$[FeCl(AsPh_3)(DiNC)_2]BPh_4$	2195m, 2156s, 2145s	3.76br[k], 4.08	6.60–7.16[j]
$[FeCl(P(OPh)_3)(DiNC)_2]BPh_4$	2201m, 2161s	3.88, 4.00	6.60–7.10[m]
$[FeCl(C_5H_5N)(DiNC)_2]BPh_4$	2190w, 2155s,br, 2144sh	3.90, 4.18	6.70–7.18[m]
$[FeCl(C_5H_5N)(DiNC)_2]BPh_4$		3.50, 4.54br[n]	6.82–7.10[n]

[a] Nujol mull. Abbreviations: w, weak; m, medium; s, strong; sh, shoulder; br, broad. [b] In $CDCl_3$ unless undicated otherwise. [c] 2195w, 2160s, 2134sh cm^{-1} in $CHCl_3$. [d] In CD_3OD. [e] Broad multiplet. [f] ν(CN) of CNMe at 2239 m cm^{-1}. [g] In $(CD_3)_2SO$; CH_3 at 3.25 ppm. [h] ν(CO) at 2085 cm^{-1}. [i] ν(CO) at 2086 cm^{-1}. [j] BPh_4^- at 7.45 ppm[k]. [k] Center of resonance. [l] BPh_4^- at 7.40 ppm[k]. [m] BPh_4^- at 7.42 ppm[k]. [n] In $(CD_3)_2SO$; BPh_4^- at 7.52 ppm[k].

with the *cis*. The lower reactivity of *trans*-$FeCl_2(DiNC)_2$ may be due to its lower solubility and/or the need for it to isomerize to the *cis* form before reacting. In the reactions described in Scheme I, *cis*-$FeCl_2(DiNC)_2$ was used.



Mercuric chloride reacts at room temperature with *cis*-$FeCl_2(DiNC)_2$ to give a complex with the composition $Fe(DiNC)_2Cl_2 \cdot HgCl_2$. Other $FeCl_2(CNR)_4$ complexes with monodentate isonitrile ligands have been observed to react with $HgCl_2$ to give analogous products $Fe(CNR)_4Cl_2 \cdot HgCl_2$ [4, 7, 8]. Mays and Prater [7] described these complexes as containing an $HgCl_3^-$ group coordinated to the iron through the Hg atom, while Bonati and Minghetti [8] suggested the chloro-bridged structure



in the solid state. The lack of definitive evidence prevents an unequivocal structural assignment to *cis*-$Fe(DiNC)_2Cl_2 \cdot HgCl_2$; however, the known [10] chloro-bridged structure of *cis*-$Pt(PMe_2Ph)_2Cl_2 \cdot HgCl_2$ and the large number of related compounds [11] suggests that *cis*-$Fe(DiNC)_2Cl_2 \cdot HgCl_2$ probably also has the chloro-bridged structure.

As *cis*-$FeCl_2(p\text{-}CNC_6H_4OMe)_4 \cdot HgCl_2$ reacts with CO and CNR to give $[FeCl(L)(p\text{-}CNC_6H_4OMe)_4]HgCl_3$ [7], so $Fe(DiNC)_2Cl_2 \cdot HgCl_2$ reacts at room temperature with CO and CNMe to yield $[FeCl(CO)(DiNC)_2]HgCl_3$ and $[FeCl(CNMe)(DiNC)_2]HgCl_3$, which are assigned *cis* structures based on the similarity of their ν(CN) absorptions (Table I) to those of *cis*-$FeCl_2(DiNC)_2$ and *cis*-$Fe(DiNC)_2Cl_2 \cdot HgCl_2$.

The room temperature reaction of *cis*-$FeCl_2(DiNC)_2$ with one equivalent of $SnCl_2 \cdot 2H_2O$ leads to *cis*-$FeCl(DiNC)_2(SnCl_3)$; using a large excess of

$SnCl_2 \cdot 2H_2O$ yields the product with two $SnCl_3^-$ ligands, *cis*-$Fe(SnCl_3)_2(DiNC)_2$. Both of these yellow to yellow-orange complexes are believed to have *cis* structures based on the similarity of their $\nu(CN)$ spectra to those of the other *cis* structures noted above and by comparison with spectra of the related *cis*-$FeCl(p\text{-}CNC_6H_4OMe)_4(SnCl_3)$ and *cis*-$Fe(SnCl_3)_2(p\text{-}CNC_6H_4OMe)_4$ complexes [7].

The substantial ionic conductivities of *cis*-$FeCl_2(p\text{-}CNC_6H_4OMe)_4$ [7] and *cis*-$FeCl_2(p\text{-}CNC_6H_4\text{-}Me)_4$ [8] in nitromethane and acetone, respectively, suggest that Cl^- dissociation occurs in these solutions. It also suggests that a Cl^- in *cis*-$FeCl_2(DiNC)_2$ could be readily displaced by other ligands. Indeed, the room temperature reactions of *cis*-$FeCl_2(DiNC)_2$ with CO, PPh_3, $AsPh_3$, $P(OPh)_3$ and C_5H_5N lead to stable $FeCl(L)(DiNC)_2^+$ complexes which are readily isolated as their BPh_4^- salts. A *cis* structure for these complexes should yield 4 IR-active $\nu(CN)$ bands, whereas a *trans* structure would give 2 $\nu(CN)$ bands assuming C_{4v} local symmetry. As can be seen in Table I, the complexes are observed to have 2 or 3 $\nu(CN)$ absorptions in Nujol mulls. The lowest frequency $\nu(CN)$ band is very broad and could obscure other bands that would be expected for the *cis* isomer. It has been noted previously that structural assignments to isonitrile complexes based on their $\nu(CN)$ spectra are often not conclusive [12], especially in the solid state where additional splittings may occur. Thus, it is not possible to specify unequivocally the structure of the $FeCl(L)(DiNC)_2^+$ complexes; their yellow-to-orange colors, however, are very similar to that of *cis*-$FeCl_2(DiNC)_2$, which hints that they may have the *cis* structure. The only previously reported complexes which are similar to these are $FeX(PPh_2OEt)(p\text{-}CNC_6H_4\text{-}Me)_4^+$, where X = Br or I [13]. They were assigned *trans* structures based on the 2 observed $\nu(CN)$ absorptions and equivalent methyl groups in all the isonitrile ligands in ^1H NMR spectra of the complexes.

Of all of the complexes studied herein, in only *trans*-$FeCl_2(DiNC)_2$ would the ethylene protons of the DiNC ligands be expected to be equivalent. However, its ^1H NMR spectrum was not obtained due to its low solubility. The ethylene protons of all other compounds should be inequivalent. Spectra of these compounds (Table I) contain at least one very broad ethylene absorption and often two broad bands. Even in the most symmetrical complex *cis*-$FeCl_2(DiNC)_2$, all 4 ethylene protons are inequivalent and should lead to a complex ^1H NMR pattern; only one broad absorption is observed. Were the $FeCl(L)(DiNC)_2^+$ complexes to have a *trans* geometry, A_2B_2 patterns would be expected for the ethylene protons. In the *cis* geometry, all 4 ethylene protons would be inequivalent. Unfortunately, the broadness of the bands prevents an unequivocal *cis* or *trans* structural assignment to the $FeCl(L)(DiNC)_2^+$ complexes.

In conclusion, the chemistry of the Fe(II)–DiNC complexes is very similar to that of analogous monodentate phenyl and substituted phenyl isonitrile complexes. Aside from requiring *cis* coordination of the isonitrile donors in DiNC, the ligand properties of DiNC are not appreciably different from those of related aryl isonitrile ligands.

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