

## Non-innocent bidentate nitrogen-ligands in electron-rich complexes of 3d-elements

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**Abstract** - Ligands with the flat N=C-C=N skeleton (1,4-diaza-1,3-dienes R<sup>Ar</sup>N=CR-CR=NR'; 2,2'-bipyridine) are both  $\sigma$ -donors and  $\pi$ -acceptors. The  $\pi$ -acceptor strength, but not the  $\sigma$ -donor strength is strongly influenced by the substituents R'. This is reflected by the half-wave potentials which decreases in the order R<sup>Ar</sup>N=CR-CR=NR' > R<sup>Al</sup>N=CR-CR=NR<sup>Al</sup> > bipy. Possibilities of a further variation of the N=C-C=N skeleton (metal extractants 2-acetylpyridine-p-toluenesulfonylhydrazone [APSH-H] and 2-quinolyl-p-toluenesulfonylhydrazone [ACSH-H]), differences in substitution reactions of nickel(0) complexes by 1,4-diaza-1,3-dienes or bipy and complex formation with the radical anions (R<sup>Ar</sup>N=CR-CR=NR')<sup>-</sup> [formation of [Li(Me<sub>4</sub>en)]<sub>2</sub>Fe(bda)<sub>2</sub> etc.] are reported.

### INTRODUCTION

The conception of "non-innocent ligands" was created in the sixties by C.K. Jorgensen. Ligands of this type, in complexes with predominantly covalent bonds, can act both as  $\sigma$ -donors and  $\pi$ -acceptors. The balance of donor and acceptor interactions and, as a consequence, the effective negative charge on these ligands to a high degree depends on the overall number of electrons available. For complexes with high numbers of such electrons, it is difficult if not impossible to establish the oxidation state of central atom correctly. This must be kept in mind, whenever a reliable interpretation of redox processes is demanded. Typical non-innocent ligands are the dithio- $\alpha$ -diketones, the o-quinones, the tetra-thiooxalate anion (ref. 1), but also the bidentate 1,4-diaza-1,3-dienes R<sup>Ar</sup>N=CR-CR=NR' and  $\alpha,\alpha'$ -bipyridine (bipy). In this connection the "spectrum" of the chromium complexes is to be mentioned which was opened by the careful preparative studies of Herzog and coworkers (ref. 2). An extremely electron-rich species, no doubt, is compound 1.

Cr(bipy) <sub>3</sub> X	1952	Cr(bipy) <sub>3</sub>	1958
[Li(THF) <sub>4</sub> ][Cr(bipy) <sub>3</sub> ]	1967	Na <sub>2</sub> [Cr(bipy) <sub>3</sub> ]·7THF	1967
Na <sub>3</sub> [Cr(bipy) <sub>3</sub> ]·7THF	1967	Ca <sub>3</sub> [Cr(bipy) <sub>3</sub> ]·7NH <sub>3</sub>	1967

1

NDDO-calculations of molecules with the flat N=C-C=N skeleton ( $\alpha$ -diimines, N $\curvearrowright$ N) have been reported by Benedix et. al. (ref. 3). They found no important difference of these ligands as to their "quasi-lone-pair" density, but a strong influence of the substituents, first of all of R', on the NDDO-LUMO energies, i.e. on the  $\pi$ -acceptor strength. These energies increases in the order



which is in a good accordance with the half-wave potentials of the one-electron steps <sup>1</sup>E<sub>1/2</sub> and <sup>2</sup>E<sub>1/2</sub> (Table 1)

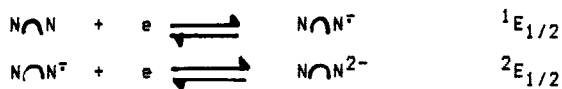



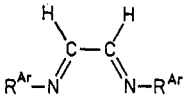
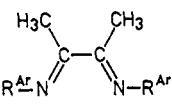
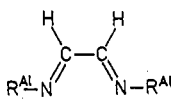
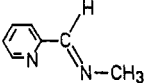
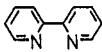
Table 1 allows us two conclusions:

- bipy is a poor  $\pi$ -acceptor (ref. 6);
- radical anions of the type (R<sup>Ar</sup>N=CR-CR=NR<sup>Ar</sup>)<sup>-</sup> are more easily reduced than the neutral molecules R<sup>Al</sup>N=CR-CR=NR<sup>Al</sup>.

