are observed. Solvent, substituent, and leaving group effects are dependent on the bulk of the β substituents, and product formation and rearrangement proceed in many cases via the free, linear, and selective α-arylvinyl cations. This and the observation of these ions by NMR give them a respectable place in the carbonium ion family.

Transition-Metal Dialkylamides and Disilylamides

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For the last quarter of a century the transition metal to carbon bond has tended to dominate inorganic chemistry. The discoveries of sandwich compounds, fluxional organometallic compounds, and stable transition-metal–carbene and –carbyne complexes, together with the development of hydrocarbon catalysis involving these compounds, led to a rapid resurgence of interest in the field of organometallic chemistry.[1] By contrast, the chemistry of the transition metal to nitrogen bond has generated less excitement. Probably the most notable exception to this generalization was the discovery of transition-metal–dinitrogen complexes.[2] This immediately raised hopes that new facile routes to nitrogen fixation would be forthcoming—hopes that for the most part still have to be realized.[3,4] There is, however, an extensive and important chemistry surrounding transition metal to nitrogen bonds. Commonly occurring nitrogen coordinating ligands include amines, pyridines, histidines, nitric oxide, nitrite, nitride, azide, cyanate, thiocyanate, nitriles, Schiff bases, amino acids, peptides, proteins, corrins, and porphyrins. Studies involving nitrogen donor ligands thus range from classical coordination chemistry to the developing field of bioinorganic chemistry.[5,6]

This Account deals with the chemistry surrounding transition metal to nitrogen σ bonds in complexes of the type ML_n where M is a transition metal coordinated by n ligands, L, L = $^-NR_2$ (R = alkyl) or $^-N(SiMe_3)_2$. The

coordination chemistry of these compounds reveals the stabilization of unusual coordination numbers and valence states of metal ions, and their reactivity leads to their unique role in the synthesis of many metalloorganic compounds of the transition elements. Also, an interesting comparison exists between the chemistry of transition metal to carbon (alkyl)[7-9] and transition metal to nitrogen (dialkylamide) σ bonds with regard to synthesis, coordination properties, and reactivity.

In addition, the steric requirements of a dialkylamido ligand can dominate the coordination chemistry of transition metals. The use of extremely bulky ligands such as N-i-Pr$_2$ and N(SiMe$_3$)$_2$ has allowed the isolation of unusually low coordination numbers and oxidation states for many metals, for example, three- and two-coordinated transition-metal ions. Less bulky ligands such as NMe$_2$ and NEt$_2$ allow higher coordination numbers, and in lower valency metal complexes oligomerization may occur either by metal–ligand bridging or by direct metal–metal bonding.

Synthetic Procedures

Although dialkylamides of zinc,[10] sodium,[11] potassium,[11] and lithium[12,13] had been prepared during the 19th century, it was not until 1935 when Dermer and

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Fernelius[14] reacted titanium tetrachloride with potassium diphenylamide that the first transition-metal dialkylamide was formed. Titanium tetrakis(diphenylamide) was isolated as a red solid. In 1956, Gilman and co-workers[15] isolated the green volatile liquid uranium(IV) diethylamide, $U(NEt_2)_4$, from a reaction of lithium diethylamide with the metal tetrachloride. However, uranium compounds derived from other amines could not be isolated by this method.

In 1959, Bradley and Thomas initiated a study of the reactions of transition-metal chlorides with lithium dialkylamides according to the general reaction 1.

