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### Stable, Two-Coordinate, Open Shell ( $d^0-d^9$ ) Transition Metal Complexes

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# Stable, Two-Coordinate, Open Shell ( $d^0-d^9$ ) Transition Metal Complexes

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Well characterized, stable, two-coordinate, open shell transition metal complexes are currently very rare species. The small number of known examples are limited to the first row metals  $Cr \rightarrow Ni$  and the majority are derivatives of amide or modified amide ligands. A characteristic feature of the compounds is the small number of electrons in their valence shells, as low as eight in the case of the Cr complexes. The compounds are very reactive toward protic reagents and nucleophiles. However, this and many other aspects of their chemistry have not been well developed. Current data available are limited to structural (X-ray and electron diffraction) and some spectroscopic and magnetic studies.

**Key Words:** *two-coordination, three-coordination, steric crowding, metal–nitrogen bonds, silylamides, borylamides, metal-amides, metal-alkoxides*

## INTRODUCTION

The coordination number two continues to remain one of the least known for open shell ( $d^0-d^9$ ) transition metal compounds. In fact, until 1984 when the structure of the  $[NiO_2]^{2-}$  ion appeared,<sup>1</sup> there were no X-ray structural characterizations of compounds in this class. Traditionally, low coordinate complexes have received much

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less attention than the more common, higher coordination numbers of four to eight. For example, the coordination numbers two and three received little consideration in a recent, comprehensive treatise on coordination chemistry.<sup>2</sup> Most current textbooks also dismiss two- and three-coordination in a few sentences. These omissions seem surprising in view of the fact that three-coordination has been the subject of a number of reviews<sup>3,4</sup> and closed shell ( $d^{10}$ ) two-coordinate complexes have been known for a long time with metals such as Pt(0), Cu(I), Ag(I), Au(I) and Hg(II). In addition, many transition metal dihalides wherein the metal is two coordinate have been studied at high temperatures in the gas phase. Currently, there is a substantial amount of information available for these species involving electron diffraction,<sup>5</sup> spectroscopic,<sup>6</sup> and theoretical data.<sup>7</sup> It is, however, true to say that the number of open shell transition metal compounds that are two-coordinate at, or near, ambient temperature is quite small. Currently, about fifteen such complexes are known and these involve the metals Cr  $\rightarrow$  Ni. The purpose of this brief review is to summarize the available information on the title compounds and to suggest possible future developments in the area.

## THE DEVELOPMENT OF BULKY, PREDOMINANTLY $\sigma$ -BONDING, UNINEGATIVE LIGANDS

A common theme in the synthesis of low coordination numbers throughout the periodic table is the use of bulky ligands to ensure stability. Other factors such as electronic and bonding consideration also play an important role as illustrated by the ionic species  $[\text{NiO}_2]^{2-}$ .<sup>1</sup> As far as low coordination numbers are concerned, however, the steric theme has received the most attention. The steric approach uses crowding ligands to prevent further ligand coordination and/or higher coordination numbers by association through ligand bridging. In effect, the coordination number of the metal may be controlled by size of the ligand. In the 1950's it was shown that the degree of association of metal alkoxides,  $\{\text{M}(\text{OR})_x\}_n$ ,<sup>8</sup> could be controlled by altering the size of the alkyl substituent. However, due to their greater steric versatility it was the amide ( $-\text{NR}_2$ ) ligands which first came into prominence in the stabiliza-

tion of low coordination numbers. Two early papers<sup>9,10</sup> demonstrated that it was possible to use the bis(trimethylsilyl)amido group,  $-\text{N}(\text{SiMe}_3)_2$ , to synthesize a series of stable low coordinate complexes of formulae  $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_3$ ,<sup>9</sup>  $\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2$ ,<sup>9</sup>  $\text{Mn}\{\text{N}(\text{SiMe}_3)_2\}_2$ ,<sup>10</sup>  $\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}_2$ ,<sup>10</sup>  $\text{Cu}\{\text{N}(\text{SiMe}_3)_2\}_2$ .<sup>10</sup> Subsequently, the  $-\text{N}(\text{SiMe}_3)_2$  ligand<sup>11</sup> has proved to be particularly effective in achieving stable three-coordination in a wide variety of transition and lanthanide metals.<sup>12</sup> In fact, the divalent lanthanide complex  $[\text{Yb}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ , which has a solid state structure similar to its transition metal counterparts, can also be synthesized.<sup>13</sup> In addition use of the isoelectronic alkyl group  $-\text{CH}(\text{SiMe}_3)_2$  has allowed many related p, d and f block alkyls to be isolated.<sup>14</sup> More recently there has been a revival of interest in sterically demanding alkoxides. As a result a new generation of very bulky  $-\text{OR}$  ligands such as  $-\text{OCH}(\text{t-Bu})_2$ ,<sup>15</sup>  $-\text{OAdamantyl}$ ,<sup>15</sup>  $-\text{OC}(\text{t-Bu})_3$ ,<sup>16</sup>  $-\text{OC}(\text{C}_6\text{H}_{11})_3$ ,<sup>17</sup>  $-\text{OCPh}_3$ ,<sup>17</sup>  $-\text{OSiPh}_3$ ,<sup>17</sup>  $-\text{OSi}(\text{t-Bu})_3$ ,<sup>18</sup>  $-\text{OAr}$ <sup>19</sup> ( $\text{Ar} = 2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2$  and similar ligands) has come into prominence. In addition, the introduction of even bulkier aryl and alkyl groups such as  $-\text{C}_6\text{H}_2\text{-2,4,6-t-Bu}_3$ <sup>20</sup> and  $-\text{C}(\text{SiMe}_3)_3$ <sup>21</sup> has demonstrated that there is plenty of scope for further development in hydrocarbyl ligands.

## WEAK ASSOCIATION IN THE METAL SILYLAMIDES $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ AND THE SYNTHESIS OF THE FIRST STABLE, TWO-COORDINATE, OPEN SHELL TRANSITION METAL COMPLEXES

Until 1985 the closest general approach to isolable, two-coordinate, open shell transition metal species had involved the original compounds  $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$  ( $\text{M} = \text{Mn}, \text{Co}$  and  $\text{Ni}$ ).<sup>9,10</sup> It was concluded that  $\text{Mn}\{\text{N}(\text{SiMe}_3)_2\}_2$  and  $\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2$  were monomeric in the vapor phase from their relatively low boiling points. Subsequently, the monomeric nature of  $\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2$  was confirmed in cyclohexane solution.<sup>22</sup> However, X-ray structural data for  $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$  ( $\text{M} = \text{Mn}$ ,<sup>23,24</sup>  $\text{Fe}$ <sup>25</sup> and  $\text{Co}$ <sup>24</sup>) show that they are associated into dimers in the solid. Data are also available for the corresponding  $-\text{NPh}_2$  derivatives<sup>25,26</sup> and these are summarized in Table I. The structures of both types of complex are exemplified

