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Recent advances in the organometallic chemistry of aryldiamine anions that can function as *N,C,N'*- and *C,N,N'*-chelating terdentate "pincer" ligands: an overview‡

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Abstract. – Monoanionic terdentate ligand systems bonded to a metal center via at least one covalent carbon-to-metal bond are interesting alternatives to the monoanionic Cp ($C_5H_5^-$) and Cp* ($C_5Me_5^-$) ligands that are commonly used in organometallic chemistry and homogeneous catalysis. This review concentrates on the metal complexes of the terdentate aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN) and the related ligand $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$ (CNN), which are characterized by the fact that NCN has two *ortho*-amine substituents whereas CNN has a single *ortho* diamine substituent.

Synthetic studies using NCN started with the synthesis of the first example of an ionic tin(IV) complex $[SnMe_3(NCN)]Br$ in 1978 and now complexes of NCN and CNN with many metals and metalloids are known. The original concept behind the use of NCN was that with metal centers this bis-(*ortho*)-chelating ligand would function as an η^3-*N,C,N* 6-electron system having all three donor atoms positioned in one plane, i.e. with the *N*-donor functions positioned mutually *trans*. However, recent structural studies have revealed that the binding of NCN and CNN in metal species is extremely versatile and in mononuclear NCN species identified bonding modes include η^1-*C* and η^2-*C,N* as well as η^3-*N,C,N* that has been found in both facial and meridional configurations with N-metal-N angles ranging from 160° to 109°.

Moreover, many NCN- and CNN-metal complexes exhibit unique physicochemical properties and/or reactivity. Some interesting examples include the stabilization of high oxidation states, such as in the first stable arylnickel(III) species $[NiX_2(NCN)]$ (X=halide or NCS) and the unusual η^1-(end-on) binding of I_2 to $[Pt(NCN)]$ leading to $[PtI(NCN)](\eta^1\text{-}I_2)]$, which can be seen as a model for the first stage of the oxidative addition of dihalogens to d^8-metal centers. The control of reactivity is nicely illustrated by a reversible C–C bond formation and cleavage process during the addition of MeI to $[Pt(NCN)(H_2O)]OTf$; this chemistry also led to the isolation of the first example of a σ-bonded metal-substituted arenonium ion. The use of NCN-metal complexes as catalysts in various homogeneous catalytic processes, including the addition of halocarbons to alkenes, transfer hydrogenation, and C–C cross-coupling reactions, is now being developed. In this context, a comparison of complexes of the aryldiamine ligand NCN and the closely related aryldiphosphine system $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$ (PCP) is timely. Recent results have shown that in some cases NCN- and PCP-metal complexes can have almost the same or complementary structural and reactivity features, whereas in other cases related NCN and PCP complexes can have entirely different and unique properties.

Our research in the chemistry of NCN is also directed to the exploration of the use of the NCN ligand and its derivatives for the synthesis of new materials, e.g. organometallic polymers (molecular wires) with special electron-conducting or photophysical properties. An example of this is $[PtCl(C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}OH\text{-}4)]$, which, as a result of the presence in the molecule of a hydrogen-bond acceptor (Cl) and a donor (the *para*-OH group), self-assembles in the solid state to infinite chains (molecular wires) by noncovalent hydrogen bonding. Other newly synthesized materials include organometallic dendrimer catalysts that comprise a carbosilane dendrimer core appended with catalytically active $[NiBr(C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Z\text{-}4)]$ units in which Z is a specially designed *para* substituent that serves as a linker to the dendrimer surface.

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The versatile bonding and unique reactivity properties in complexes of aryldiamine ligands such as NCN and CNN indicate that these ligands (as well as PCP) are primary candidates as alternative donor systems to the well-known Cp and Cp* ligands in transition metal chemistry. This review illustrates that the NCN ligand, and most probably the CNN ligand too, could be as broadly applicable in organometallic chemistry and homogeneous catalysts as the cyclopentadienyl fragment.

Key words : metal complexes, monoanionic aryldiamine ligands, overview, "pincer" ligands, terdentate *N,C,N'*- and *C,N,N'*-chelation.

1. Introduction

The monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN) found its introduction in 1978 in the ionic Sn(IV) complex $[Sn(NCN)(Me)Ph]^+Br^-$ [1]. Since then this ligand has found wide application and complexes with many metals and metalloids have been prepared [1-32].

The original concept behind the development of NCN was that it would be a bis(*ortho*)-chelating "pincer" ligand that would function as a *N,C,N'*-terdentate 6-electron donor system and thereby form metal complexes with the N-donor functions mutually *trans*, as shown schematically in Figure 1, A. This meridional η^3-*N,C,N'*-bonding mode of NCN has been identified in complexes of Ti(IV) [2], Ta [3], Fe(III) [4], Ru(II) [5], Co(II) [6], Rh(III) [7], Ni(II) [8a-c], Ni(III)[8d-f], Pd(II) [9], Pt(II) [9, 10], Pt(IV) [11], Hg [9d], Al [12a], Ga [12b, c], In [12d, e], Tl [9a], Si [13], Sn(II) [14a], Sn(IV) [1, 14b, c], Sb [15], Y [16], and Lu [16]. In X-ray structural studies of specific complexes the N–M–N angles are significantly less than 180° (i.e. ±160-150°) due to the geometrical restriction of the two five-membered rings and in most species of this type the rings have C_2 (rotation)-related puckering with the aryl ring twisted approximately 12° out of the C_{ipso}, N, N, metal plane; such studies include complexes of Ti(IV) [2], Ta [3], Ru(II) [5], Rh(III) [7a], Ni(II) [8a, b], Ni(III) [8e], Pd(II) [9a, b, f], Pt(II) [9c, e, 10j, k, l], Pt(IV) [11a, b], Al [12a], Ga [12b, c], In [12d, e], Sn(II) [14a], Sn(IV) [14b], and Lu [16].

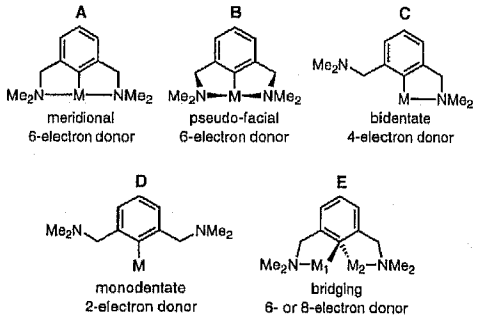


Figure 1. – Bonding modes reported for $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN).

During the development of NCN chemistry it soon became apparent that this ligand could access other coordination modes. Firstly a number of organometallic species were found in which the *N,C,N'*-coordination was no longer meridional with the two five-membered rings having C_S (mirror plane)-related puckering and the N-donor atoms being positioned on the same side of the aryl plane. This situation was characterized by X-ray molecular structure determinations for complexes of Fe [4], Co [6], Ni(III) [8d, f], and Pt(II) [10a, b, h, i]. Later it was found that this distortion from meridional *N,C,N'*-bonding could be even more severe and in recent years we have isolated NCN species of Ti [2], Ta [3b, 17], Re [18], Ru [5], Si [19], Sb [20], Bi [20], Lu [16], and La [21] in which the bonding mode can now be best described as pseudo-facial with N–M–N angles ranging from approximately 110-120° (Fig. 1, **B**).

Apart from these terdentate "pincer" *N,C,N'*-bonding modes, the NCN ligand can also engage in bidentate η^2-*C,N*-bonding (Fig. 1, **C**) (Ta [22], Rh(I) [23], Ir(I) [24a], Ir(III) [24b], Au(I) [25], B [26], Ga [12b, d], Si [27]) and monodentate η^1-*C*-bonding (Fig. 1, **D**) (Pt(II) [28], Au(I) [25]), as well as act as an *N,C,N'*-bridging system between metal centers in di- and multinuclear complexes (Fig. 1, **E**) ($M_1 = M_2$: Li [29], Na [30], Cu [31]; $M_1 \neq M_2$: Ta/Zn [3a, 32]).

During the development of NCN chemistry we found that this ligand system has some very specific and unique properties that can lead not only to the stabilization of a variety of metal oxidation states but can also control the reactivity and stereochemistry of its complexes as a result of its electronic properties and the geometric restrictions it imposes. An example of control of the reactivity is illustrated by a reversible aryl-to-cyclohexadiene conversion occurring in a Pt(II) complex; this system enabled the isolation and characterization of a stable σ-metal-substituted arenonium ion (i.e. cyclohexadienyl carbonium ion) analogous to the Wheland intermediate formed during electrophilic substitution reactions on free aromatic systems [33]. As regards both the number of coordination sites it can occupy and the number of bonding electrons it can provide, the NCN ligand when acting as a facially bonded η^3-*N,C,N'*-coordinated system

may be considered as an interesting alternative to the commonly used $C_5H_5^-$ (Cp) ligand system.

A very useful property of the NCN ligand is that substituents can be introduced at many places in its skeleton to enable fine tuning of its coordination and electronic properties. For example complexes have been prepared with substituents other than Me on the N-donor atom (Li [34], Ga [12e], Ni(II) [35], Pt(II) [36], Cu [37]) and with substituents on the aryl ring (Li [38, 39a], Ru [39], Ni(II) [40]). In this context the NCN ligand and its many derivatives offer in several senses a more varied chemistry than that of the related aryldiphosphine ligand $[C_6H_3(CH_2PPh_2)_2\text{-}2,6]^-$ and other analogous terdentate *P,C,P'*-bonding ligand systems [41].

More recently we have extended our study to the bonding modes of aryl ligands having one diamine substituent, by synthesizing complexes containing the monoanionic mono(*ortho*)-aryldiamine ligand $[C_6H_4(CH_2N(Me)CH_2NMe_2)\text{-}2]^-$ (CNN) (Fig. 2) [42]. The CNN system is also a potential terdentate ligand but differs from NCN in two ways. First, when coordinated as a "pincer" terdentate ligand, it should always give N-donor atoms coordinated mutually *cis*. Second, when the $CH_2CH_2NMe_2$ unit is not coordinating its flexibility can still enable the N-donor atom to come close to the metal center. In this situation this unit, which is actually a Lewis base, may become an active spectator moiety and possibly provide anchimeric assistance of metal-centered reactions [42-44]. It should be noted that the N atom of the $ArCH_2N(Me)$ unit is a stereogenic center when this nitrogen donor is involved in coordination to the metal center and this feature provides a very useful stereochemical probe in NMR spectroscopy. Like NCN, the CNN ligand has versatile bonding properties comprising a terdentate η^3-*C,N,N'*-bonding mode, a bidentate η^2-*C,N*-bonding mode, as well as a monodentate η^1-*C*-bonding mode. In the case of terdentate *C,N,N'*-bonding it can provide, like NCN, both meridional and facial coordination.

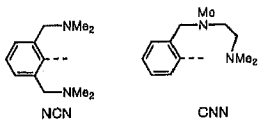


Figure 2. – The monoanionic potentially terdentate "pincer" ligands NCN and CNN.

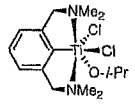
In 1989 a review appeared devoted to research in the area of oxidative addition reactions that employ d^8 metal centers that are bonded by the NCN ligand, but this was restricted to research done in our own group [45]. In the present review we concentrate on the variety of structural forms and unusual coordination modes established with NCN (*Section 2*) and CNN ligand systems (*Section 3*) that have been reported by our own group and others in the period from 1989 to 1996; this review includes a few earlier references that were previously not incorporated, and some mention of other terdentate *C,N,N'*- and *N,C,N'*-bonding ligand systems.