Assuming a correlation between the half-wave potential and the  $\pi$ -acceptor strength, we can expect the radical anions  $(R^{Ar}-N=CR-CR=N-R^{Ar})^{\cdot-}$  to be  $\pi$ -acceptors superior or at least comparable to  $R^{Al}-N=CR-CR=N-R^{Al}$  and bipy. We were interested in three questions:

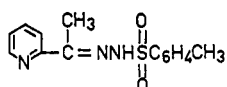
- What other, the ligands in table 1 surpassing variations of the  $N=C-C=N$  skeleton are possible without an essential variation in the redox behaviour?
- Are the differences in the  $\pi$ -acceptor strength of bipy and the 1,4-diaza-1,3-dienes also reflected in the course of substitution reactions?
- What is the coordinative behaviour of the above-mentioned radical anions?

TABLE 1. NDDO-LUMO-energies (eV) (first lines) and half-wave potentials (V) of  $\alpha$ -diimine ligands (second lines:  $^1E_{1/2}$ , third lines:  $^2E_{1/2}$ ).

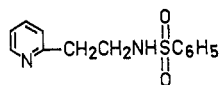
			
0.22		1.86	$R^{Ar} = C_6H_5$
?		-0.904	} $R^{Ar} = pCH_3C_6H_4$ (ref. 4)
?		-1.358	
			
?		2.24	$R^{Al} = CH_3$
-1.310	$R^{Ar} = C_6H_5$	-1.65	} $R^{Al} = C_6H_{11}$ (ref. 4)
-1.593		-	
			
2.39		2.54	
?		-2.14	(ref. 5)
?		-2.40; -2.64	

### SULFONAMIDE SUBSTITUTED $\alpha$ -DIIMINE LIGANDS

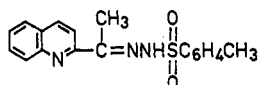
In connection with our studies on the extraction of late 3d-element ions by chelating ligands (ref. 7), we synthesized the arenesulfonylhydrazones APSH-H and ACSH-H. APSH-H is, as is shown by the  $pH_{1/2}$ -values (pH at which the distribution ratio of the metal between water and the organic phase is unity) for copper(II), comparable to LIX 34, a proprietary metal extractant produced by the Henkel Corp. (ref. 8). We were interested in the coordinative behaviour of these ligands as well and obtained always 1,2-chelates  $M^{II}(APSH)_2$  or  $M^{II}(ACSH)_2$ , not only with copper(II), nickel(II), cobalt(II), and zinc(II) but also with iron(II) and manganese(II). This was somewhat surprising, we had studied a lot of heterocyclic sulfonamides, for instance PEB-H (ref. 9), but never succeeded in the preparation of iron(II) and manganese(II) chelates.



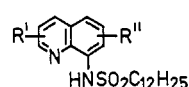
APSH-H  
 $pH_{1/2}(Cu^{2+}) = 1,4$



PEB-H  
 $pH_{1/2}(Cu^{2+}) = 6,4$



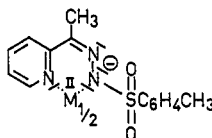
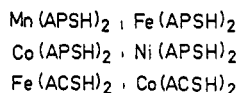
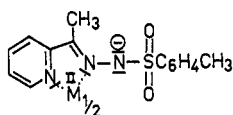
ACSH-H  
 $pH_{1/2}(Cu^{2+}) = 3,3$