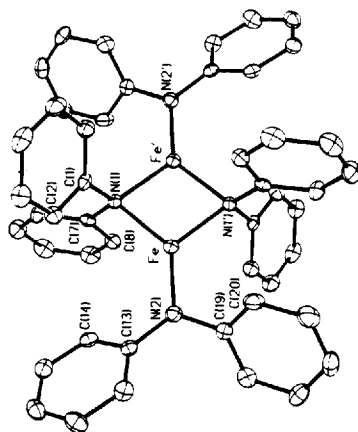
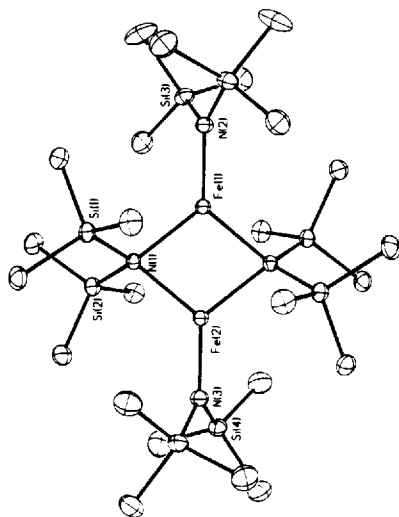
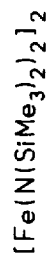
TABLE I

Important structural data for the monomeric and dimeric complexes  $M(NR_2)_2$ ,  
( $M = Mn \rightarrow Ni$ ) ( $R = SiMe_3, Ph$ )

$\{M(NR_2)_2\}_2$ $R = SiMe$	Mn	Fe	Co	Ni
M—M, Å	2.811(1)	2.663(1)	2.583(3)	
M—N(t), Å	1.998(3)	1.925(3)	1.916(5)	
M—N(b), Å	2.174(3)	2.086(2)	2.062(4)	
M—N—M	80.6(1)°	79.4(1)°	77.6(2)°	
R = Ph				
M—M, Å		2.715(1)	2.566(3)	2.327(2)
M—N(t), Å		1.895(3)	1.889(8)	1.828(9)
M—N(b), Å		2.038(2)	1.998(5)	1.911(9)
M—N—M		83.6(1)°	79.9(3)°	75.0(3)°
$M\{N(SiMe_3)_2\}_2$	Vapor Electron Diffraction for the Linear Monomers			
M—N, Å	1.95(2)	1.84(2)	1.84(2)	

by the dimeric iron species in Fig. 1. A notable absence in Table I are data for the nickel complex  $Ni\{N(SiMe_3)_2\}_2$ <sup>9</sup> which distills as a red oil. However, this quickly decomposes at room temperature. One explanation for its instability involves the greater crowding, as a result of short Ni—N bonds, which may lead to ligand dissociation. Nevertheless, the alacrity of its decomposition is puzzling in view of the excellent thermal stability of the, albeit less crowded,  $[Ni(NPh_2)_2]_2$  species.<sup>26</sup> For the remaining complexes the long bridging M—N distances, the low boiling points and the monomeric nature of  $Co\{N(SiMe_3)_2\}_2$  in cyclohexane<sup>22</sup> and  $Mn\{N(SiMe_3)_2\}_2$  and  $Fe\{N(SiMe_3)_2\}_2$  in toluene<sup>25</sup> show that the association to give dimers is fairly weak. Conclusive evidence of the weak nature of the association comes from recent electron diffraction data<sup>27</sup> (Table I) on  $M\{N(SiMe_3)_2\}_2$  ( $M = Mn, Fe$  or  $Co$ ) which show that they have monomeric structures very similar to that reported for the linear compound  $Zn\{N(SiMe_3)_2\}_2$ .<sup>28</sup> Other evidence for weak bridging comes from the reactivity of the complexes. For example, the dimers in Table I are easily cleaved by nucleophiles and if the synthesis of  $Fe\{N(SiMe_3)_2\}_2$  is carried out in THF instead of  $Et_2O$ , the pale green complex  $Fe\{N(SiMe_3)_2\}_2(THF)$ <sup>25</sup> (Fig. 2) distills and crystallizes at room temperature.

Even though it has been known since 1963<sup>9,10</sup> that the bis amido derivatives are probably weakly associated in the solid, the first


$$\text{Fe} \cdots \text{Fe} = 2.715(1) \text{ \AA}$$
$$\text{Fe}-\text{N}(t) = 1.895(3) \text{ \AA}$$
$$\text{Fe}-\text{N}(\text{b}) = 2.038(3) \text{ \AA}$$


2.663(1) Å

1.925(3) Å

2.086(2) Å

FIGURE 1 Computer generated thermal ellipsoid plots, with important bond distances and angles, for  $[\text{Fe}(\text{NR}_2)_2]_2$  ( $\text{R} = \text{Ph}, \text{SiMe}_3$ ).

Fe-N = 1.916(5) Å

Fe-O = 2.071(6) Å

N-Fe-N' = 144.0(3)°

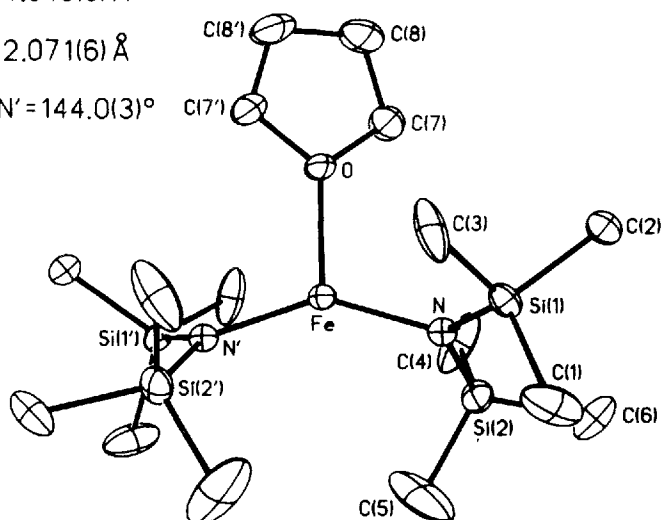


FIGURE 2 Computer generated thermal ellipsoid plot, with important bond distances and angles, for  $\text{Fe}(\text{THF})\{\text{N}(\text{SiMe}_3)_2\}_2$ .

open shell, molecular, two-coordinate transition metal complexes were not structurally characterized until 1985. The reaction between  $\text{LiC}(\text{SiMe}_3)_3$  and  $\text{MnCl}_2$  in a 2:1 molar ratio gave  $\text{Mn}\{\text{C}(\text{SiMe}_3)_3\}_2$ <sup>29</sup> as shown in Fig. 3. The coordination is two-fold and the complex is rigorously linear as indicated by a center of inversion at manganese. Distances and angles in the  $\text{C}(\text{SiMe}_3)_3$  ligand are within the expected ranges and no agostic interactions involving C-H groups and manganese are apparent. Almost simultaneously electron diffraction data showed that  $\text{Mn}(\text{CH}_2\text{-t-Bu})_2$ <sup>30</sup> (Fig. 3) was also monomeric in the vapor with linear coordination at manganese and very similar Mn-C bond lengths to those seen in  $\text{Mn}\{\text{C}(\text{SiMe}_3)_3\}_2$ . The compound  $\text{Mn}\{\text{CH}(\text{SiMe}_3)_2\}_2$  is also linear and monomeric in the gas phase.<sup>31</sup>

## EXTENSION OF TWO-COORDINATION TO IRON AND COBALT

The synthesis and structure of  $\text{Mn}\{\text{C}(\text{SiMe}_3)_3\}_2$  and also  $\text{Mn}(\text{CH}_2\text{-t-Bu})_2$  marked a significant advance. However, attempts to extend