2. Organometallic chemistry of NCN and related ligand systems

2.1. Groups 1 (IA) and 2 (IIA): Li, Na, Mg

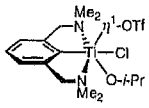
We reported the dimeric lithium complex of the NCN ligand, $[Li_2(NCN)_2]$, in 1982 [29a] and have been able to obtain an X-ray molecular structure of a related complex, $[Li\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}]_2$, **1**, which contains four aryl CH_2NMe_2 substituents [38a]. This latter molecule exists as a dimeric unit in which each aryl group bridges two lithium atoms in a 3-center, 2-electron interaction. The distorted tetrahedral coordination sphere of each of the lithium atoms is completed by two *N*-coordinating *ortho*-CH_2NMe_2 substituents. Complex **1** was the first dimeric aryllithium species to be characterized in which coordination around lithium is completed solely by intramolecular heteroatom bonding to the metal center [38a]. We have also prepared the potentially pentadentate, monoanionic ligand $[C_6H_3(CH_2N(Me)CH_2CH_2NMe_2)_2\text{-}2,6]^-$ (N'NCNN') that can be seen as being derived from NCN by replacement of one methyl group of each NMe_2 unit by a $CH_2CH_2NMe_2$ group. The aryllithium complex $[Li_2(N'NCNN')Br]$, **2**, containing this ligand has been prepared from the reaction of the arylbromide compound $C_6H_3Br(CH_2N(Me)CH_2CH_2NMe_2)_2\text{-}2,6$ with two equivalents of *n*-BuLi [34]. The X-ray crystallographic determination of **2** shows a novel structural feature: a Li_2ArBr core in which the bromide anion bridges the two lithium atoms and in which C_{ipso} is involved in a 3-center 2-electron bond. The coordination sphere of each lithium is completed by coordination of two *N*-donor atoms of the *ortho*-$CH_2N(Me)CH_2CH_2NMe_2$ substituents [34]. In this crystallographic study of **2** the unit cell was found to contain two enantiomeric molecules, i.e. the S_NS_N and R_NR_N complexes, that arise from the presence of two stereogenic –N(Me)– centers in each complex (compare the CNN ligand that has one stereogenic –N(Me)– center, Fig. 2). The structure of the *para*-substituted NCN complex $[Li\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-Ph-}4\}]_2$ has also been recently reported [39a].

The trimeric organosodium NCN complex $[Na_3(NCN)_3]$, **3**, which was synthesized by reaction of $[Li_2(NCN)_2]$ with sodium *tert*-amylate, is the first example of a totally intramolecularly solvated organosodium species [30]. The



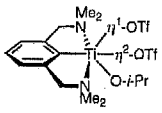
4

C_{ipso}-Ti 2.090 Å
N-Ti-N 113.23°



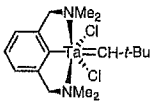
5

C_{ipso}-Ti 2.086 Å
N-Ti-N 147.86°



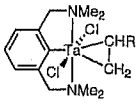
6

C_{ipso}-Ti 2.098 Å
N-Ti-N 147.26°



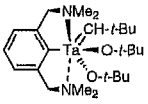
7

C_{ipso}-Ta 2.154(4) Å
N-Ta-N 118.63(14)°
Ta-C_α-H_α 76(3)°
Ta-C_α-C_β 170.6(3)°



8: R = *t*-Bu
9: R = Me

(8) C_{ipso}-Ta 2.165(7) Å
N-Ta-N 145.0(2)°

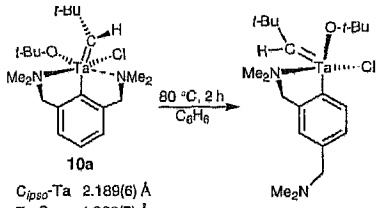


12

C_{ipso}-Ta 2.242(4) Å
N-Ta-N 99.70(10)°

NCN ligand is meridionally η^3-*N,C,N'*-bonded to the metal [3b, 17]. A Wittig-type reaction of **7** with acetone or benzaldehyde affords the dimer $[TaCl_2(NCN)(\mu\text{-}O)]_2$, which contains a bridging oxo function. A similar reaction of **7** with PhCH=NR yields the imido complexes $[TaCl_2(NCN)(NR)]$ (R = Me, $SiMe_3$) [6b].

In order to obtain active metathesis catalysts and to avoid the reductive rearrangement of the intermediate tantalacyclobutane, which leads to inactive alkene-coordinated complexes like **8** and **9**, we have tried to substitute chloride groups in **7** by alkoxide groups; the latter should stabilize this type of tantalacyclobutane intermediate and protect the alkylidene function from bimolecular decomposition. Transmetallation of **7** with Li–O–*t*-Bu and KOMe, respectively, affords the monoalkoxide complexes [TaCl(=CH–*t*-Bu)(NCN)(OR)] (R = *t*-Bu, **10a**; Me, **10b**) [22]. Interestingly, complex **10a** is thermally unstable and at 80 °C an irreversible isomerization reaction takes place in which the metal moves from a position between the two CH_2NMe_2 coordination arms of the NCN ligand to a position *ortho* to one of these coordination arms and [TaCl(=CH–*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*4*}(O–*t*-Bu)], **11**, is formed (eq 2) [47]:



10a

C_{ipso}-Ta 2.189(6) Å
Ta-C_α 1.962(7) Å
N-Ta-N 113.59(15)°
Ta-C_α-C_β 140.7(5)°

11

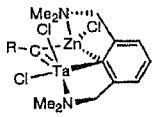
(2)

A similar rearrangement reaction, which involved conversion of the Ir(I) complex [Ir{$C_6H_3(CH_2NMe_2)_2$-2,*6*}(COD)] (COD = cycloocta-1,5-diene) to the product [Ir{$C_6H_3(CH_2NMe_2)_2$-2,*4*}(COD)], was previously reported by van der Zeijden et al. [24a].

The bisalkoxide complex [Ta(=CH–*t*-Bu)(NCN)(O–*t*-Bu)$_2$], **12**, has been obtained by the reaction of $[Li_2(NCN)_2]$ with [TaCl(=CH–*t*-Bu)(O–*t*-Bu)$_2$(PMe_3)] [22]. The pentacoordinate tantalum center in **12** has a distorted trigonal-bipyramidal geometry with one NMe_2 unit of the η^2-*C,N*-bidentate-bonded NCN ligand and one of the alkoxide groups in axial positions, while the second *ortho*-CH_2NMe_2 substituent is free from the metal center (Ta–N = 3.426(3) Å) although its N-donor atom is positioned opposite to the alkylidene carbon atom [22]. Complex **12** reacts with (trimethylsilyl)ethene to afford its (trimethylsilyl)methylidene analog [22]. A bisalkoxide complex directly related to **12** is the $[C_6H_4CH_2NMe_2]^-$ complex [Ta(=CH–*t*-Bu)($C_6H_4CH_2NMe_2$-2)(O–*t*-Bu)$_2$], which can be prepared in a one-pot procedure by a sequence of transmetallation reactions starting from [$TaCl_3$(=CH–*t*-Bu)(THF)$_2$], [Zn($C_6H_4CH_2NMe_2$-2)$_2$], and Li–O–*t*-Bu [22]. The alkoxide complexes **12** and [Ta(=CH–*t*-Bu)($C_6H_4CH_2NMe_2$-2)(O–*t*-Bu)$_2$] are fluxional in solution at room temperature and undergo dissociation/association processes involving the coordinative Ta–N bonds of the arylamino ligands [22]. The reactivity of the mono- and bisalkoxide complexes **10a** and **12** with simple alkenes varies from unclean (probably reductive rearrangement) reactions to very clean alkene metathesis reactions [22].

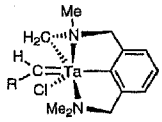
The NCN alkylidene complex **7** is easily accessible and we have used this species to make the new bimetallic bridging alkylidyne complex [$TaCl_2$(μ-NCN)(μ-C–*t*-Bu)ZnCl], **13**, through its 1:1 reaction with neopentylzinc chloride [3a, 32]. Surprisingly, reaction of bimetallic **13** with $Me_2N(CH_2)_2NMe_2$ (tmeda) at 60 °C leads to elimination of zinc chloride and formation of the alkylidene complex [TaCl(=CH–*t*-Bu){C_6H_3(CH_2N(Me)CH_2)-2-(CH_2NMe_2)-6}], **14**, which arises from an alkylidyne activation reaction of a methyl C–H bond in a NMe_2 group [32]. In the presence of [Pd($C_6H_4CH_2NMe_2$-2)(μ-X)]$_2$ (X = Cl, I) the reaction of **13** with tmeda generates [$TaCl_2$(=C-(*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2, 6})($C_6H_4CH_2NMe$-2)], **15**,

and this, as such, is an unprecedented, new palladium-mediated alkylidyne functionalization reaction [32].

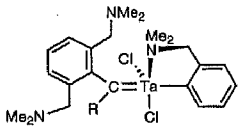


13: R = t-Bu

C_{ipso}-Ta 2.321(6) Å
C_{ipso}-Zn 2.258(6) Å
C_{ipso}-Ta-C_{α} 102.5(2)°
C_{ipso}-Zn-C_{α} 96.9(2)°



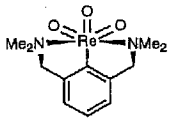
14: R = t-Bu



15: R = t-Bu

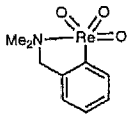
2.3. Group 7 (VIIB): Re

Through the use of *C,N*-coordinating $[C_6H_4CH_2NMe_2\text{-}2]^-$ and *N,C,N'*-coordinating $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ we have introduced a new type of chelating ligand to rhenium oxide chemistry and we have been able to synthesize the bis(*ortho*)-chelated arylaminorhenium trioxide complex $[ReO_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, **16** and the mono(*ortho*)-chelated arylaminorhenium trioxide complex $[ReO_3(C_6H_4CH_2NMe_2\text{-}2)]$, **17** [18]. Complex **16** has been characterized by X-ray molecular structure determination, which shows that the rhenium center has a bicapped tetrahedral geometry in which the NCN ligand is pseudo-facially η^3-*N,C,N'*-bonded [18]. Although these new arylaminorhenium trioxide complexes with intramolecular *C,N*-coordination are not active catalysts in the epoxidation of alkenes their easy accessibility and good thermal stability make them excellent potential starting materials for the synthesis of other aryltrioxorhenium(VII) species.