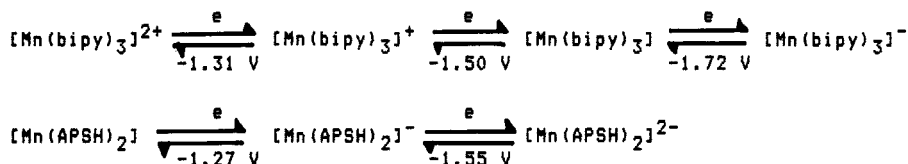
LIX 34  
 $pH_{1/2}(Cu^{2+}) = 1,5$

extraction in the system water-chloroform

We think the speciality of the ligands APSH-H and ACSH-H is the E-Z-isomerism of their anions. These type of isomerism is well-known for 1,2-dioximes, where E-Z-isomerisation is catalysed by transition metal ions (ref. 10, 11). Therefore, in normal cases the real structure of metal complexes with 1,2-dioximes is determined by the thermodynamic stability of these complexes and not by the original structure of the protonated ligand. We think the same rule to be valid for the complexes of our ligands APSH-H and ACSH-H, and our results are in accordance with the E-structure of these ligands in all but one case. These results come mainly from electrochemical measurements.



The E-isomers, as to their electronic structures, are to be classed with the  $\alpha$ -diimine ligands and a comparison with bipy is obvious. Tris-bipyridine chelates of the late 3d-elements have been thoroughly investigated by electrochemical methods (ref. 5, 12), and it was demonstrated that in the course of the reduction of these chelates the electrons first of all occupy MOs which are primarily localized on the ligands. Three one-electron steps with half-wave potentials close to one another are recorded. For an example the data of the manganese complex are shown.



Remarkably, the first and the second steps of the  $[\text{Mn}(\text{bipy})_3]^{2+}$ - and  $[\text{Mn}(\text{APSH})_2]$ -reduction have nearly the same half-wave potentials (ref. 13). As to our opinion, this is not an accident, but it is an expression of analogous structures. This means, as already indicated, an E-structure of both ligands in  $\text{Mn}(\text{APSH})_2$ .

TABLE 2. Half-wave potentials of the complexes  $\text{M}^{\text{II}}(\text{APSH})_2$  and  $\text{M}^{\text{II}}(\text{ACSH})_2$  (ref. 13)

	${}^0E_{1/2}$ (V)	${}^1E_{1/2}$ (V)	${}^2E_{1/2}$ (V)
Fe(APSH) <sub>2</sub>	+0.86	-1.10	-1.60
Co(APSH) <sub>2</sub>	-	-1.10	-1.88
Ni(APSH) <sub>2</sub>	-	-1.435	-2.07
Cu(APSH) <sub>2</sub>	-0.41	-	-
Fe(ACSH) <sub>2</sub>	+0.80	-1.19	-1.69
Co(ACSH) <sub>2</sub>	-	-1.16	-1.82
Zn(ACSH) <sub>2</sub>	-	-1.39	-1.62

$5 \cdot 10^{-3} \text{ M}$  solutions in acetonitrile,  $(\text{NEt}_4)\text{ClO}_4$ , Hg-dropping electrode, calomel electrode as a reference

The electrochemical behaviour of the most other complexes of the ligands APSH<sup>-</sup> and ACSH<sup>-</sup> is similar to that of  $\text{Mn}(\text{APSH})_2$  (Table 2). But three differences must be mentioned:

- In the case of the iron(II) chelates an additional anodic step is discovered ( ${}^0E_{1/2}$ ) which is doubtlessly connected with an oxidation of the central atom  $[\text{Fe}(\text{II}) \rightarrow \text{Fe}(\text{III})]$ .
- For  $\text{Mn}(\text{APSH})_2$  the difference  ${}^1E_{1/2} - {}^2E_{1/2}$  is 0.28 V, in all other cases it is higher. Probably this is an expression of an electronic interaction between the two ligands which is favoured by an unsymmetrical occupation of  $t_2$ - or e-levels of the central atom.
- The electrochemical behaviour of  $\text{Cu}(\text{APSH})_2$  is abnormal (Because of its low solubility a study of  $\text{Cu}(\text{ACSH})_2$  was impossible). Only one step is observed which can be attributed to the copper(II)/copper(I)-pair. We have a reference to a structural background of this behaviour and it comes from ESCA-data (ref. 13). For all electrochemical normal chelates these data are in accordance with the E-structure of the ligands, but for  $\text{Cu}(\text{APSH})_2$  they point out a coordination of the Z-isomer.

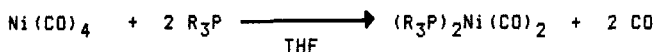
**SUBSTITUTION REACTIONS OF NICKEL(0) COMPLEXES WITH 1,4-DIAZA-1,3-DIENES OR  $\alpha,\alpha'$ -BIPYRIDINE**

In the following only reactions of electron-rich nickel complexes will be discussed. Considering a great number of experimental data two rules have been derived (ref. 14):

- The reaction of binary complexes containing only  $\pi$ -acceptor ligands with other  $\pi$ -acceptor ligands is connected with a total exchange of the ligands (msa = maleic anhydride, COD = cyclo-octadiene(1,3)). Complete conversion of  $\text{Ni}(\text{CO})_4$  only becomes possible if the carbon monoxide can escape.



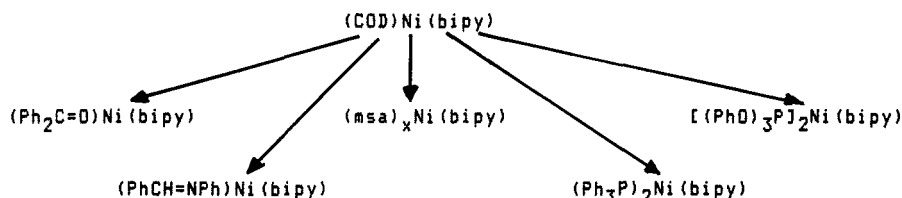
- A combination of  $n$ -donor and  $\pi$ -acceptor ligands is a stabilizing factor for ternary complexes. Therefore binary complexes of nickel(0) containing  $\pi$ -acceptor ligands react smoothly with  $n$ -donor ligand by a partial substitution



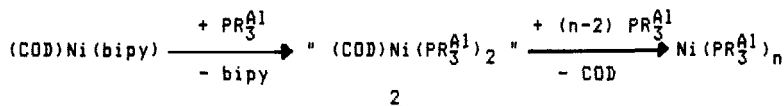
The following reactions demonstrate the strong  $\pi$ -acceptor behaviour of 1,4-diaza-1,3-dienes and the function of the poor  $\pi$ -acceptor bipy mainly as an  $n$ -donor.



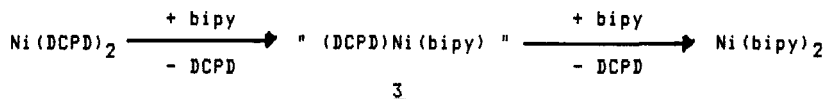
$(\text{COD})\text{Ni}(\text{bipy})$  is a good feed for the synthesis of other ternary nickel(0) complexes. But we find a specific influence of the donor-acceptor balance of the reagent on the course of the reaction. In general  $\pi$ -acceptors substitute the  $\pi$ -acceptor COD, and remarkably in this special case there is no difference between  $\text{PPh}_3$  and the strong  $\pi$ -acceptor  $\text{P}(\text{OPh})_3$ .



Stronger  $n$ -donor ligands substitute bipy. But we never succeeded in the isolation of intermediates such as 2. In the case of tert.-aliphatic phosphines  $\text{PR}_3^{\text{Al}}$  as reagents this is not so much surprising, because it is well-known that binary phosphine complexes are easily obtained by substitution of COD in complexes of type 2.