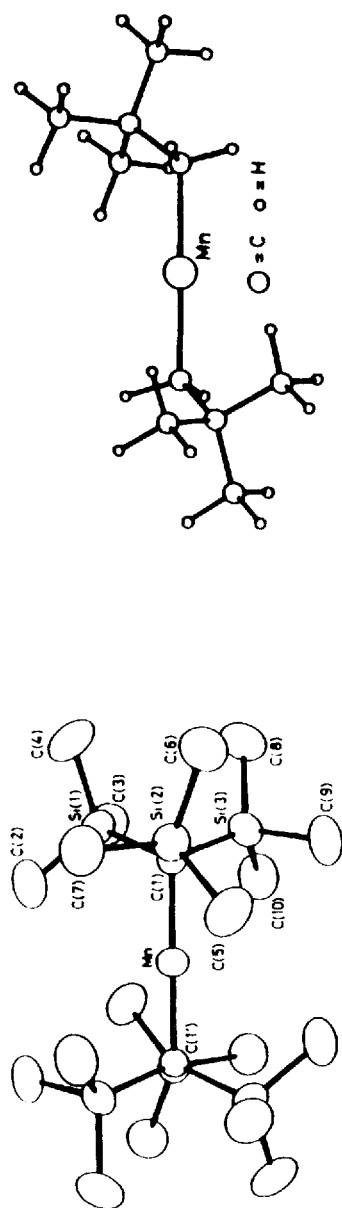


FIGURE 3 Molecular drawings of the linear two-coordinate manganese dialkyls  $\text{Mn}(\text{C}(\text{SiMe}_3)_{3/2})_2$  (a) and  $\text{Mn}(\text{CH}_2\text{-t-Bu})_2$  (b). Reproduced from Refs. 29 and 30. For (a)  $\text{Mn-C}(1) = 2.102(4) \text{ \AA}$ , for (b)  $\text{Mn-C} = 2.104(6) \text{ \AA}$ .



the use of  $-\text{C}(\text{SiMe}_3)_3$  or other bulky alkyls to achieve two-coordination in other first row transition metals have been unsuccessful so far. This could be so for a number of reasons which include (i) weak  $\text{M}-\text{C}$  bonds compared to  $\text{M}-\text{N}$  or  $\text{M}-\text{O}$  bonds; (ii) a special stability in the case of manganese owing to its half-occupied d-orbitals. In view of these difficulties it seemed that the easiest route to further examples of two-coordinate complexes lay with the use of amide ligands bulkier than  $-\text{N}(\text{SiMe}_3)_2$ . The main reason is that the bulky amide ligands (necessary for kinetic stability) can be obtained readily or conveniently synthesized. In addition, metal amides are, generally speaking, more stable than the corresponding alkyls or aryls owing to the greater strength of the  $\text{M}-\text{N}$  bond.<sup>32</sup> On the other hand alkoxides or aryloxides should be even more stable than the amides (bond strength  $\text{M}-\text{O} > \text{M}-\text{N} > \text{M}-\text{C}$ ).<sup>33</sup> However, the  $-\text{OR}$  ligand bears only one organic group and is not as sterically versatile as the amide having two organic substituents. In effect, the amide ligand combines high metal-ligand bond strength (thermodynamic factors) and high steric requirements (kinetic factors) and is thus a good ligand for the synthesis of low coordinate complexes with high stability.

These considerations suggested that if the size of the amide ligands such as  $-\text{N}(\text{SiMe}_3)_2$  were increased further, a variety of two-coordinate crystalline species might result. This proved to be true in the case of the readily obtainable  $-\text{N}(\text{SiMePh}_2)_2$ <sup>34</sup> ligand. Straightforward treatment of the metal dihalides  $\text{MnI}_2$ ,  $\text{FeBr}_2$  or  $\text{CoCl}_2$  with two equivalents of  $\text{LiN}(\text{SiMePh}_2)_2$  in  $\text{Et}_2\text{O}$  gave good yields of  $\text{M}\{\text{N}(\text{SiMePh}_2)_2\}_2$  ( $\text{M} = \text{Mn}$ ,<sup>35</sup>  $\text{Fe}$ <sup>36</sup> or  $\text{Co}$ <sup>36</sup>). The most important structural parameters for these complexes are given in Table II and the structures of the iron and cobalt complexes are illustrated in Figs. 4 and 5.<sup>36</sup>

TABLE II

Important structural parameters for  $\text{M}\{\text{N}(\text{SiMePh}_2)_2\}_2$ , ( $\text{M} = \text{Mn, Fe, Co}$ )

$\text{M}\{\text{N}(\text{SiMePh}_2)_2\}_2$	Mn	Fe	Co
N-M-N	170.7(1)°	169.0(1)°	147.0(1)°
M-N(av.) Å	1.989(3)	1.917(2)	1.901(3)
M-C(<2.8 Å)	2.774(5)	2.695(4)	2.584(7)
			2.588(7)
Color	pale pink	pale amber	green

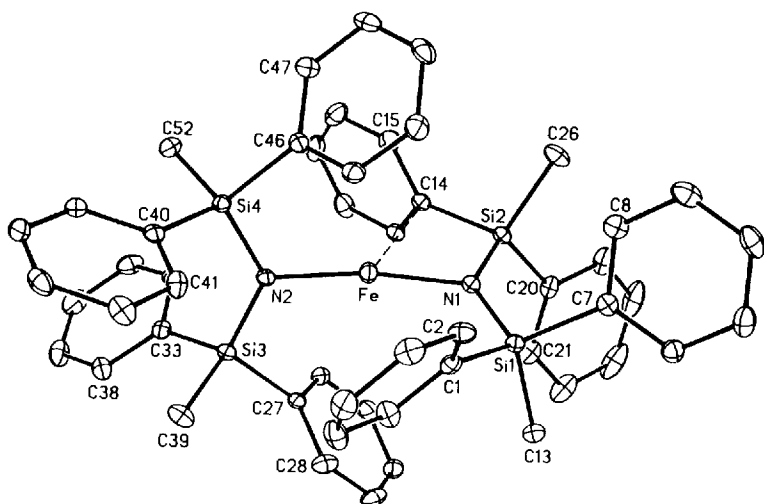


FIGURE 4 Computer generated thermal ellipsoid plot of  $\text{Fe}(\text{N}(\text{SiMePh}_2)_2)_2$ . Structural details are in Table II.

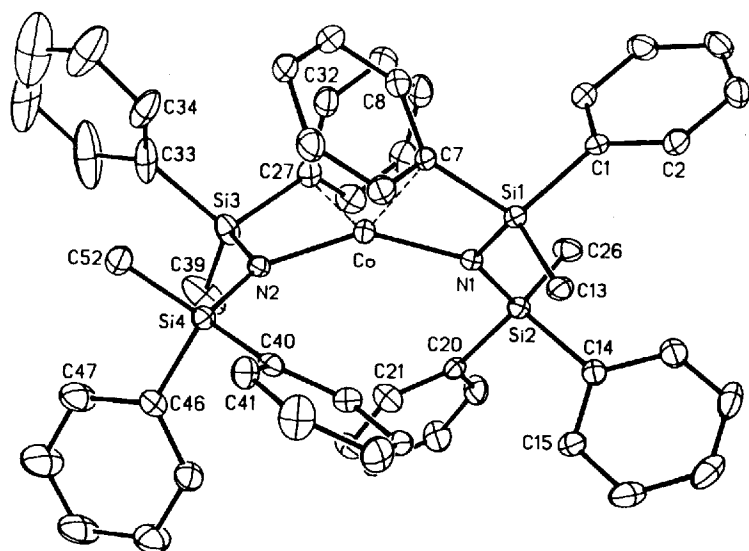


FIGURE 5 Computer generated thermal ellipsoid plot of  $\text{Co}(\text{N}(\text{SiMePh}_2)_2)_2$ . Structural details are in Table II.