16

C_{ipso}-Re 2.112(11) Å
N-Re-N 107.7(3)°



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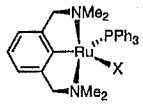
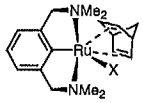
2.4. Group 8 (VIII): Ru

In the course of our studies directed towards the development of new metal complex catalysts for oxidation and hydrogenation reactions, we have realized the synthesis of the new NCN complexes [Ru(NCN)-X(PPh$_3$)] (X=Cl, **18a**; X=I, **18b**), [Ru(NCN)Cl-(nbd)] (nbd=norbornadiene), **19**, and [Ru(NCN)(OTf)-



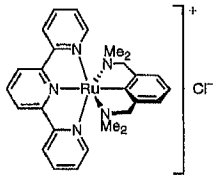
18a: X = Cl
18b: X = I

(**18a**) C_{ipso}-Ru 1.967(2) Å
N-Ru-N 147.59(7)°



19: X = Cl
20: X = OTf

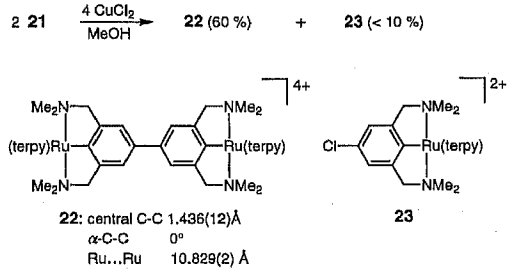
C_{ipso}-Ru ~ 2.0 Å
N-Ru-N ~ 110°



21

C_{ipso}-Ru 1.982(7) Å
N-Ru-N 156.2(2)°

(nbd)], **20** [5]. The flexibility that the NCN ligand exhibits in its terdentate *N,C,N'*-bonding in these complexes is unprecedented. This is demonstrated by the different N–Ru–N angles, which range from 147.59(7)° in **18b**, to 110.09(7)° in **19** and 109.35(6)° in **20** [5]. Moreover, in combination with other ligands at the ruthenium center the NCN ligand stabilizes a five-coordinate, square-pyramidal, 16-electron configuration in **18** (with bulky PPh$_3$) as well as a six-coordinate, octahedral, 18-electron configuration in **19** and **20** (with bidentate norbornadiene) [5]. A ligand-substitution reaction of the 16-electron complex **18a** with the terdentate nitrogen ligand 2,2′:6′,2″-terpyridine (terpy) affords a product formulated as [Ru(NCN)(terpy)]Cl, **21** [5]. The NMR spectroscopic data for **21**, for example, show only one NMe$_2$ resonance, which indicates that this Ru(II) species most likely consists of an octahedral ruthenium (18-electron) cation in which both the NCN and the terpy ligands are terdentate coordinated, and a chloride anion; this ionic character is corroborated by its excellent water solubility and an X-ray structure determination [5]. Subsequent reaction of **21** with copper(II) dichloride unexpectedly affords the dinuclear ruthenium(III) complex $[\{Ru(terpy)\}_2(bis\text{-}NCN)]^{4+}$ (bis-NCN is the biaryl ligand $[4,4'\text{-}(C_6H_2(CH_2NMe_2)_2\text{-}2,6)_2]^{2-}$), **22**, (in 60% yield), as well as the *para*-chloro analog of **21**, i.e. complex **23**, in less than 10% yield (eq 3) [39b, c]:



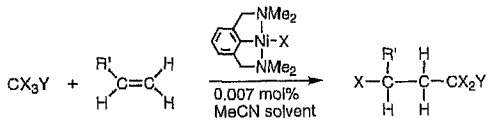
(3)

This reaction to afford complex **22** in good yield involves not only an oxidation of the Ru(II) center to Ru(III) but also a subsequent efficient C–C bond formation that results from oxidation of two NCN *para* C–H bonds. An X-ray diffraction study has shown that the tetracation **22** has a central 2,2′,6,6′-tetrakis[(dimethylamino)methyl]biphenyldiyl dianion that bridges two identical ruthenium(III) centers, which are both bis(chelate)-η^3-*N,C,N′*-bonded by this double "pincer" system [39b, c]. The dinuclear complex **22** has strong electronic communication between the metal centers as evidenced by large intervalence charge-transfer bands at 1875 nm ($\epsilon = 33000\ M^{-1}\ cm^{-1}$) in its near infrared spectrum and a high value for the comproportionation constant (K_c) in cyclic voltammetry measurements (Ru^{II}·Ru^{III}: $K_c = 950$) [39b, c].

2.5. Group 10 (VIII): Ni, Pd, Pt

Wenschuh and co-workers have reported that Ni(II) complexes of the type $[NiBr\{C_6H_3(CH_2NRR')_2\text{-}2,6\}]$, in which NRR′ represents derivatives of the cyclic amines piperidinyl and pyrrolidinyl, show reversible binding of SO_2 (detected by means of IR photoacoustic spectroscopy) and that they react with CS_2 and PhNSO. In contrast the complexes where NRR′ is NEt_2, $N(i\text{-}Pr)_2$, and NMeCy did not react with SO_2, CS_2, and PhNSO [35c]. It should be noted that in our laboratory it has been found that the square-planar platinum(II) and nickel(II) NCN complexes [MX(NCN)] (M = Ni, Pt; X = Cl, Br, I) do react reversibly with SO_2 and that the X-ray molecular structure of $[PtBr(NCN)(SO_2)]$ contains a square-pyramidal Pt(II) center to which SO_2 is η^1-*S*-bonded at the apical position [10i].

We have also reported that organonickel(II) complexes of the type $[NiX\{C_6H_3(CH_2NRR')_2\text{-}2,6\}]$ (X = halide) containing a range of alkylamino substituents are excellent homogeneous catalysts for the Kharasch addition reaction (eq 4) [35a, b, d, e]:

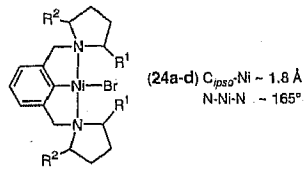


(4)

X = halogen; Y = H, halogen, CF_3 or other electronegative group.

This particular catalytic system is based on the redox properties of the metal complex and it has been found that the Ni^{II}/Ni^{III} redox potential for $[NiX\{C_6H_3(CH_2NMe)_2\text{-}2,6\}]$ dissolved in water has a remarkably low $E_{1/2}$ of +0.14 V vs. SCE. It is relevant to note that the NCN system is capable of stabilizing d^7 Ni(III) species and that the air-stable square-pyramidal species $[Ni^{III}X_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (X = Cl, Br, I, NO_3, and NO_2) [8d, f] and octahedral species $[Ni^{III}(NCN)(NCS)_2(py)]$ [8e] have been isolated; ESR data as well as the X-ray molecular structures of $[NiI_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ [8d, f] and $[Ni(NCS)_2(NCN)(py)]$ [8e] have been reported.

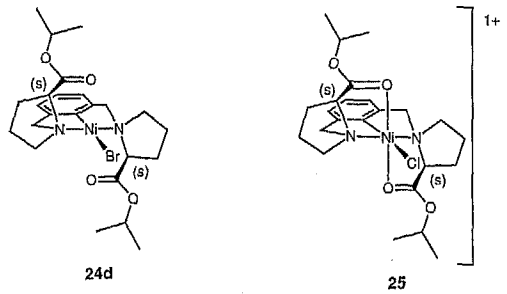
When an alkene with a prochiral center is used as a substrate in the Kharasch addition reaction a chiral center is formed in the product and the use of an arylnickel complex containing derivatives of NCN as a catalyst could possibly lead to chiral induction. With Ni^{2+} ions ligands of the type $[C_6H_3(CH_2NRR')_2\text{-}2,6]^-$ form square planar d^8 Ni(II) complexes in which there is meridional η^3-*N,C,N′*-bonding of the ligand, i.e. they contain a metal-carbon σ-bond and two mutually *trans*-positioned nitrogen-donor sites; this bonding mode gives a restricted geometry that offers several possibilities for obtaining chiral organometallic complexes. In this context chiral organonickel(II) complexes **24a-d** have been synthesized containing monoanionic *N,C,N′*-terdentate ligands based on the 2,6-bis[1-(pyrrolidinyl)methyl]phenyl system. In these ligands chirality is introduced at the nitrogen donor atoms, which are part of pyrrolidynyl ring systems, by placing substituents on the 2 or 5 positions of the rings [35d].



24a: R^1 = Me, R^2 = H (racemic; [Ni(pyr(2-Me)NCN)Br]
24b: R^1 = Me, R^2 = H (*S*-enantiomer); [Ni(pyr(2*S*-Me)NCN)Br]
24c: R^1 = Me, R^2 = Me (*R,R*-enantiomer); [Ni(pyr(2*R*, 5*R*-Me_2)NCN)Br]
24d: R^1 = C(O)O-*i*-Pr, R^2 = H (*S*-enantiomer); [Ni(pyr(2*S*-CO_2-*i*-Pr)NCN)Br]

It was found that the catalytic ability of these and related nickel complexes in the Kharasch addition reaction is markedly influenced by the ligand geometry around nickel and only **24a** and **24b** proved to be effective catalysts. The highest enantiomeric excess of 16-17% obtained with **24b** and L-menthyl methacrylate as the substrate in this catalytic reaction indicates that the C_2 chiral fence produced by the Me-substituted pyrrolidinyl rings is not very effective for the transfer of chiral information [35d]. An attempt was made to use the enantiopure arylnickel(II) complex [Ni(L*–*N,C,N′*)Br] (L* is the monoanionic ligand 2,6-bis[(2-(*S*)-2-isopropoxycarbonyl-

1-pyrrolidinyl)methyl]phenyl), **24d**, as a catalyst for the Kharasch addition reaction of CCl_4 to alkenes but this reaction led instead to the formation of a new ionic nickel(III) complex $[(Ni(L^*)Cl]_2[NiCl_4]$, **25** [35e].



24d **25**

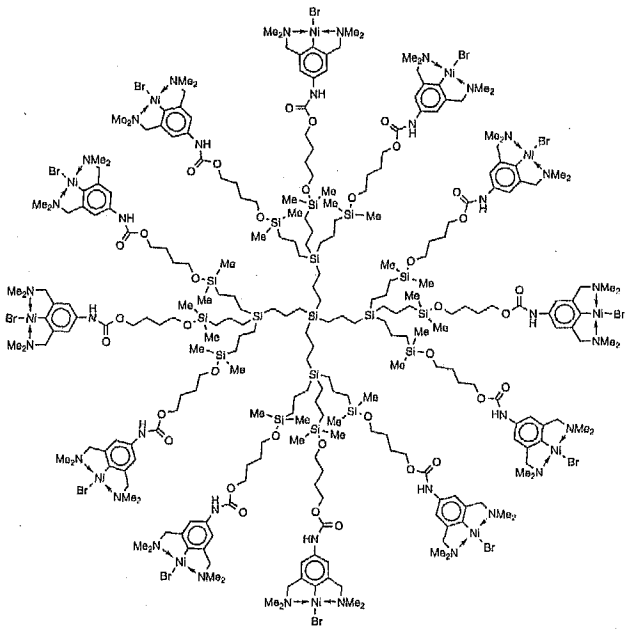
C_{ipso}-Ni 1.900(5) Å
N-Ni-N 162.21(19)°

The X-ray molecular structure of **25** reveals that this complex comprises two identical monocations $[(Ni(L^*)Cl]^+$ that have octahedrally coordinated d^7 Ni(III) centers and a single dianionic $[Ni^{II}Cl_4]^{2-}$ unit [35e]. The octahedral ligand sphere of the Ni(III) center in the cation $[(Ni(L^*)Cl]^+$ is best described as tetragonally compressed, with the meridional coordination comprising N_2,O_2-donative bonding from the two N atoms of the pyrollidine groups and two carbonyl O atoms of the ester groups of L*. The mutually *trans*-positioned apical sites are occupied by a Cl atom and the C atom of the Ni–C_{aryl} bond; i.e. the monoanionic organic ligand L* binds as a monoanionic O,N,C,N',O'-pentadentate system [35e].