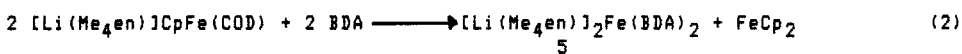
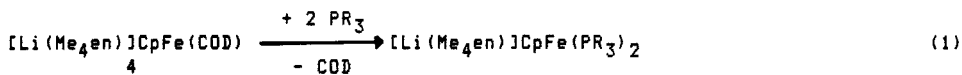


$(\text{COD})\text{Ni}(\text{bipy})$  is not a suitable educt for  $\text{Ni}(\text{bipy})_2$ . D. Walther prepared the latter compound starting with the polymeric Bis(dicyclopentadiene)nickel  $\text{Ni}(\text{DCPD})_2$ . DCPD is a diolefine, but in contrast to COD is it not a chelating ligand. Therefore an intermediate such as 3, which is comparable to  $(\text{COD})\text{Ni}(\text{bipy})$  as to the composition but not as to the structure, will react with a second molecule of bipy by substitution as well.

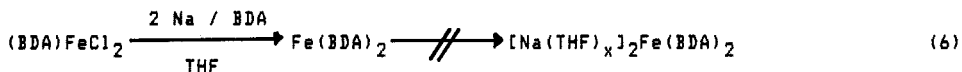
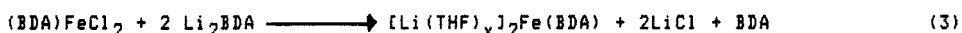


COMPLEX FORMATION WITH THE RADICAL ANIONS ( $R^{Ar}N = CR-CR = NR^{Ar}$ ).

Whenever, as might be expected on account of the half-wave potentials (table 1), the radical anions ( $R^{Ar}N=CR-CR=NR^{Ar}$ )<sup>-</sup> are comparable both to the neutral ligands  $R^{Al}N=CR-CR=NR^{Al}$  and bipy as to their  $\pi$ -acceptor strenght, then we can ask the question for the existence of such a pair of compounds as  $Fe(R^{Al}N=CR-CR=NR^{Al})_2$  (ref. 15) and  $M_2^I[Fe(R^{Ar}N=CR-CR=NR^{Ar})_2]$ . Starting with the complex 4 (ref. 16) and considering the reaction of this compound with phosphines (1), we tried to substitute COD by benzildianil (BDA). However we did not obtain  $[Li(Me_4en)]CpFe(BDA)$ , but ferrocene and 5, i.e. the products of a ligand redistribution (ref. 17).



The complexes of type 5 can be prepared in a simple way by the reaction of  $(BDA)FeCl_2$  and  $Li_2(BDA)$  in THF (3). But the failure of the reactions (5) and (6) marks the limited area of the stability of these compounds.

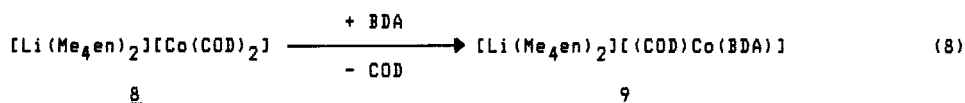
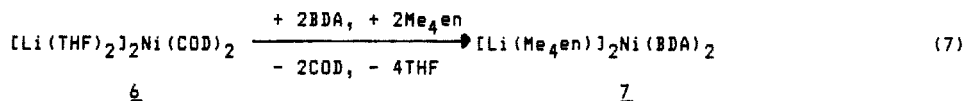


GDT = glyoxal-bis(4-methylphenylimine)

GDIP = glyoxal-bis(isopropylimine)

Complexes of type 5 with aliphatic N-substituted 1,4-diaza-1,3-dienes (and with bipy) are not obtainable. But lithium is also a inevitable component. As is shown by the low content of  $Me_4en$  or THF, a specific interaction between iron and lithium is a stabilizing factor (ref. 16). But also the fact that, among the alkali metals in organic solvents, lithium is the strongest reductant, should be of same importance.

ate-complexes related to 5 are obtained with cobalt and nickel as well. Again the best method is the substitution of COD (7,8). Only one equivalent of lithium is present in the complex 8. This should be the reason, why only one equivalent of COD is substituted by BDA.