The iron and cobalt species were the first, solid state, structurally characterized examples of two-coordination for these elements. Both the data in Table II and the figures illustrate that the complexes are non-linear with N–M–N angles near 170° for the Mn and Fe complexes. For the cobalt complex the deviation is much more marked with the relatively small N–Co–N angle of 147°. A feature of this complex is the possible interaction between the cobalt center and the C(7) and C(27) aromatic rings. The Co  $\cdots$  C(7) and C(27) distances are 2.588(7) Å and 2.584(7) Å. Longer interactions are seen in the Fe and Mn cases where the closest approaches involve C(14) at 2.695(5) for iron and C(7) at 2.74(5) Å for manganese. However, close examination of bond distances and angles within the ligands in all three complexes reveal no unusually long SiN or SiC bonds, but there are large asymmetries ( $\approx 27^\circ$ ) in the Co–N–Si angles which are 103.4(2)° (av.) for Co–N–Si (1 and 3) and 130.5(2) (av.) for Co–N–Si (2 and 6). Even smaller angular distortions are apparent in the iron and manganese compounds. Clearly, a case can be made for some M  $\cdots$  C interaction on the basis of the electron deficiency of the metal centers which encourages interaction between the metal and the electron-rich aromatic rings. However, it is quite probable that the N–M–N angle is a “soft” one, and relatively weak interactions, evident from the long M  $\cdots$  C distances, or perhaps crystal packing forces can effect large changes in the angular parameters.

These considerations aside, it is obvious that the presence of phenyl rings instead of methyl groups on silicon effect the monomeric structure seen. Inspection of the structures in Figs. 4 and 5 show that four of the eight available phenyl rings shield the metal center from further attack. Imaginary lines connecting the centroids of these phenyl rings to the metals, in addition to the two metal nitrogen bonds, afford an approximately octahedral arrangement. This effect is underlined by considering the structure of the species  $\text{Fe}\{\text{N}(\text{SiMe}_2\text{Ph})_2\}_2$ <sup>37</sup> shown in Fig. 6. This compound is distinct from those in Table II and Figs. 4 and 5 in that it involves only one phenyl group on each silicon. Yet, the phenyl groups are observed to surround the metal, as illustrated in Fig. 7, even though the structures in Figs. 4 and 5 show clearly that there is room for the phenyl groups on the periphery of the molecule. This arrangement, of course, lends further support to the importance of the interaction between the metal centers and the aromatic rings.

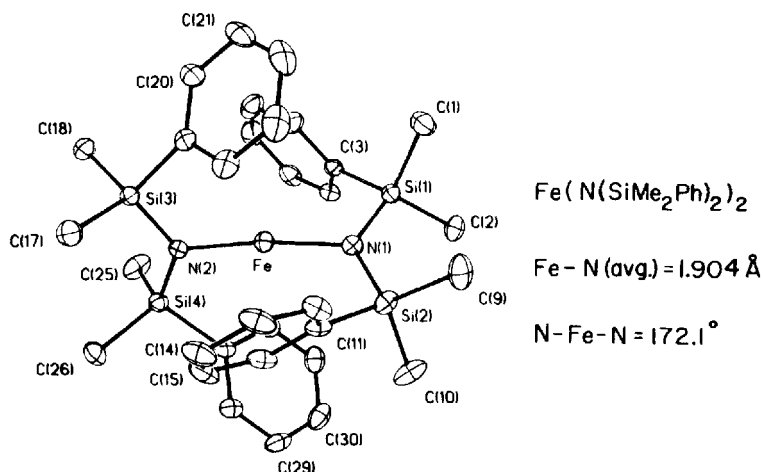
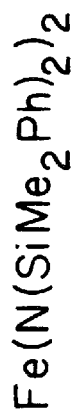


FIGURE 6 Computer generated thermal ellipsoid plot with important structural parameters for  $\text{Fe}\{\text{N}(\text{SiMe}_2\text{Ph})_2\}_2$ .

In addition to the angle seen at the metals, the metal–nitrogen bond lengths also merit comment. The values observed, by X-ray data at 130 K, in Table II average ca. 0.05 Å longer than the values observed by electron diffraction (see also Table II) in the gas phase (at ca. 320 K) for  $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$ . The M–N distances in Table II are, in fact, quite close to the M–N (terminal) values seen in the dimers  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$  in Table I. The consistency of the terminal M–N distances in the X-ray structures of the monomers in Table II and both the  $-\text{N}(\text{SiMe}_3)$  and  $-\text{NPh}_2$  dimers in Table I suggest that these are more accurate than those given by the electron diffraction studies. The authors point out<sup>27</sup> that the latter figures probably have a reduced reliability since the M–N distances are strongly correlated with the closely similar Si–C bond lengths. However, the electron diffraction results do give the correct trend in M–N distances for the series  $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$  (M = Mn, Fe or Co). An alternative explanation for the longer terminal M–N bonds seen in the crystal phase lies in the fact that all the compounds in Table I are dimers. Hence, the metals are three-coordinate and more crowded and longer M–N distances might be expected. However, the weight of evidence is that the dimerization is weak, suggesting that the nominal increase in coordination has only a small



$$\text{Fe} - \text{centroid Ph's} = 3.028 - 3.118 \text{ \AA}$$

$$\text{Fe} - \text{N} = 1.904 \text{ \AA}$$

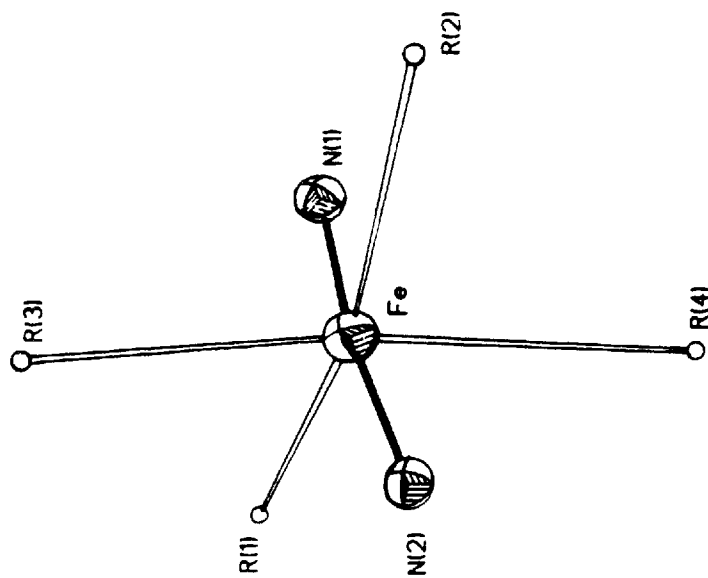


FIGURE 7 Computer generated plot illustrating the pseudo-octahedral geometry of the iron in  $\text{Fe}[\text{N}(\text{SiMe}_2\text{Ph})_2]_2$ .

effect on the terminal M–N distance. In support of this argument there are now a number of different X-ray structures of three-coordinate mononuclear Mn(II), Fe(II) (e.g., Fig. 2) and Co(II)<sup>38</sup> compounds available which also indicate a relatively minor increase in M–N distance between two- and three-coordination for these complexes.