Ligands formed from NCN by replacement of the *para* H with another substituent should form metal-complex derivatives with altered properties. To investigate the effect that such substituents have on the electronic properties of a metal center the Ni(II) complexes $[NiBr\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4\}]$ (R = NH_2, MeO, H, Cl, MeC(O)) were synthesized in our group [40b]. The electrochemical results show that electron-donating *para*-substituents increase the ease of oxidation from Ni(II) to Ni(III), and a direct correlation exists between ^{13}C NMR chemical shift data for the carbon atom bonded to nickel and appropriate Hammett parameters [40b].

At the interface between heterogeneous and homogeneous catalysis there is great need for the development of new materials that combine the advantages and/or minimize the disadvantages associated with each of these classes. In particular there is an interest in homogeneous catalysts with properties that allow their ready removal from a product-containing solution. One approach to such materials is to anchor homogeneous catalysts to soluble polymer supports. With the knowledge that it is relatively easy to functionalize the *para* position of the aromatic ring of the NCN ligand (vide supra) our group was able to synthesize a new type of grafted polysiloxane polymer in which a substituted NCN system is the terminal aryldiamine group that provides a pendant terdentate ligand environment for a catalytically active (organonickel) center [40a]. The novel strategy employed involves initial grafting of the aryl bromide $(C_6H_2(CH_2NMe_2)_2\text{-}1,3\text{-}Br\text{-}2\text{-}NH_2\text{-}5)$ into the side chain of poly(2-(chlorocarbonyl)ethyl)methylsiloxane followed by nickel incorporation through an oxidative addition reaction with $[Ni(COD)_2]$ [40a]. The resulting polymeric materials having immobilized organonickel(II) centers show good catalytic activity in the Kharasch addition reaction of polyhalogenated alkanes to alkenes, which is of the same order of magnitude as for the comparable model organonickel(II) complex $[Ni\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}NHC(O)Me\text{-}4\}Br]$ [40a].

One disadvantage encountered when anchoring homogeneous catalysts to polymers is the difficulty of accurately controlling the number and locations of these sites. For this reason we started to synthesize carbosilane dendrimers that are functionalized at their periphery with metal-containing catalytically active sites. Such a compound is the dendrimer **26**, which contains twelve active nickel(II) sites [48].

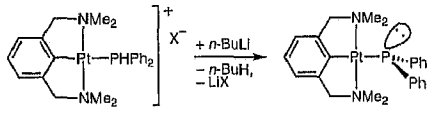


26

Attractive properties of this type of dendrimer are the regular and precise polymeric structure, the inertness of the carbosilane core, and the fact that all the Ni-containing catalytic sites are equivalent and well-defined. Two examples: the dendrimers G0-$\{SiMe_2\text{–}ArNiBr\}_4$ and

G1-{$SiMe_2$–ArNiBr}$_{12}$, **26**, show regiospecific catalytic activity for Kharasch addition of polyhalogenated alkanes to carbon-carbon double bonds [48]. It should be possible to remove nanoscale catalytic macromolecules of this type from solutions of products using ultra-filtration methods.

The chemistry of platinum and palladium NCN complexes has been a major topic in our group and this overview affords an opportunity to present some recent developments in this area. Reaction of diphenylphosphine with the ionic complexes [Pt(NCN)(H_2O)]X (X=BF_4, OTf) leads to substitution of the H_2O ligand to afford the ionic Pt(II) complexes [Pt(NCN)($PHPh_2$)]X, (X=BF_4, **27a**; X=OTf, **27B**) [10k]. Deprotonation of the $PHPh_2$ ligand of **27** with *n*-BuLi (eq 5) affords the neutral complex [Pt(NCN)PPh_2)], **28**, which is unprecedented in being the first mononuclear Pt(II) species containing a terminal phosphido ligand [10k]:



27a: X = BF_4
27b: X = OTf

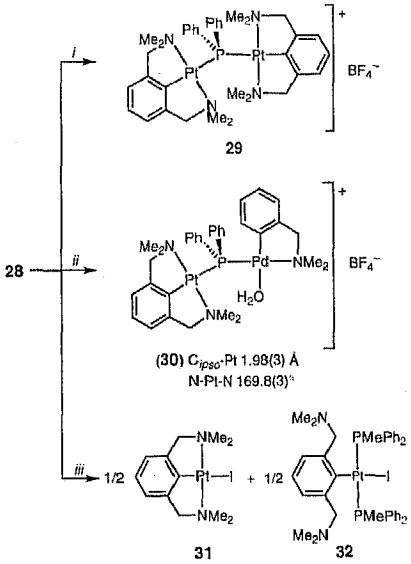
(**27b**) C_{ipso}-Pt ~ 1.98 Å
N-Pt-N ~ 160°

28 (5)

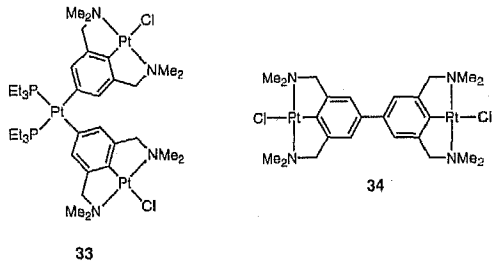
Complex **28** reacts with the complex cations of [Pt(NCN)-(H_2O)][BF_4] and [Pd{$C_6H_4CH_2NMe_2$-2}(N≡CMe)$_2$]-[BF_4] to afford the new ionic dinuclear phosphido-bridged complexes [{Pt(NCN)}$_2$(μ-PPh_2)] [BF_4], **29**, and [Pt(NCN)(μ-PPh_2)Pd($C_6H_4CH_2NMe_2$)(H_2O)][BF_4], **30**, respectively (Scheme 1). The reaction of MeI with **28** gives, rather than Pt(IV) oxidative addition products, the new Pt(II) *trans*-bis(methyldiphenylphosphine) complex [Pt{η^1-*C*-(NCN)}(I)($PMePh_2$)$_2$], **32**, and the known [Pt{η^3-*N,C,N'*-(NCN)}(I)], **31** [10k].

In another study it has been found that the new di-arylplatinum complex *cis*-[(PEt_3)$_2$Pt{C_6H_3(CH_2NMe_2)$_2$-3,5}$_2$], containing four free amine coordination sites, undergoes directed *ortho*-lithiation with *t*-BuLi in hexane. Subsequent transmetallation of this latter dilithio platinum complex with [$PtCl_2$(SEt_2)$_2$] gives a unique triplatinum species *cis*-[(PEt_3)$_2$Pt{C_6H_2(CH_2NMe_2)$_2$-3,5-(PtCl)-4}$_2$], **33**, which, with selective C–C bond formation, reductively eliminates the diplatinum complex [ClPt(bis-NCN)PtCl], **34** [49].

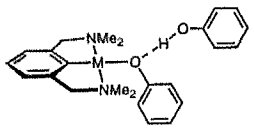
The new NCN arylmetal complexes [M(OPh)(NCN)] (M=Pd, Pt) with η^3-*N,C,N'*-bonded NCN were synthesized by reacting known [M(NCN)(H_2O)][BF_4] with sodium phenoxide [9c]. Both new complexes react with excess phenol to form the corresponding phenol adducts [M(OPh)(NCN)]·HOPh (M=Pd, **35a**; M=Pt, **35b**) containing an intramolecular O–H···O hydrogen bond [9c]. In a similar way the new monodentate catecholate complexes [M(OC_6H_4OH-2)(NCN)] (M=Pd, **36a**; M=Pt, **36b**) have been synthesized and they also contain an intramolecular O–H···O hydrogen bond [9c]. In solution the arylpalladium phenoxide complex **35a** undergoes fast exchange between phenoxide and associated phenol and this illustrates the large *trans* effect of the aryl ligand. In the corresponding platinum complex this exchange is slow on the ^{1}H NMR timescale. Similarly, intramolecular phenol/phenoxide exchange is fast on the ^{1}H NMR timescale in the Pd catecholate complex **36a** but slow in the Pt catecholate **36b** [9c].



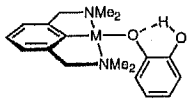
Scheme 1. – Formation of complexes **29-32** from complex **28**. Conditions: (*i*) [Pt(NCN)(H_2O)][BF_4], (*ii*) [Pd{$C_6H_4CH_2NMe_2$-2}-(N≡CMe)$_2$][BF_4], (*iii*) MeI.



The substitution-reaction behavior of the organometallic cation [Pt(NCN)(OH_2)]$^+$ has been studied with a series of nucleophiles (Cl^-, Br^-, I^-, N_3^-, NCS^-, thiourea, *N,N'*-dimethylthiourea, *N,N,N'N'*-tetramethylurea) as a function of nucleophile concentration ([Nu]), pH, temperature, and pressure [10l]. This complex affords pseudo-first-order rate constants, k_{obs}, for the complex-formation reaction given by $k_{obs}=k_1[Nu]+k_{-1}$; the k_{-1} term is due to the reverse aquation reaction and is

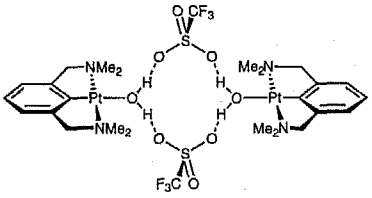


35a: M = Pd
35b: M = Pt
(35a) C_{ipso}-Pd 1.901(5) Å
O---O 2.567(6) Å
N-Pd-N 162.93(17)°



36a: M = Pd
36b: M = Pt

insignificant for stronger, S-donor nucleophiles. This complex cation has high substitution reactivity that can be ascribed to labilization, which arises from the σ-bonded carbon atom of the NCN ligand, in combination with backbonding to the in-plane aryl ligand that increases the electrophilic character of the Pt(II) center. The X-ray structure of the ionic complex $[Pt(NCN)(OH_2)]^+[OTf]^-$, **37** shows an aggregate of two complex cations and two triflate anions [101]. The structure contains two fully equivalent square-planar coordinated Pt(II) centers with an O-ligated neutral H_2O molecule *trans* to the Pt–C_{aryl} bond; the aggregate results from involvement of both H atoms of the two H_2O molecules in asymmetric hydrogen bonding to the oxygen atoms of the two triflate anions.

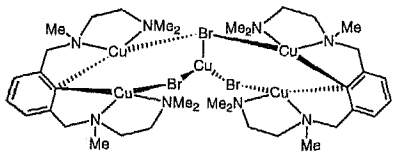


37
C_{ipso}-Pt 1.903(2) Å
N-Pt-N 164.95(9)°

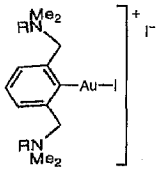
2.6. Group 11 (IB): Cu, Au

In recent years there have been no new publications concerning the use of NCN in copper chemistry, though it has been shown that treatment of $[Li_2(N'NCNN')Br]$, **2** (see *Section 1.2.1*), with two equivalents of CuBr yields the pentanuclear species $[Cu_5(N'NCNN')_2Br_3]$, **38** [37]. The molecular structure of this complex can best be described as two cationic organocopper moieties $[Cu_2(N'NCNN')]^+$ linked by a $[CuBr_3]^{2-}$ dianion [37, 50].