We didn't succeed in the synthesis of 7 starting with  $Ni(BDA)_2$  and lithium nor did we obtain any crystalline compound by the reaction of  $Co(BDA)_2$  and lithium.

The problems which are connected with an interpretation of the magnetic moment of transition metal complexes with non-innocent ligands are well-known. Therefore it is somewhat astonishing that the magnetic moments of our new ate-complexes can be explained in a simple way by Paulings classic valence bond model.

TABLE 3. Electronic configuration and magnetic moments of 1,4-diaza-1,3-diene complexes

			number of un- paired electrons	$\mu_{\text{eff.}}$ (20°C) (B.M.)
$\text{Fe}(\text{R}'\text{N}=\text{CR}=\text{CR}=\text{NR}')_2$	$3d^8$	$4(sp^3)^8$	2	2.98 (ref. 15)
$\text{Co}(\text{R}'\text{N}=\text{CR}=\text{CR}=\text{NR}')_2$	$3d^9$	$4(sp^3)^8$	1	2.1 (ref. 19)
$\text{Ni}(\text{R}'\text{N}=\text{CR}=\text{CR}=\text{NR}')_2$	$3d^{10}$	$4(sp^3)^8$	0	diam.
<u>5</u>	$3d^8$	$4(sp^3)^8$	4	5.5
<u>9</u>	$3d^9$	$4(sp^3)^8$	2	2.82
<u>7</u>	$3d^{10}$	$4(sp^3)^8$	2	2.76
<u>8</u>	$3d^{10}$	$4(sp^3)^8$	0	diam.
<u>6</u>	$3d^{10}$	$4(sp^3)^8$	0	diam.
<u>10</u>	$3d^{10}$	$4(sp^3)^8$	0	diam.

For steric reasons the neutral complexes of the type  $\text{M}(\text{R}'\text{N}=\text{CR}=\text{CR}=\text{NR}')_2$  cannot have a planar structure. A tetrahedral structure is favoured, but for special nickel complexes a diminution of the dieder angle ( $< 90^\circ$ ) is found (ref. 18). Assuming a roughly tetrahedral structure, the four  $sp^3$ -orbitals are occupied by the free electron pairs of the ligands and the valence electrons of the central atoms are concentrated in the 3d-level. The experimental magnetic moments are in accordance with this proposal (Table 3).

The explanation of the magnetic behaviour of the ate-complexes is based in the proposal that there is no change of the "inner" electronic configuration, but one electron is added to each N-arylated 1,4-diaza-1,3-diene ligand. Then, in comparison to the neutral complexes, the number of unpaired electrons should increase by one (9) or two (5 and 7). This is what is found indeed.

Summing up we have to say the magnetic behaviour of the formal 18-electron species 5 is quite unusual. This is clearly demonstrated by a comparison with  $[\text{Li}(\text{Me}_4\text{en})]_2\text{Fe}(\text{COD})_2$  (10), another 18-electron species of iron. But on the contrary, among the formal 20-electron species of nickel (6 and 7) the latter seems to be the normal one. The explanation is as follows, 6 has a fluxional structure (ref. 16). On average, out of the four  $\pi$ -electron pairs of the two COD-ligands, only three are coordinated to nickel. Therefore, in practice 6 is an 18-electron species and as such is equivalent to  $\text{Ni}(\text{R}'\text{N}=\text{CR}=\text{CR}=\text{NR}')_2$ .

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