## SPECTROSCOPIC STUDIES

Photoelectron spectra of the complexes  $M\{N(SiMe_3)_2\}_2$  ( $M = Mn, Fe$  or  $Co$ ) and theoretical calculations on the simple  $M(NH_2)_2$  systems have provided considerable insight into the bonding in such molecules.<sup>27</sup> The He-I and He-II photoelectron data for these and other silylamides indicate little or no M–N  $\pi$ -bonding. This is, most probably, due to delocalization of the nitrogen lone pairs onto silicon.<sup>27,39</sup> Magnetic data are also becoming available.<sup>23</sup> These show that for the dimers  $[M\{N(SiMe_3)_2\}_2]_2$  and  $[M(NPh_2)_2]_2$  high spin M(II) units are coupled and they do not follow the Curie–Weiss law. At high temperatures the magnetic susceptibility becomes temperature independent. Magnetic data for the monomers  $M\{N(SiMe_3)_2\}_2$  are unavailable but data for the monomers  $M\{N(SiMePh_2)_2\}_2$  indicate high spin configurations in all cases. Photoelectron spectroscopic studies on  $M\{N(SiMe_3)_2\}_2$  show a band at around 8.5 eV which has been assigned to the ionization of the nitrogen lone pairs. The MO calculations on  $M(NH_2)_2$  are in close agreement and show the degenerate lone pair orbitals to be the HOMO. A significant feature of the calculations involves the results of population analysis which suggests that the M–N bonds are very polar and that metal nitrogen d-p  $\pi$ -bonding is negligible. This result implies that all the silylamides in both Tables I and II are quite electron poor. Thus, the monomeric Mn, Fe, Co complexes are 9, 10 and 11 electron species, respectively. As a result, these and other two-coordinate complexes are expected to be particularly reactive toward any non-bulky nucleophile.

Absorption spectroscopy has been reported for the complexes  $Co\{N(SiMe_3)_2\}_2$ ,<sup>22</sup>  $Co\{N(SiMePh_2)_2\}_2$ <sup>36</sup> and  $Fe\{N(SiMePh_2)_2\}_2$ .<sup>36</sup> In the case of  $Co\{N(SiMe_3)_2\}_2$  three absorptions are seen in the solid at 20,600  $cm^{-1}$ , 17,200  $cm^{-1}$  and 14,700  $cm^{-1}$ . In hexane

solution bands are observed at 24,400  $\text{cm}^{-1}$ , 17,100  $\text{cm}^{-1}$  and 14,600  $\text{cm}^{-1}$ . In the case of  $\text{Co}\{\text{N}(\text{SiMePh}_2)_2\}_2$  three bands are also present at 19,010  $\text{cm}^{-1}$  ( $\epsilon = 70$ ), 15,770  $\text{cm}^{-1}$  ( $\epsilon = 125$ ), and 12,470  $\text{cm}^{-1}$  ( $\epsilon = 50$ ). If a two-coordinate geometry is assumed in hexane solution then these bands can be assigned to the  $^4\Sigma_g \rightarrow ^4\Pi_g(\text{P})$ ,  $^4\Sigma_g \rightarrow ^4\Sigma_g(\text{P})$  and  $^4\Sigma_g \rightarrow ^4\Delta_g(\text{F})$  transitions. There is a frequency change in only one of the bands when the solution and solid state spectra of  $\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2$  are compared. It is notable that the same number of bands is also observed for  $\text{Co}\{\text{N}(\text{SiMePh}_2)_2\}_2$  in toluene; however, all the bands are shifted to lower energy compared to those observed for  $\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2$ . It is unlikely that a large shift difference could be the result of the use of different solvents PhMe and hexane. No UV-visible data have been published for the manganese or nickel compounds. The spectrum of  $\text{Fe}\{\text{N}(\text{SiMePh}_2)_2\}_2$  displays a slow rise in absorption toward the UV. A very weak shoulder at 17,900  $\text{cm}^{-1}$  is apparent.<sup>35</sup>

Thus far the UV-visible spectra of the compounds have played a relatively minor role in their characterization and structural assignments. Of the four different transition metals for which homoleptic bivalent silylamides are known, only two, the green Co compounds and the red Ni complex, display significant colors in the visible region. Little unambiguous information regarding structure could be obtained even in the most studied Co species. Although the three bands observed for the cobalt complexes are consistent with a linear structure they could also be rationalized on the basis of a bent ( $C_{2v}$ ) or an approximate trigonal planar (as in the dimer) geometry.<sup>36</sup>

In the conclusion of this section it may be noted that stable two-coordinate transition complexes with silylamide ligands are currently known only in the case of Mn(II), Fe(II) and Co(II). As previously noted,  $\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}_2$  is unstable and although a bis-silylamide of Cr(II) is known it has only been isolated as square planar adducts such as *trans*- $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ .<sup>40</sup>

## A Cr–Ni SERIES OF TWO-COORDINATE METAL COMPLEXES USING BORYLAMIDE LIGANDS

It has been implicit in the discussion thus far that steric considerations are a principal factor in producing low coordination num-

bers. However, as the example of  $[\text{NiO}_2]^{2-}$  shows,<sup>1</sup> this is not the whole story and electronic considerations must also play a role. For example, a characteristic feature of the  $-\text{N}(\text{SiMe}_3)_2$  ligand (and indeed silylamines in general) is the low basicity of the nitrogen lone pair and its weak bridging tendency.<sup>11</sup> The classical and controversial explanation for this lies in the removal of lone pair density from nitrogen into the d-orbitals on silicon (see Ref. 39 for supporting evidence). The  $-\text{NPh}_2$  ligand appears to bridge somewhat more strongly judging by the slightly shorter M–N distances. It is, however, possible that here, too, some lone pair electron density could be delocalized into antibonding  $\pi$ -orbitals of the phenyl substituents. In the context of the lower basicity of the  $-\text{N}(\text{SiMe}_3)_2$  and  $\text{NPh}_2$  ligand it is notable that there are very few low coordinate dialkyl amides of transition metals known at present (a rare exception is  $\text{Cr}\{\text{N}(\text{i-Pr})_2\}_3$ ).<sup>41</sup> These observations suggest that electronic factors are significant in the stability and not just the degree of association of the complexes. As a result it could be argued that a restriction on the lone pair availability might enhance metal amide stability.

Consideration of these factors led to the use of an alternative type of amido ligand in which the lone pair is rendered unavailable for bridging by use of a boryl ( $-\text{BR}_2$ ) substituent. The resultant borylamide ligand  $-\text{NR}'\text{BR}_2$  (R and R' may be a variety of alkyl and aryl groups) involves a double bond between nitrogen and boron and is the BN analog of an alkenyl ligand. Metal borylamides, e.g.,  $\text{LiNMeBMe}_2$ , had in fact been generated in situ some years ago.<sup>42</sup> These were allowed to react further to give Hg and Sn compounds with interesting structures.<sup>43</sup>