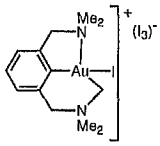
Dimeric $[Au^I(NCN)]_2$ reacts with both methyl iodide and ethyl iodide to give the unexpected heteroaurate(I) species $[Au(I)\{\eta^1\text{-}C\text{–}C_6H_3(CH_2NMe_2R)_2\text{-}2,6\}]I$ (R = Me, **39a**; R = Et, **39b**), which are zwitterionic complexes containing two quaternarized (non-coordinating) *ortho* amine substituents and an η^1-*C*-bonded aryl ligand system [25]. Reaction of $[Au(NCN)]_2$ with CH_2I_2 affords the zwitterionic Au(III) complex **39c**, which is formed in a sequence of reaction steps that probably involves



38
C_{ipso}-Cu ~ 2.0 Å
Cu-C_{ipso}-Cu ~ 73°



39a: R = Me
39b: R = Et
(39a) C_{ipso}-Au 2.047 Å
C_{ipso}-Au-I 172.9°

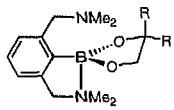


39c
C_{ipso}-Au 1.98 Å
C-Au 1.96 Å
C_{ipso}-Au-I 180.0°

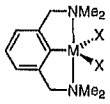
quaternarization of one *ortho*-(dimethylamino)methyl CH_2NMe_2 substituent followed by oxidative addition of the resulting NCH_2I group to the Au(I) center [25].

2.7. Group 13 (IIIA): B, Al, Ga, In, Tl

Toyota and co-workers have reported the synthesis of the NCN boronate complexes $[B(NCN)(OCR_2CH_2O)]$ (R = H, **40a**; Ph, **40b**) [26]. An X-ray molecular structure determination of **40b** indicates that the NCN ligand is η^2-*C,N*-coordinated to a tetrahedral boron atom; i.e. one *ortho*-CH_2NMe_2 substituent remains uncoordinated [26].

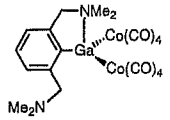


40a: R = H
40b: R = Ph
(40b) C_{ipso}-B 1.599(3) Å



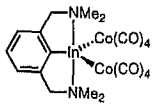
41a: M = Al, X = Cl
41b: M = Ga, X = Cl
41c: M = In, X = Cl
41d: M = Al, X = H
(41d) C_{ipso}-Al 1.949(5) Å
N-Al-N 157.8(2)°

In separate publications the syntheses of $[AlCl_2(NCN)]$, **41a** [12a], $[GaCl_2(NCN)]$, **41b** [12b], and $[InCl_2(NCN)]$, **41c** [12e], from the reaction of $[Li_2(NCN)_2]$ with the corresponding metal trichloride were described. Furthermore, Cowley and co-workers have reported the synthesis of $[AlH_2(NCN)]$, **41d**, not only from the reaction of $[Li_2(NCN)_2]$ with $AlH_2Cl{\cdot}NMe_3$ but also, interestingly, from the transmetallation reactions of **41a-c** with $LiAlH_4$ [12a]. Molecular structure determinations of the aluminium species **41a** and **41d** show both to be monomeric in the solid state [12a]; it is also relevant to note that the structure of the closely related complex $[InMeCl\{C_6H_3(CH_2NEt_2)_2\text{-}2,6\}]$ has been reported [12e].



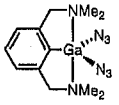
42

C_{ipso}-Ga 1.983(14) Å
Ga-Co ~ 2.57 Å
Co-Ga-Co 116.8(5)°
C_{ipso}-Ga-Co ~ 117°



43

C_{ipso}-In 2.158(6) Å
In-Co ~ 2.6 Å
N-In-N 143.1(2)°
Co-In-Co 118.6(1)°
C_{ipso}-In-Co ~ 120°



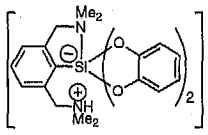
44

C_{ipso}-Ga 1.922(4) Å
Ga-N(azide) ~ 1.9 Å
N-Ga-N 158.7(1)°
C_{ipso}-Ga-N(azide) ~ 125°

Reaction of $[MCl_2(NCN)]$ (M = Ga, In) and $Na[Co(CO)_4]$ affords the heterotrimetallic derivatives $[M\{Co(CO)_4\}_2(NCN)]$ (M = Ga, **42**; M = In, **43**) [12d]. An X-ray diffraction study of **42** reveals that only one of the CH_2NMe_2 substituents is coordinated and as a consequence the Ga coordination sphere is approximately tetrahedral; the indium complex **43** has a distorted trigonal-bipyramidal geometry of the metal center with a planar $C_{ipso}InCo_2$ unit. The arylgallium diazide $[Ga(N_3)_2(NCN)]$, **44**, which has been prepared by a metathesis reaction of $[GaCl_2(NCN)]$, **41b**, with NaN_3 is stabilized by intramolecular coordination of the nitrogen donors of both CH_2NMe_2 substituents [12c].

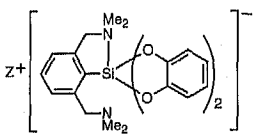
2.8. Group 14 (IVA): Si, Sn

There is continuing interest in the use of the NCN ligand in the stabilization of Si(IV) species. Corriu et al. have shown that the reaction of $[Si(OMe)_3(NCN)]$ with catechol in methanol yields the zwitterionic species $[Si(O_2C_6H_4\text{-}1,2)_2\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(CH_2NMe_2H)\text{-}6\}]$, **45** [27a]. With potassium hydride the N–H proton of **45** can be abstracted and $K[Si(O_2C_6H_4\text{-}1,2)_2(NCN)]$, **46a**, is formed [27a]. The potassium cation of **45a** can be replaced by the bis(triphenylphosphoranylidene)ammonium cation PNN (by reaction with (PNN)Cl) to form $(PNN)[Si(O_2C_6H_4\text{-}1,2)_2(NCN)]$, **46b**.



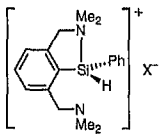
45

C_{ipso}-Si 1.943(4) Å

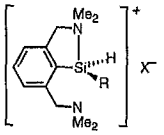


46a: Z = K
46b: Z = PNN

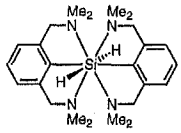
A novel and general route for the preparation of the species $[Si(\eta^2\text{-}C,N\text{-}NCN)(Ph)H]^+$, **47**, $[Si(\eta^3\text{-}N,C,N'\text{-}NCN)H_2]^+$, **48a**, and $[Si(\eta^3\text{-}N,C,N'\text{-}NCN)Me(H)]^+$, **48b** was also reported [13]. The ionic diorganosiliconium species **48b** is closely related to the tin species $[Sn^{IV}\text{-}(NCN)(Me)(Ph)]Br$, **52e**, (vide infra) which marked the start of our studies in NCN chemistry.



47a: X = I
47b: X = Br
47c: X = Cl
47d: X = BF_4
47e: X = OTf



48a: X = I, R = H
48b: X = CF_3SO_3, R = Me

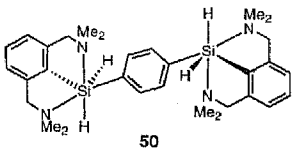


49

C_{ipso}-Si 1.901(5) Å
N-Si-N 116.7(1)°

The fluorosilicate species $[SiF_4(NCN)]^-$ [K, 18-crown-6]$^+$ has been obtained by a reaction between $[SiF_3(NCN)]$, KF, and 18-crown-6 [27b]. Reaction of mono(aryl)silane $[SiH_3(NCN)]$ with $[Li_2(NCN)_2]$ affords the diarylsilane complex $[SiH_2(NCN)_2]$, **49** [19a]. An X-ray molecular structure determination of **49** shows that both NCN ligands are primarily η^1-*C*-bonded but subsidiary *N*-donor coordination affords an overall geometry that can be described as a tetracapped tetrahedron, in which the Si atom is (4+4)-coordinated. ^1H NMR spectroscopy of **49** at room temperature shows the equivalence of the four NMe_2 groups and this result can be explained by dynamic coordination, i.e. the NMe_2 groups displace each other on the ^1H NMR timescale. Treatment of **49** with $Ph_3C^+BF_4^-$ or 0.5 equivalent of I_2 gives the monocationic silane species $[SiH(NCN)_2]^+X^-$ (X = BF_4, I), while reaction of **49** with 2 equivalents of HX affords the dicationic species $[Si(NCN)_2]^{2+}(X^-)_2$ [19a]. Reaction of the 1,4-disubstituted aryl compound $C_6H_4(Si(OMe)_3)_2$-1,4 with 1 equivalent of dimeric $[Li_2(NCN)_2]$ affords $[C_6H_4\{SiH_2(NCN)\}_2\text{-}1,4]$, **50**, a complex in which the aryl nucleus is now substituted with two $[SiH_2(NCN)]$ units [19b].

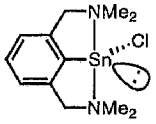
In previous studies the group of van Koten has shown that monomeric di- and tetravalent organotin complexes can be isolated by making use of the coordinating properties of potentially *C,N*-chelating ligands; the stabilizing factor in these tin complexes seems to be the formation of five-membered chelate rings. The reaction of $[Li_2(NCN)_2]$ with $SnCl_2$ in a 1:2 molar ratio affords the Sn(II)



50

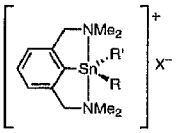
C_{ipso}-Si 1.884(2) Å
N-Si-N 117.4(1)°

complex [SnCl(NCN)], **51**, which can be converted to the mixed (aryl)alkyltin(II) species [SnR(NCN)] (R = 4-tolyl, neopentyl, neophyl) by reaction with the corresponding alkyllithium reagents [14a]. A molecular structure determination of [SnCl(NCN)] shows that this complex has a pseudo-trigonal-bipyramidal structure with an electron lone pair occupying one of the meridional positions [14a].



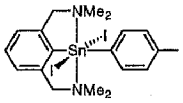
51

C_{ipso}-Sn 2.158(8) Å
N-Sn-N 142.0(4)°



52a: R = Me, R' 4-tolyl, X = I
52b: R = Me, R' neopentyl, X = I
52c: R = R' = Me, X = Br
52d: R = R' = Ph, X = Br
52e: R = Me, R' = Ph, X = Br

(**52e**) C_{ipso}-Sn 1.95 Å



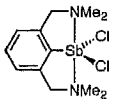
53

C_{ipso}-Sn 2.109(9) Å
N-Sn-N 150.7(3)°

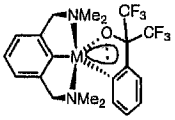
The ionic triorganotin(IV) iodide species [SnMeR(NCN)]I (R = 4-tolyl, **52a**; R = neopentyl, **52b**) were obtained from oxidative addition reactions of methyl iodide with the diorganotin(II) complexes [SnR(NCN)] [14a]. Reaction of the diorganotin dibromides [SnRR'Br_2] with [Li_2(NCN)$_2$] affords the corresponding ionic triorganotin bromides [SnRR'(NCN)]Br, **52c-e** [1]. When [Sn(4-tolyl)(NCN)] is reacted with 1 molar equivalent of I_2 the diorganotin(IV) complex [SnI_2(4-tolyl)(NCN)], **53**, is formed and its structure in the solid state has been determined by X-ray diffraction methods [14b]. As a result of intramolecular coordination of both nitrogen donors to the tin center, the geometry about tin in **53** is octahedral.

2.9. Group 15 (VA): Sb, Bi

The trigonal-bipyramidal antimony complex [$SbCl_2$(NCN)], **54**, in which the NCN ligand adopts an η^3-*N,C,N'*-coordination mode has been reported by the group of Cowley [15a].



54



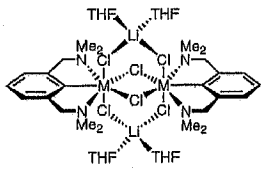
55a: M = Bi
55b: M = Sb

C_{ipso}-Bi 2.27(1) Å
C_{ipso}-Sb 2.167(3) Å
N-Bi-N 117.6(3)°
N-Sb-N 116.24(8)°

The synthesis of the Bi(III) and Sb(III) species [M{C_6H_4(CF_3)$_2$O)-2}(NCN)] (M = Bi, **55a**; M = Sb, **55b**) has been reported by Yamamoto et al. [20]. These complexes were characterized by X-ray molecular structure determinations and in both cases the NCN ligand is pseudo-facially η^3-*N,C,N'*-bonded to the metal. NMR studies of these two species showed that a fast configuration inversion of the metal center takes place in solution. The proposed mechanism for this inversion involves, rather than Bi–N or Sb–N dissociation, the formation of a transition state in which the two electron pairs of the nitrogen-donor atoms coordinate to a vacant *p*-type metal orbital so that a 3-center 4-electron bond is generated [20].

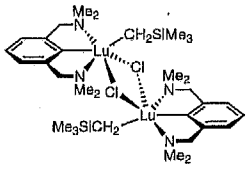
2.10. Lanthanides

We have used the NCN ligand in the preparation of coordinatively unsaturated lanthanide complexes that might be used to activate aromatic halides toward nucleophilic substitution. One very recent report arising from this study concerned the synthesis of [MCl_2(NCN)(μ-Cl)(μ-Li(THF)$_2$)]$_2$ (M = Lu, **56a**; M = Y, **56b**) [16].



56a: M = Lu
56b: M = Y

(**56a**) C_{ipso}-Lu 2.351(7) Å
N-Lu-N 135.8(2)°

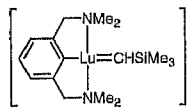


57

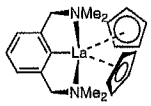
C_{ipso}-Lu 2.32(2) Å
N-Lu-N 123.1(6)°

Reaction of the lutetium complex **56a** with one molar equivalent of trimethylsilylmethyllithium (i.e. neosilyllithium) affords a 1:1 mixture of the dimeric mono(alkyl) complex [LuCl(NCN)(CH_2SiMe_3)], **57**, and the bis(alkyl) complex [Lu(NCN)(CH_2SiMe_3)$_2$] [16]. In

contrast, reaction of the yttrium complex **56b** with neosilyllithium leads to instantaneous decomposition of the mixture, with formation of the parent arenediamine, NCN-H, and tetramethylsilane (TMS) [16]. The five-coordinate, coordinatively unsaturated bis(alkyl) complex $[Lu(NCN)(CH_2SiMe_3)_2]$ is surprisingly stable in benzene. However, it decomposes significantly within a few days, both in the pure state (as an oil) and when dissolved in hexane, with liberation of TMS and NCN-H. The proposed decomposition route involves α-hydrogen transfer from one neosilyl group to the other, and subsequent loss of TMS. This implies formation of an unstable intermediate carbene complex $[Lu(=CHSiMe_3)(NCN)]$, **58**, which however has neither been isolated nor detected.



58



59

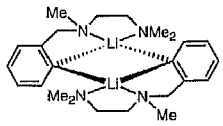
C_{ipso}-La 2.548(3) Å
N-La-N 121.98(9)°

Mono(alkyl) complex **57** and bis(alkyl) complex $[Lu(NCN)(CH_2SiMe_3)_2]$ illustrate the potential of the NCN ligand for stabilizing salt- and solvent-free lanthanide alkyl complexes. The latter are difficult to obtain using the "traditional" cyclopentadienyl ligand and are especially of interest with respect to their reactivity towards simple alkenes.

Lanthanide aryl complexes containing potentially intramolecularly coordinating substituents can be seen as useful precursors for the immobilization of lanthanide ions in zeolites, provided that they are small enough to enter the zeolite microporous structure. For this reason our attention turned to complexes in which one or two cyclopentadienyl ligands in Cp_3M complexes are replaced by aryldiamine groups [21]. Reaction of $[Cp_3La{\cdot}THF]$ with one molar equivalent of $[Li_2(NCN)_2]$ affords $[LaCp_2(NCN)]$, **59** [21]. A molecular structure determination of this complex shows a central lanthanum ion surrounded by two η^5-coordinated cyclopentadienyl ligands and a pseudofacially, η^3-*N,C,N'*-bonded aryldiamine ligand. Unfortunately the NCN ligand in **59** is more susceptible to attack by proton donors such as alcohols than the cyclopentadienyl ligand. It may be that prior protonation of an amino substituent assists the alcoholysis of the highly polar La–C_{ipso} bond [21].

3. Organometallic chemistry of the CNN ligand

Many of the organometallic NCN complexes described in recent years were obtained by transmetallation reactions of pure $[Li_2(NCN)_2]$ with the corresponding metal salts, whereas earlier studies often employed this species generated in situ, together with LiBr from $C_6H_3Br(CH_2NMe_2)_2$-2,6 (NCN–Br) and Li metal in Et_2O. Since we have found that the success of many transmetallation reactions (particularly in copper chemistry) depends on whether or not the organolithium reagent employed is free from alkyl halides and lithium halides, we have also studied in detail the synthesis and structure of pure $[Li_2(CNN)_2]$, **60** [42a].



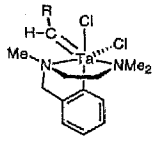
60

C_{ipso}-Li ~ 2.17 Å
Li-C_{ipso}-Li ~ 111°

We have prepared pure aryllithium complex **60** by reaction of the *ortho*-diamine aryl bromide $BrC_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2 with *n*-BuLi in hexane. This complex has been shown by cryoscopy to exist as a dimer in benzene solution. Its solid state structure as determined by X-ray crystallographic methods was found to be dimeric. In this structure each lithium atom has a distorted tetrahedral geometry afforded by ligation of two nitrogens atoms of a single *ortho* substituent and the two C_{ipso} carbons of the bridging aryl rings. Each C_{ipso} atom is bonded to two lithium atoms in a 3-center 2-electron interaction with characteristic acute Li–C–Li angles of 66.3(4) and 66.6(5)°, and a Li···Li distance of 2.444(15) Å. ^1H and ^{13}C NMR spectroscopic data of **60** in benzene-d_6 are consistent with both nitrogen-donor atoms of one ligand being coordinated to the same lithium center and the data furthermore reveal that each dimeric molecule, as in the solid state, is one of two enantiomeric pairs in which the two central nitrogen atoms of the *ortho*-diamine substituents both have the same absolute configuration [42a].

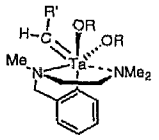
Based on the success we had experienced in preparing and characterizing stable tantalum(V) alkylidene complexes that contain the NCN ligand (*Section 1.2.2*), we wondered whether it would be possible to prepare analogous complexes containing CNN and, if so, what the effect of this monoanionic aryldiamine ligand would be on the reactivity of the alkylidene functionality. We have been able to prepare the dichloro complex $[TaCl_2(CNN)(=CH\text{–}t\text{-Bu})]$, **61**, and dialkoxide

complexes [Ta(CNN)(=CHR)(O–*t*-Bu)$_2$] (R = *t*-Bu, **62a**; R = CMe$_2$Ph, **62b**), by transmetallation of the aryllithium complex **60** with (TaCl$_3$(=CH–*t*-Bu)(THF)$_2$] and [TaCl(=CHR)(O–*t*-Bu)$_2$(PMe$_3$)], respectively [42f].

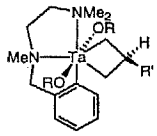


61: R = *t*-Bu

C_{ipso}-Ta	2.201(11) Å
Ta-C_α	1.849(10) Å
C_{ipso}-Ta-N(outer)	88.8(4)°
Ta-C_α-C_β	167.0(9)°



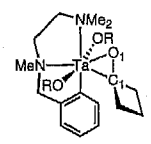
62a: R' = *t*-Bu, R = *t*-Bu
62b: R' = CMe$_2$Ph, R = *t*-H



63a: R' = H, R = *t*-Bu
63b: R' = Me, R = *t*-Bu
63c: R' = Ph, R = *t*-Bu

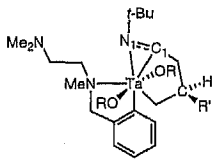
C_{ipso}-Ta	~ 2.2 Å
Ta---C_β	~ 2.8 Å
C_{ipso}-Ta-N(outer)	~ 143°
C_α-Ta-C_α	~ 60°

^{1}H and ^{13}C NMR spectroscopy of complex **61** in solution indicates the presence of three species, which are most probably isomers that arise from different mutual positions around the metal center of the η^3-*C,N,N'*-bonded aryldiamine ligand, the two chlorides, and the alkylidene functionality. In the X-ray crystal structure of the major isomer of complex **61** the metal center has facially-bonded CNN, two *cis*-positioned chlorides, and the neopentylidene group *trans* to the *N*Me$_2$ nitrogen-donor atom [42f]. Unfortunately complex **61** shows no reactivity with ethene nor does it show ring-opening metathesis polymerization (ROMP) reactivity with norbornene. In contrast, reaction of the dialkoxide species **62a** and **62b** in pentane with ethene at 298 K affords the tantalacyclobutane complex [Ta{(CH$_2$)$_3$-1,3}(CNN)(O–*t*-Bu)$_2$], **63a**. An X-ray structure of **63a** shows it to be a heptacoordinate pentagonal-bipyramidal tantalum species in which two mutually *trans* alkoxide groups are in the apical positions; the meridional ligation comprises η^3-*C,N,N'*-bonding of the CNN ligand and σ-bonding of two carbon atoms of the metallacycle [42f]. Reaction of **62b** in hexane at 69 °C with ethene gives a mixture of the new tantalum alkene complex [Ta(CNN)(O–*t*-Bu)$_2$(H$_2$C=CH$_2$)] and **63a** in a 5:2 ratio [42f]. The dialkoxide complexes **62** and complex **63a** all initiate ROMP with strained cyclic olefins; dicyclopentadiene produces cross-linked polymers, whereas norbornene produces polycyclopentamers with approximately 90% *trans*-vinylene bonds. From the reaction of the unsubstituted tantalacyclobutane complex **63a** with propene and styrene we obtained the substituted tantalacyclobutane complexes [Ta{CH$_2$CH(Me)CH$_2$-1,3}(CNN)(O–*t*-Bu)$_2$], **63b**, and [Ta{CH$_2$CH(Ph)CH$_2$-1,3}(CNN)(O–*t*-Bu)$_2$], **63c**, respectively [42g]. The X-ray molecular structures of **63b** and **63c** show them to be seven-coordinate species with overall structures similar to that of the unsubstituted tantalacyclobutane complex **63a**. The substituent of the metallacycle in **63b** and **63c** is positioned on the β carbon. Reaction of **63a** with carbon monoxide yields the oxytantalacyclopropane complex [Ta{C(O)((CH$_2$)$_3$-1,3)}(CNN)(O–*t*-Bu)$_2$], **64**, whose X-ray molecular structure reveals a seven-coordinate metal center that has a pentagonal-bipyramidal geometry, similar to that found for complexes **63a-c**; complex **64** can be described as a cyclobutanone adduct with the C=O function bonded side-on to the metal center [42g]. Although complexes **63b** and **63c** also slowly react with CO, no stable product could be isolated. Reaction of the tantalacyclobutane complexes **63a-c** with one equivalent of *t*-BuNC affords the 1:1 insertion products [Ta{C(=N–*t*-Bu)CH$_2$CH(R)CH$_2$-1,4}(CNN)(O–*t*-Bu)$_2$] (R = H, **65a**; R = Me, **65b**; R = Ph, **65c**), respectively. ^{1}H and ^{13}C NMR spectroscopy of complexes **65b** and **65c** indicate that in solution each complex is present as two isomers. The X-ray molecular structure of **65c** shows the presence of two adjacent fused tantalacyclic rings of different sizes, the smaller three-membered ring contains the metal center and both the nitrogen and the carbon atom of an η^2-iminoacyl fragment, while the larger five-membered ring consists of the metal center and four carbon atoms. A particular feature in complexes **65a-c** is that the CNN ligand is η^2-*C,N*-bonded by the aryl C_{ipso} carbon and the *N*(Me) nitrogen donor [42g].