The first borylamide ligands to be successfully applied to transition elements involved the crowded precursors  $\text{HNPhBMe}_2$  and  $\text{HNMeBMe}_2$  which used two mesityl groups to protect the boron center from further attack.<sup>44</sup> They were synthesized in good yield by the reaction of  $\text{LiNHPh}$  or  $\text{LiNHMe}$  and  $\text{Me}_2\text{BF}$ . Treatment of the amine precursor with  $n\text{-BuLi}$  gave the lithium salts  $\text{Li}(\text{Et}_2\text{O})_2\text{NRBMe}_2$ <sup>45</sup> (R = Ph or Mes). Their monomeric nature is notable because most etherate adducts of lithium amides are associated even when bulky substituents are present, such as in  $[\text{Li}(\text{Et}_2\text{O})\text{N}(\text{SiMe}_3)_2]_2$ .<sup>46</sup> Reaction of  $\text{LiNMeBMe}_2$ , generated in situ, with the dihalides  $\text{MnBr}_2$ ,  $\text{FeBr}_2$  or  $\text{CoCl}_2$  gave the monomeric species  $\text{M}\{\text{NMeBMe}_2\}_2$  (M = Mn, Fe or Co). In the case of Cr



and Ni it was found that the solvated halides *trans*-[CrCl<sub>2</sub>(THF)<sub>2</sub>]<sup>47</sup> and NiBr<sub>2</sub>·<sup>5</sup>/<sub>3</sub> THF<sup>47</sup> gave moderate yields of Cr{NMesBMes<sub>2</sub>}<sub>2</sub><sup>48</sup> and Ni{NMesBMes<sub>2</sub>}<sub>2</sub>.<sup>48</sup> The most important structural parameters for these five complexes are given in Table III. Clearly, all the complexes are monomeric. However, there are important variations in structure between Cr and Ni. The crystals of the iron, cobalt and nickel complexes are isomorphous and the molecules are almost isostructural. As in the case of the -N(SiMe<sub>2</sub>Ph)<sub>2</sub> and -N(SiMePh<sub>2</sub>)<sub>2</sub> derivatives their structures deviate from linearity. However, there do not appear to be any strong interactions between the metals and the aromatic carbon atoms. The closest M · · · C interactions in the three complexes are about 2.6 Å so that the compounds are essentially two-coordinate. The nickel species (Fig. 8) is in fact the first neutral, molecular, two-coordinate derivative of that element to be characterized. The B–N bond length in Mn, Fe and Co compounds are close to 1.4 Å, confirming that the nitrogen lone pair is involved in π-bonding to boron and has a low availability for bridge bonding. The twist angles between the boron and nitrogen planes in the Fe, Co and Ni complexes are also low.

The Cr and Mn compounds show more deviation from linearity. This is particularly true for chromium where the NCrN angle is 112.2°. There are also close Cr · · · C contacts of 2.39 Å. In addition, there is considerable asymmetry (ca. 15°) in the NBC angles in

TABLE III  
Important structural parameters for M{NMesBMes<sub>2</sub>}<sub>2</sub>, (M = Cr → Ni)

M{NMesBMes <sub>2</sub> } <sub>2</sub>	Cr	Mn	Fe	Co	Ni
N–M–N	112.3(3)°	160.4(2)°	166.6(1)°	168.4(1)°	167.9(1)°
M–N(av.), Å	1.984(7)	2.046(4)	1.938(2)	1.910(3)	1.866(2)
M–C(<2.8 Å)	2.383	2.536	2.521	2.629	2.611
	2.391			2.734	2.703
B–N(av.), Å	1.377(12)	1.402(7)	1.409(4)	1.406(6)	1.412(4)
B–C, Å	1.598(14)	1.603(8)	1.592(4)	1.598(5)	1.595(3)
	1.624(14)		1.598(4)	1.592(5)	1.596(3)
			1.607(5)		
B–C(–M), Å	1.647(14)	1.618(8)	1.622(5)	1.612(6)	1.617(4)
	1.646(14)			1.624(7)	1.619(4)
Dihedral between	18.7°	45.8°		24.1°	23.1°
MNC(–M) planes					
Color	turquoise	pale pink	pale amber	green	dark red

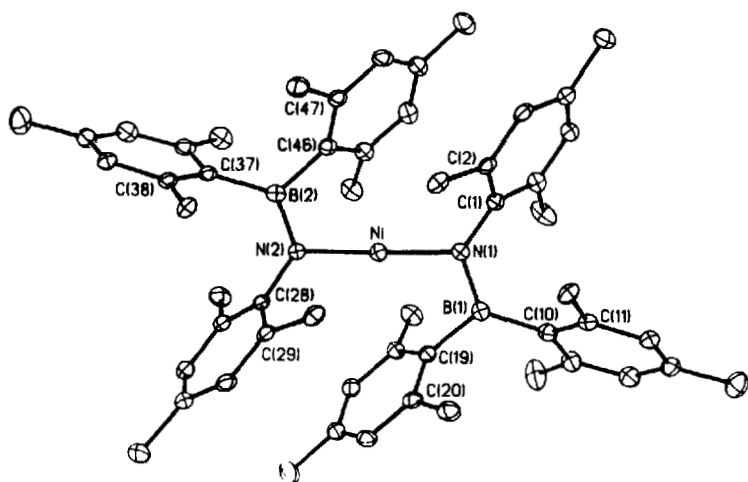


FIGURE 8 Computer generated thermal ellipsoid plot of  $\text{Ni}\{\text{NMesBMes}_2\}_2$ . Structural details are in Table III.

agreement with the  $\text{Cr} \cdots \text{C}$  contacts.  $\text{Cr}\{\text{NMesBMes}_2\}_2$ <sup>47</sup> (Fig. 9) is also the first homoleptic chromium(II) amide to be reported. It is nominally two-coordinate but the coordination at Cr could also be described as quasi-square planar. This is because the angles at Cr total near to  $360^\circ$  with a small ( $18.7^\circ$ ) dihedral between the two CrNC planes. It is not clear why the *cis* configuration is adapted and it is difficult to justify on steric grounds. The only reported comparable species is the square planar *trans*- $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ .<sup>40</sup> Here the Cr–N bonds are  $2.089(10)$  Å which are  $0.1$  Å longer than those in the borylamide. However, this lengthening is to be expected due to the higher coordination number of the Cr in the silylamide derivative. The manganese complex also shows considerable, though not as severe, deviation from linearity with a NMnN angle of  $160.4^\circ$ . There is also an  $\text{Mn} \cdots \text{C}$  interaction of  $2.536(5)$  Å as well as a large asymmetry ( $17^\circ$ ) in the NBC angles. For comparison purposes the NBC angle asymmetries in  $\text{HNPhBMes}_2$ ,  $\text{Li}(\text{Et}_2\text{O})_2\text{NPhBMes}_2$ ,  $\text{M}(\text{NMesBMes}_2)_2$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ) are  $3.7^\circ$ ,  $8.1^\circ$ ,  $15^\circ$ ,  $13.1^\circ$  and  $13.5^\circ$ , respectively. There is a significant difference, however, between the types of coordination in Cr and Mn. Whereas the Cr geometry may be regarded as distorted square planar, the Mn geometry is closer to distorted tetrahedral with a

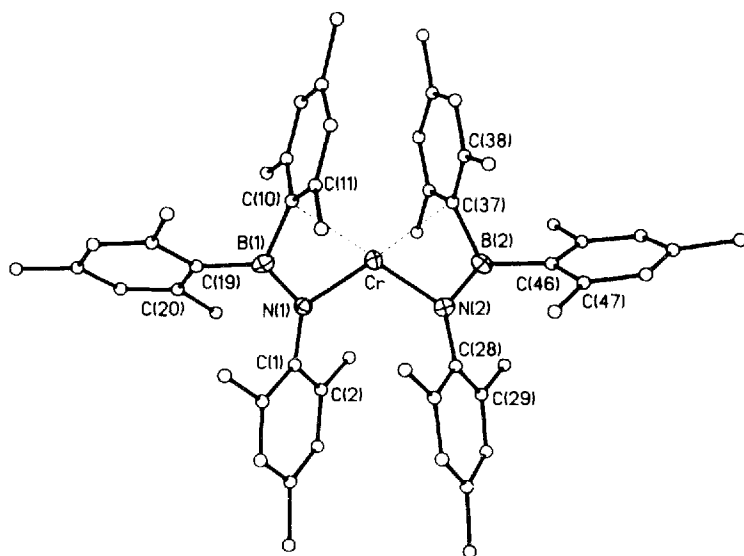


FIGURE 9 Computer generated thermal ellipsoid plot of  $\text{Cr}\{\text{NMesBMes}_2\}_2$ , structural details are in Table III, with important bond distances and angles.