64: R = *t*-Bu

C_{ipso}-Ta	2.261(15) Å
C_1-O_1	1.401(17) Å
Ta-O_1	1.971(11) Å
C_{ipso}-Ta-N(outer)	147.5(10)°
C_1-Ta-O_1	39.6(5)°

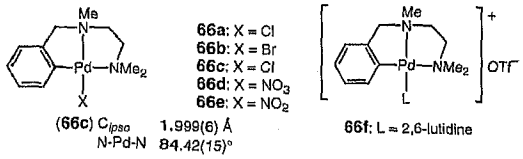


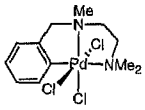
65a: R = *t*-Bu, R' = H
65b: R = *t*-Bu, R' = Me
65c: R = *t*-Bu, R' = Ph

(**65c**) C_{ipso}-Ta	2.246(5) Å
Ta-N_1	2.442(4) Å
C_1-Ta-N_1	31.64(16)°

During our work on the reactivity of organopalladium compounds towards inorganic peroxo species like [MoO(O$_2$)$_2$·HMPT·H$_2$O] (HMPT = hexamethylphosphoric triamide) we have prepared several Pd(II) complexes containing η^3-*C,N,N'*-bonded CNN and related aryldiamine ligands [42b, c]. For example, the complexes [PdX(CNN)] (X = Cl, **66a**; Br, **66b**; I, **66c**) were prepared by a direct palladation reaction of the arene C$_6$H$_5$(CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$) with [Pd(OAc)$_2$],

followed by anion metathesis with an appropriate alkali metal salt [42d].

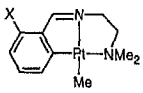




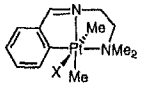
67

These terdentate-bound CNN organopalladium compounds are thermally stable solids (dec. temp. > 200 °C), which are not air-sensitive [42d]. From **66a-c** standard halide substitution reactions with silver salts can be used for the preparation of the analogous nitrate (**66d**) or nitrido (**66e**) complexes and for the synthesis of cationic derivatives like the lutidine complex **66f**. The *o*-methoxy-substituted CNN derivative [PdCl{$C_6H_3(CH_2N(Me)CH_2CH_2NMe_2)$-2-OMe-3}] was prepared by treatment of the coordination adduct [$PdCl_2${$MeOC_6H_4(CH_2NMeCH_2CH_2NMe_2)$-2}] (obtained by direct methoxylation of **66d** using [$MoO(O_2)_2 \cdot HMPT \cdot H_2O$] followed by treatment with LiCl) with 2 equivalents of $AgNO_3$ and subsequent heating in methanol in the presence of sodium acetate [42d]. Another method for the synthesis of the CNN palladium halides involves oxidative addition of *ortho*-halogenated organic compounds $XC_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2 to [$Pd(dba)_2$] (dba = dibenzylidene acetone) [42d]. Oxidative addition of Cl_2 to chloride complex **66a** results in the octahedral Pd(IV) complex [$PdCl_3$(CNN)], **67**, which is reasonably thermally stable in solution and which was identified by means of NMR spectroscopy at room temperature [42d]. A molecular structure determination of [PdI(CNN)], **66c**, shows the CNN ligand to be meridionally η^3-*C,N,N'*-bonded to the metal center [42d].

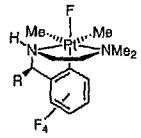
In related work Puddephatt and co-workers have reported a series of complexes [$PtMe_2${$ArCH{=}NCH_2CH_2NMe_2$}] that contain arylimines, which like the CNN ligand provide terdentate η^3-*C,N,N'* coordination. When Ar is 2-BrC_6H_4, 2-ClC_6H_4, or 2-IC_6H_4 these complexes undergo oxidative addition of the aryl-halogen bond to afford Pt(IV) species, **69a-c**, but when the Ar group is C_6H_4F and C_6H_5 they undergo orthometallation to afford complexes **68a** and **68b**, respectively. An oxidative addition reaction also occurs in the case where Ar is C_6F_5 and this affords [$Pt^{IV}(F)Me_2${$C_6F_4(CH{=}NCH_2CH_2NMe_2)$-2}], which adds acetone across its imine bond, yielding complex **70** containing a facial η^3-*C,N,N'*-coordinating ligand that has a chiral benzylic carbon center, i.e. an ArC*(H)(R)N– unit [44]. Complex **70** has been characterized by an X-ray crystallographic study, which shows that it exists as hydrogen-bonded N–H···F–Pt dimers in the solid state [44c].



68a: X = F
68b: X = H



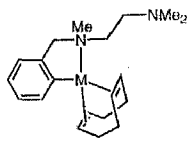
69a: X = Br
69b: X = Cl
69c: X = I



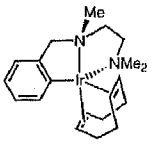
70: R = CH_2COMe,
C_{ipso}-Pt 1.978(9) Å

In the period covered by this review there has also been a number of reports employing the unsubstituted CNN ligand with d^8 metal centers. For example transmetallation reactions of [$Li_2(CNN)_2$] with dimeric [$MCl(COD)]_2$ (M = Rh, Ir) and [$PtCl_2(SEt_2)_2$] yield the complexes [M(CNN)(COD)] (M = Rh, **71a**; M = Ir, **71b**) and [PtCl(CNN)], **72**, respectively [42e]. In solution these three complexes have square-planar structures with CNN coordinated as an η^2–*C,N*-bidentate in **71a** and **71b** and as an η^3-*C,N,N'*-terdentate in **72**. However, the solid state structure of **71b** shows it to be a square-pyramidal species with a facial η^3-*C,N,N'*-terdentate coordination mode of the CNN ligand [19e]. The neutral monodentate ligands CO and PPh_3 replace the bidentate COD ligand in **71a** and **71b** to afford complexes that in solution are fluxional on the NMR timescale and in which the CNN ligand is either bidentate or terdentate bonded to the metal [42e].

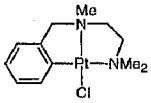
Before considering the tungsten chemistry of CNN it is worthwhile mentioning a small number of studies in which other *C,N,N'*-bonding ligands have been used in this area. For example Richmond and co-workers have reported that the bis(aryldiimine) compounds **73a-c** can undergo aryl carbon-halogen bond cleavage with [$W(CO)_3(EtCN)_3$] to afford seven-coordinate tungsten(II) complexes **74a-c**, respectively, in which terdentate bis(chelate) *C,N,N'*-coordination is present [43a-c].



In solution:
71a: M = Rh
71b: M = Ir



71b in the solid state:
C_{ipso}-Ir 2.048(9) Å
C_{ipso}-Ir-N(outer) 77.3(3)°



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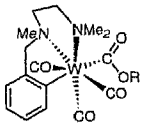
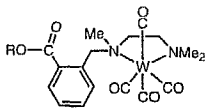
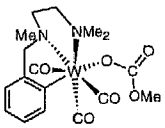


76a: R = Me
76b: R = C_6H_4-4-Me
76c: R = $CH_2C_6H_4$-4-Me



77a: R = Me
77b: R = C_6H_4-4-Me
77c: R = $CH_2C_6H_4$-4-Me



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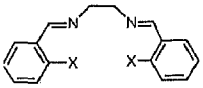
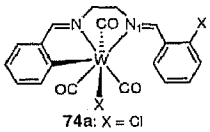


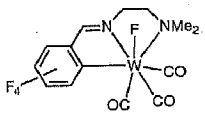
73a: X = Cl
73b: X = Br
73c: X = I



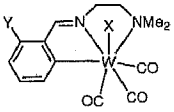
74a: X = Cl
74b: X = Br
74c: X = I

(**74b**) C_{ipso}-W 2.219(16) Å
C_{ipso}-W-N_1 128.2(6)°

A similar example is provided by the chelate-assisted insertion of tungsten into an *ortho*-C–X (X = F, Cl) bond of an unsymmetrical Schiff base compound; the reaction proceeds readily to afford the tungsten(II) complexes **75a-d** [43d-f].



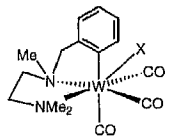
75a



75b: X = F, Y = H
75c: X = F, Y = F
75d: X = Cl, Y = F

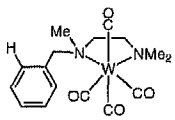
In the area of CNN chemistry it has been found that the tungsten(II) alkoxide and aryloxide complexes $[W(OR)(CNN)(CO)_3]$ (R = Me, C_6H_4Me-4, $CH_2C_6H_4Me$-4) can be synthesized by a reaction of $[WBr(CNN)(CO)_3]$ with silver triflate and subsequent reaction of the formed $[W(OTf)(CNN)(CO)_3]$ with the corresponding sodium alkoxide or aryloxide salt [43g]. Carbonyl insertion into a W–O bond in these tungsten(II) alkoxides and aryloxides results in the generation of alkoxycarbonyl and aryloxycarbonyl species **76a-c**, which undergo a reductive elimination reaction whereby a new C_{keto}–C_{aryl} bond is formed and the resulting complexes **77a-c** contain a *N,N'*-chelating system [43g].

When carbon dioxide is used, insertion into the W–OMe alkoxide bond generates an η^1-carbonate ligand that retains its coordination to the metal center to form a CNN complex $[W(O_2COMe)(CNN)(CO)_3]$, **78** [20g]. A two-electron reduction of the tungsten halides $[WX(CNN)(CO)_3]$ with either Na/Hg amalgam or potassium naphthalide affords the W(0) anion $[W(CNN)(CO)_3]^-$ [43h]. Reaction of this anion with Ph_3SnCl affords the air-stable triphenyltin adduct $[W^{II}(CNN)(CO)_3(SnPh_3)]$, **79a** [43h]. The related complexes $[WX(CNN)(CO)_3]$ (X = I, **79b**; H, **79c**) are obtained from the reaction of $K[W(CNN)(CO)_3]$ with I_2 and H^+, respectively.



79a: X = $SnPh_3$
79b: X = I
79c: X = H

(**79a**) C_{ipso}-W 2.20(1) Å
C_{ipso}-W-N(outer) 85.2(3)°



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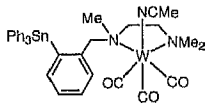
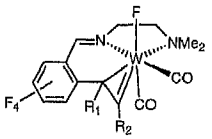


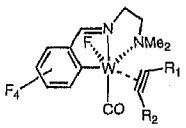
81

With CO the tungsten hydride complex **79c** is converted to the W(0) complex **80**, which contains protonated CNN, $C_6H_5CH_2N(Me)CH_2CH_2NMe_2$, functioning as a *N,N'*-chelate. The tungsten(0) complex $[W(CO)_3(EtCN)_3]$ undergoes an oxidative addition reaction with the Sn(IV) complex $[SnPh_3(CNN)]$ whereby the adduct complex $[W(CNN)(CO)_3SnPh_3]$, **79a**, results. The tungsten(II)

center in the latter complex can be reduced in reactions with CO, pyridine, and MeCN to form the tungsten(0) species $[W(CO)_6]$, $[W(CO)_3(py)_3]$, and $[W(CO)_3(MeCN)_3]$, respectively, together with $[Ph_3Sn(CNN)]$. In the case of the reaction of **79a** with MeCN a dinuclear species **81** is formed in which CNN is η^1-*C*-bonded to Sn and η^2-*N,N'*-chelated to W. The tungsten(II) Schiff base complex **75a**, which has a tetrafluoroaryl system involved in the *C,N,N'*-chelate bonding, has an interesting chemistry with symmetrically disubstituted alkynes RC≡CR. Reaction with electron-poor PhC≡CPh and $F_3CC{\equiv}CCF_3$ under mild conditions leads to formation of the η^2-vinyl complexes **82a** and **82b**, respectively, as a result of migratory insertion into the C_{ipso}–W bond [43i, j]. For electron-rich alkynes a competitive reaction that affords the four-electron-donor alkyne complexes **83a** and **83b** is favored. No evidence for interconversion of alkyne donor complexes of this type and corresponding η^2-vinyl complexes (analogous to **82**) was found even in the presence of carbon monoxide [43i].



82a: $R_1 = R_2 = CF_3$
82b: $R_1 = R_2 = Ph$
(**82b**) C_α-C_α 1.448(7) Å
C_α-W-C_α 40.4(2)°



83a: $R_1 = R_2 = CF_3$
83b: $R_1 = R_2 = Ph$

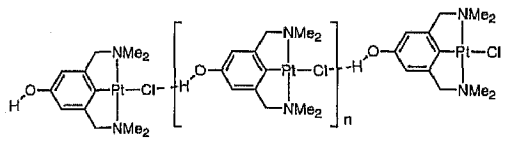
4. Outlook

The aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, NCN, has found widespread use for the synthesis of arylmetal complexes. Whereas it was initially designed for planar η^3-*N,C,N'*-coordination, and as such has been frequently encountered in our chemistry, we and others now have given ample demonstration that the NCN ligand is extremely versatile in its coordination behavior. This includes η^1-*C* 2-electron and η^2-*N,C* 4-electron bonding modes, as well as facial and meridional η^3-*N,C,N'* 6-electron terdentate chelation. Furthermore, both 6-electron and 8-electron donation have been established in cases where (aryl)C_{ipso} is bridging two similar (e.g. two Li or Cu atoms) or two different (e.g. Ta and Zn) Lewis acidic metal atoms.

Through the combination of an anionic sp^2-hybridized C-donor atom and two neutral amine N-donor atoms, which have exclusively σ-donating properties, the metal center in NCN-metal complexes becomes more susceptible to electrophilic attack, in particular when the attacking species has also π-accepting properties. For η^3-*N,C,N'*-terdentate binding in square-planar and octahedral coordination complexes the aryl plane of the NCN ligand coincides with the coordination plane of the d^8 or d^6 metal center; in contrast similar nonchelated aryl systems with these metal ions would (for steric reasons) normally have the aryl ring twisted by 90° out of the coordination plane. Accordingly in NCN complexes overlap between metal orbitals and suitable arene π orbitals is possible and this is a special feature of the NCN ligand. One example of this effect has been nicely demonstrated by *para*-substituted complexes derived from [NiBr(NCN)], i.e. $[NiBr\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4\}]$ (R = NH_2, MeO, H, Cl, MeC(O)) (*Section 2.5*). Substitution of the *para* position of the arene ring with substituents with different electron-withdrawing or electron-releasing properties allows variation of the redox potential of the metal as well as of the catalytic activity of these complexes [40b].

The electron-donating character of the *N,C,N'*-donor sites in NCN seems particularly suited for the stabilization of unusual species that may have the metal center in its higher oxidation states. Unique examples of this latter feature are the arylnickel(III) species $[NiX_2(NCN)]$ (X = Cl, Br, I, NO_3, and NO_2) (see *Section 2.5*) [8f], easily formed as a result of the low Ni(II)/Ni(III) redox potential. The $[Pt(I)(NCN)(\eta^1\text{-}I_2)]$ complex, which contains an end-on coordinated I_2 molecule, is an intermediate in the oxidative addition reaction of I_2 to a Pt(II) center and this illustrates the potential of NCN to stabilize reaction intermediates [10a-c].

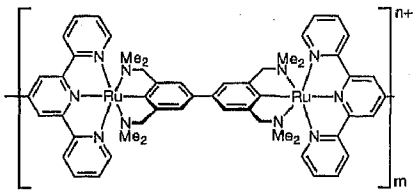
Presently our research on NCN chemistry is concentrated on exploring the use of the NCN ligand for the synthesis of new materials, in particular of organometallic polymers with special electron-conducting or photophysical (e.g. nonlinear optical) properties. A recent example is $[PtCl\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}OH\text{-}4\}]$, **84**, which, as a result of the presence in the molecule of acceptor (Cl) and donor (OH) ends, self-assembles in the solid state to infinite chains (molecular wires) by noncovalent hydrogen bonding [51a]; the related system $[PtCl\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}(C{\equiv}CH)\text{-}4\}]$ behaves similarly [51b].



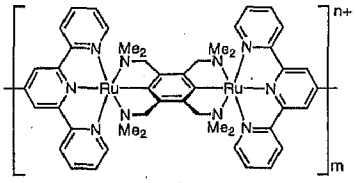
84

Another approach to "molecular wires" is based on the use of either a 4,4'-dimetallobiphenylenediyl unit (as

found in $[\{(terpy)Ru\}_2(bis\text{-}NCN)]^{n+}$, **22** [39b, c], and the diplatinum(II) complex **34** [49]) or of the 1,4-phenylenediyl unit (as recently found in, for example, $[\{ClPd\}_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ [52]); in combination with ligands that can link such units by directed self-assembly one can anticipate the formation of linear (potentially conducting) polymeric organometallic species such as **85** and **86**.



85

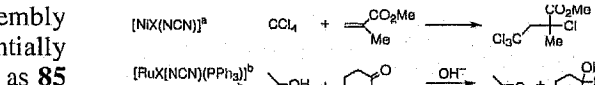
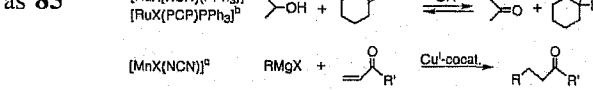
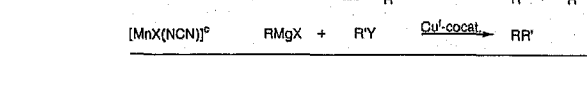


86

Another direction in which we are further developing our chemistry is the design and use of NCN-metal complexes in homogeneous catalysis. Presently known examples employing Ni(II) [8c, 35a, d, e], Ru(II) [53], and Mn(II) [54] species in this area can be found in Table I. Striking features are the high reactivity and selectivity of the catalytic species, as well as the stability of the σ-*C*-metal bond under the catalytic conditions employed. Moreover, the fact that this σ-bond is so stable is also an advantage of NCN-metal catalysts compared to other catalysts that contain neutral terdentate ligands. For the latter a common deactivation process is leaching of the metal from the catalyst or catalyst dimerization but these are high energy processes in the case of NCN-metal complexes. This is one of the reasons that our organometallic dendrimer catalyst (see *Section 2.5*, complex **26** [48]) can be employed successfully.

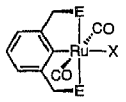
However, there is one process, which so far seems unique to NCN-metal complexes, which can lead to catalyst deactivation. This is the intramolecular rearrangement process shown in eq 2 (*Section 2.2*) for the tantalum(V) complex $[TaCl(=CH\text{–}t\text{-}Bu)(O\text{–}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, **10a**, and that was reported earlier in the literature for the NCN iridium(I) complex $[Ir(\eta^2\text{-}N,C\text{-}NCN)(COD)]$ [24a]. We have found that a similar process can also occur in the case of the ruthenium(II) complexes $[Ru(NCN)(Cp)PPh_3]$ and $[RuCl(NCN)\{\eta^6\text{-}(MeC_6H_4\text{-}4\text{-}CH(Me)_2)\}]$, both of which have been the subject of X-ray crystallographic studies [55]. This intramolecular

Table I. – Examples of NCN-metal complexes used as homogeneous catalysts [56].

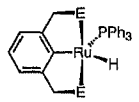
Complex	Process	Catalyst / Substrate molar ratio
[NiX(NCN)][a]	CCl_4 + 	7 / 1000
[RuX(NCN)(PPh$_3$)][b] [RuX(PCP)PPh$_3$][b]		1 / 10000 1 / 30000
[MnX(NCN)][c]	RMgX + 	3 / 100
[MnX(NCN)][c]	RMgX + R'Y $\xrightarrow{Cu^I\text{-cocat.}}$ RR'	3 / 100

ligand rearrangement was one of the reasons that prompted us to explore complexes of other monoanionic terdentate ligand systems such as the *C,N,N'*-"pincer" system CNN and the *P,C,P'*-chelating aryldiphosphine system $\{C_6H_3(CH_2PPh_2)\text{-}2,6\}^-$ (PCP).

It is particular to ruthenium(II) chemistry that the η^3-facial and η^3-meridional binding of the NCN and PCP ligands to the metal is operative and in such species the aryldiamine and aryldiphosphine "pincer" systems can have binding properties comparable to the commonly used monoanionic ligands $C_5H_5^-$ and $C_5Me_5^-$ (Cp and Cp*, respectively). In fact we have found that interesting similarities exist between related NCN- and PCP-metal complexes. For example, the 16-electron complexes $[RuCl(NCN)(PPh_3)]$, **18a** [5], and $[RuCl(PCP)(PPh_3)]$ [53] are isostructural. An interesting parallel with ruthenium Cp chemistry is that the latter reacts with CO and $NaBH_4$ to give complexes **87** and **88**, respectively, which both have their counterparts in Cp chemistry.



87a: E = NMe_2, X = Cl
87b: E = NMe_2, X = I
87c: E = PPh_2, X = Cl
87d: E = PPh_2, X = I



88a: E = NMe_2
88b: E = PPh_2

Finally, it is interesting to note that whereas both $[RuCl(NCN)(PPh_3)]$ and $[RuCl(PCP)(PPh_3)]$ are excellent hydrogen-transfer catalysts it is the PCP system that is the most active [53b]. In summary it can be concluded that new directions in organometallic chemistry have been opened with the use of the terdentate aryldiamine ligand NCN and of the related aryldiphosphine ligand PCP and that these "pincer" systems provide access to new homogeneous catalysts and organometallic materials as well as to exciting coordination chemistry of the species themselves.

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