dihedral angle of  $45.8^\circ$  between the MNC planes. There is thus a roughly linear decrease in the severity of angular distortion from Mn to Ni. In addition, an important feature of the data in Table III is the appearance, for the first time, of asymmetry in bond distances within the ligand. This concerns the two B–C(mesityl) bonds which display the largest asymmetry ( $0.035 \text{ \AA}$ ) in the case of the Cr complex and a lower (ca.  $0.02 \text{ \AA}$ ) asymmetry for the remaining complexes. Even greater asymmetries are found in the complexes in Table IV *vide infra*. Presumably, these distortions are the result of the close  $\text{M} \cdots \text{C}$  contacts which remove electron density from one of the B–C bonds in each ligand.

The chromium compound, because of its tendency toward planar coordination, is unique. Presumably, the  $d^4$  electron configuration is mainly responsible. In addition, the larger size of Cr(II) facilitates the more crowding flattened geometry. Perhaps for a similar reason the angular distortions within the ligand are not quite as severe. An imposition of planar geometry might also have been expected for the Ni(II)  $d^8$  complex. However, either this geometry

TABLE IV

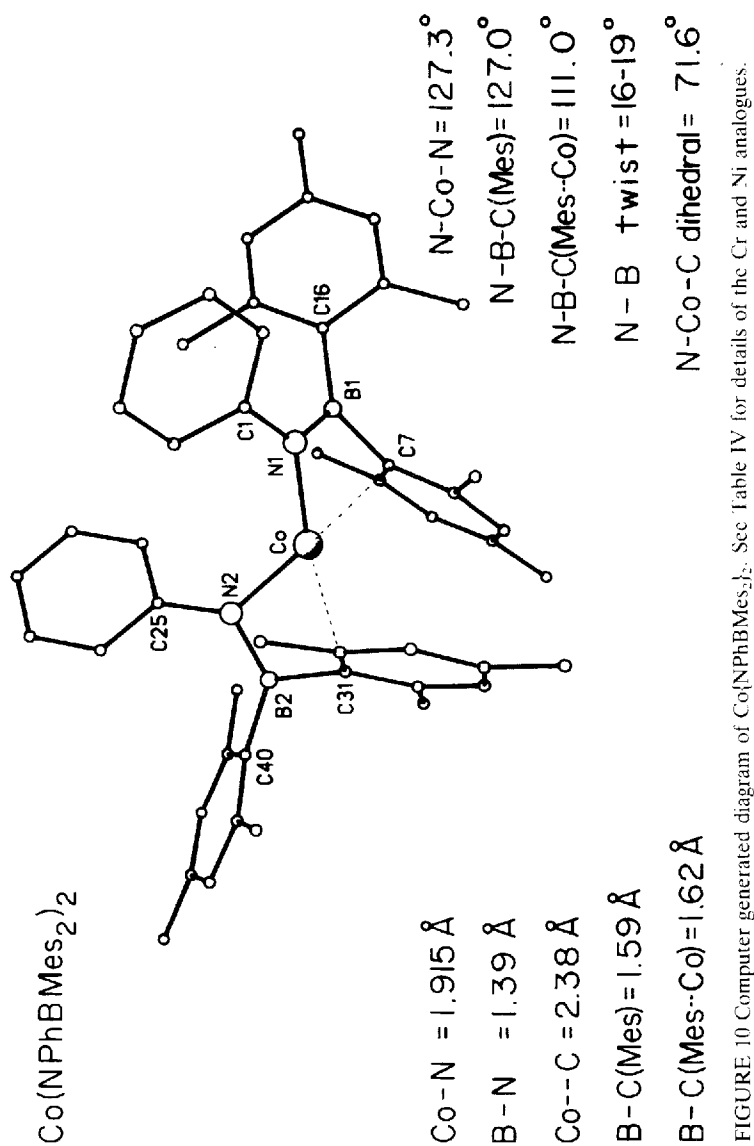
Important structural parameters for  $M\{NPhBMes_2\}_2$ , ( $M = Cr, Co, Ni$ )

$M\{NPhBMes_2\}_2$	Cr	Co	Ni
N–M–N	110.8(1)°	127.1(2)°	135.7(1)°
M–N(av.), Å	1.982(2)	1.909(5)	1.885(4)
M–C(<2.8 Å)	2.328(2)	2.388(6)	2.370(3)
	2.406(2)	2.387(5)	2.402(4)
B–N(av.), Å	1.389(3)	1.398(8)	1.403(6)
B–C, Å	1.585(4)	1.596(9)	1.586(5)
	1.591(3)	1.592(9)	1.575(7)
B–C(–M), Å	1.630(4)	1.639(8)	1.624(7)
	1.632(4)	1.600(9)	1.629(6)
Dihedral between MNC(–M) planes	37.5°	71.7°	87.4°
Color	green	green	dark red

is not favored over tetrahedral or the nickel is too small to allow the type of coordination seen in the case of Cr(II).

Another structural feature of interest concerns the trend in B–N bond lengths across the series Cr to Ni. The length varies between 1.377 Å in Cr and 1.415 Å in Ni. There is no corresponding trend in the ligand N–C and B–C distances which remain fairly constant across the series. This tends to rule out steric effects as a cause of this increase. One explanation may lie in metal–ligand  $d \rightarrow p\pi$  back bonding in which electron density is transferred from the metal d-orbitals into the  $\pi^*$  antibonding B–N orbitals. The number of electrons in the d-orbitals increases from left to right and it is possible that the back bonding ability has the same trend. In other words Ni should be more effective at back bonding than Cr. Another explanation is that the complexes become more ionic upon proceeding from right to left owing to the increasing size of the metal. This would imply a greater negative charge at nitrogen which effects greater electron density in the B–N  $\pi$ -bond which results in shorter B–N bond lengths.

It is also possible to obtain monomeric species using the smaller  $-NPhBMes_2$  ligand. In certain cases it is even possible to crystallize three coordinate derivatives as in the species  $[THF(Et_2O)_2LiClCo\{NPhBMes_2\}_2]$ .<sup>45</sup> Heating this complex in toluene eliminates LiCl and gives free  $Co(NPhBMes_2)_2$ <sup>48</sup> (Fig. 10) which can be also obtained by carrying out the reaction in  $Et_2O$ .

FIGURE 10 Computer generated diagram of  $\text{Co}(\text{NPhBMes}_2)_2$ . See Table IV for details of the Cr and Ni analogues.

Structural details for this and its Cr(II) and Co(II) analogs are given in Table IV. The bonding parameters for the Cr compound are similar to those of Cr(NMesBMes<sub>2</sub>)<sub>2</sub>. However, close examination of these reveal that the Cr–N distances in Table IV are slightly shorter, the NCrN angle is more acute and the Cr···C distances are also slightly decreased. The structure of Cr(NPhBMes<sub>2</sub>)<sub>2</sub> is thus even “tighter” than Cr(NMesBMes<sub>2</sub>)<sub>2</sub>. These differences can be attributed mainly to the smaller size of Ph compared to Mes.

As already mentioned the distortion of the bond distances and angles within the –NPhBMes<sub>2</sub> ligands are even more severe than those found with –NMesBMes<sub>2</sub> derivatives. The decreased steric requirements of the –NPhBMes<sub>2</sub> species result in much larger structural differences for the cobalt and nickel derivatives. The NMN angles are reduced from near 170° to 127.1° and 135.7°, respectively. There is also a large, ca. 0.2 Å, reduction in the M···C distances. It is apparent that these changes and the tighter structure are a result of steric factors. The coordination in both the Co and Ni complexes are closer to quasi-tetrahedral rather than quasi-square planar as seen in the Cr(II) case.

Preliminary UV-Vis absorption spectra (Table V) for the Cr, Co and Ni complexes of Tables III and IV show that there are significant spectral changes which depend on the type of metal coordination present. The spectra of both Cr compounds, which are broadly similar structurally, each feature two peaks. The Co and Ni –NMesBMes<sub>2</sub> complexes, which are almost linear, have

TABLE V

Absorption spectra for M(NRBMes<sub>2</sub>)<sub>2</sub>, (M = Cr, Co, Ni; R = Ph, Mes).  
Values given in cm<sup>-1</sup> with ε values in parenthesis

M	Cr	Co	Ni
M(NMesBMes <sub>2</sub> ) <sub>2</sub>	16,026(252)	12,580(50)	17,420(914)
	12,530(77)	12,820(31) 16,000(76)	23,040(1100) 28,985(1200)
M(NPhBMes <sub>2</sub> ) <sub>2</sub>	14,880(54)	15,240(78)	20,325(1300)
	12,350(36)	16,395(89) 20,010(95) 24,290(386)	16,670(sh)

three absorptions each. The spectra of the corresponding  $\text{-NPhBMes}_2$  derivatives, however, are very different. The Co spectrum involves four peaks. These are really two absorptions which are split as a result of the imposition of  $C_{2v}$  symmetry on an idealized  $T_d$  geometry. The Ni complex involves an absorption at  $20,325\text{ cm}^{-1}$  with a weak shoulder at  $16,670\text{ cm}^{-1}$  which is very different from the absorption spectrum of the corresponding linear complex.

## CONCLUSION AND OUTLOOK

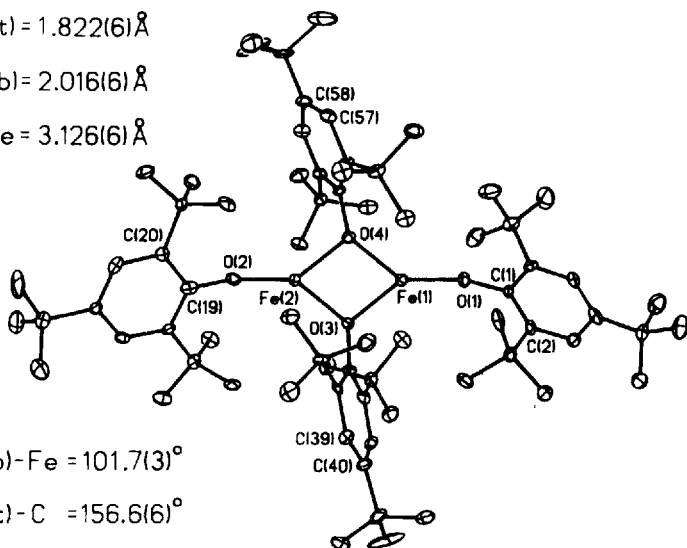
Currently, two-coordination in open shell, stable, transition metal compounds is limited to the metals  $\text{Cr} \rightarrow \text{Ni}$  and with a few important exceptions to amide ligands. This restricted range of compounds is unlikely to continue in the future. Already, alkoxides and aryloxides which have crystal structures very closely related to those of the  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$  dimers are known (Fig. 11).<sup>17,25</sup> Moreover, variable temperature NMR studies have indicated that their barriers to terminal/bridging ligand exchange are fairly low. For example in the alkoxide  $[\text{Co}\{\text{OCPh}_3\}_2]_2$  the barrier for the coalescence of the bridging and terminal  $^1\text{H}$  NMR signals is ca. 14 kcal/mole.<sup>17</sup> This indicates that electronic modification of the alkoxide or aryloxide ligand, for example as in the boryloxide ligand  $\text{-OBTrip}_2$  ( $\text{Trip} = 2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2$ )<sup>49,50</sup> or the use of  $\text{-CF}_3$ <sup>51</sup> substituents may prevent bridging and allow monomers to be isolated. Similarly, bulky aryl ligands such as  $2,4,6\text{-Ph}_3\text{C}_6\text{H}_2$  may allow the synthesis of various two-coordinate complexes. This ligand has already proved itself to some extent successful at stabilizing low coordination numbers via the synthesis of the one-coordinate copper and silver derivatives  $\text{M}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Ph}_3)$  ( $\text{M} = \text{Cu}$  or  $\text{Ag}$ ).<sup>52</sup> Another ligand type which may prove useful is the substituted alkenyls which are isoelectronic to the borylamides. The synthesis of two-coordinate heteroleptic complexes, wherein two different substituents are present, may also be expected.<sup>53</sup>

The synthesis of the salt  $\text{K}_2[\text{NiO}_2]$ , involving a 16-electron, two-coordinate nickel ion  $[\text{NiO}_2]^{2-}$  has shown that bulky ligands are not a requirement for two-coordination.<sup>1</sup> Presumably other two-coordinate dioxometallates involving a range of metals will appear. Other two-coordinate anions involving ligands isoelectronic to oxygen may also be anticipated.

$$\text{Fe}-\text{O}(\text{t}) = 1.822(6) \text{ \AA}$$

$$\text{Fe}-\text{O}(\text{b}) = 2.016(6) \text{ \AA}$$

$$\text{Fe} \cdots \text{Fe} = 3.126(6) \text{ \AA}$$



$$\text{Fe}-\text{O}(\text{b})-\text{Fe} = 101.7(3)^\circ$$

$$\text{Fe}-\text{O}(\text{t})-\text{C} = 156.6(6)^\circ$$

FIGURE 11 Computer generated thermal ellipsoid plot, with important bond distances and angles, for  $\{\text{Fe}(\text{O}-2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2)_2\}_2$ .

The limitation of the range of two-coordinate complexes to the metals  $\text{Cr} \rightarrow \text{Ni}$  is also likely to change. For example, although the +2 oxidation state is known for both Ti and V the known stable derivatives for Ti(II) and V(II) involve either high coordination numbers or  $\pi$ -acid ligands. Good starting materials for the synthesis of Ti(II) and V(II) are unfortunately scarce. One suspects that this, rather than any inherent instability, is the main reason for the absence of a more extensive range of +2 oxidation state compounds. Extension of two-coordination to second and third row transition elements and the lanthanides<sup>13</sup> may also be expected.

In conclusion the known range of two-coordinate, open shell transition metal compounds is currently very small and limited to a few ligands. Little is known concerning their reactivity. Their low coordination number and small number of electrons in the valence shell should give rise to a rich and varied chemistry. Significant developments in the variety and reactivity of such compounds may be expected in the future.



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