$$MCl_n + nLiNR_2 \rightarrow M(NR_2)_n + nLiCl \qquad (1)$$
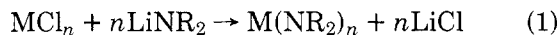
Work proceeded across (group 4A to 8) and down (1st to 3rd row) the periodic table. The volatile dialkylamides of Ti(IV),[16] Zr(IV),[16] Hf(IV),[17] V(IV),[18] Nb-(IV),[19,20] Nb(V),[19] Ta(V),[21] Cr(III),[22-25] Mo(III),[26-28] Mo(IV),[29] W(III),[30-32] and W(VI)[33] were isolated in this way. These dialkylamides are all solids or liquids at room temperature and are appreciably soluble in alkane solvents. They are readily hydrolyzed, though quite stable in the absence of hydroxylic reagents. The dialkylamides of V(IV), Nb(IV), Cr(III), Mo(III), Mo(IV), and W(III) are all exceedingly oxygen sensitive, the metal being readily oxidized in these compounds.
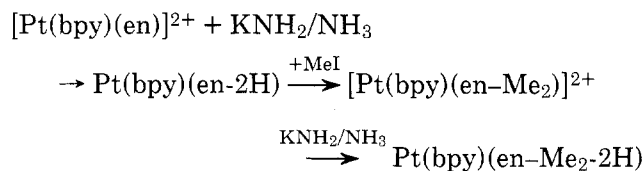
An interesting comparison is seen here with the synthesis of transition-metal alkyls, MR_n.[7-9] The latter are synthesized by metathetic reaction analogous to eq 1 employing either alkyllithium or alkylmagnesium (Grignard) reagents, but are only stable when the alkyl group does not accommodate a kinetically favorable decomposition route involving an initial β-hydride elimination reaction. The analogous decomposition pathway for transition-metal dialkylamides, involving metal hydride and imine formation, is clearly not a dominant factor in their chemistry since they are all thermally stable at room temperature and can be distilled or sublimed under vacuum at more elevated temperatures.

The successful preparation of transition-metal dialkylamides according to eq 1 is limited and is not applicable to the later transition metals. Indeed, for Mn, Fe, Co, Ni, and Cu stable compounds of the type $M(NR_2)_n$ have not been isolated. Instead the reactions lead to the formation of diiminato complexes of the type shown below (M = Co, Ni, Cu.[34]). Thus there appears
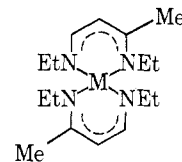
to be a reluctance for the later transition metals to form stable $M-NR_2$ bonds. This is in sharp contrast to the preparation of stable $M-C(alkyl)$ bonds. For example, the compounds $[Me_3PtX]_4$[35] were the earliest examples of stable transition-metal alkyl compounds, whereas $Pt-NR_2$ bonds are formed and are stable only under severe conditions:[36,37]

$$[Pt(bpy)(en)]^{2+} + KNH_2/NH_3$$

$$\rightarrow Pt(bpy)(en\text{-}2H) \xrightarrow{+MeI} [Pt(bpy)(en\text{-}Me_2)]^{2+}$$

$$\xrightarrow{KNH_2/NH_3} Pt(bpy)(en\text{-}Me_2\text{-}2H)$$

The trends apparent in $M-NR_2$ stability may be rationalized in terms of the bonding properties of the dialkylamide ligand, $^-NR_2$, which acts as both a two-electron σ donor and a two-electron π donor (see later). Thus it should form stronger bonds with early transition metals containing vacant d orbitals (π-acceptor metals) than with later transition metals which are electron rich (π-donor metals).

Reaction 1 employing $LiN(SiMe_3)_2$ has been successful in preparing a complete series of first row transition-metal disilylamides.[38-42] This synthetic procedure has also been extended to the successful synthesis of several disilylamides of the lanthanides.[43,44] The more general application of eq 1 involving the disilylamido ligand, $^-N(SiMe_3)_2$, may be due, at least in part, to the different electronic properties of this ligand relative to $^-NR_2$.

Finally two other synthetic aspects of eq 1 should be noted. First, this reaction does in some cases lead to a change in valency state of the metal. For example, the reaction between $MoCl_5$ and $LiNMe_2$ leads to a mixture of $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$. This type of valence change is also observed in metal alkyl synthesis, e.g.,[45,46] in the preparation of Mo_2R_6 from $MoCl_5$ and LiR. Second, although the reaction $TaCl_5$ with $LiNMe_2$ (5 equiv) leads only to $Ta(NMe_2)_5$, the reaction of other lithium dialkylamides leads to the unusual imido or nitrene compounds $Ta(NR_2)_3(NR)$.[21,47] Again an in-

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teresting comparison with transition-metal alkyl chemistry is seen, cf.[48] the recent preparation of $TaMe_5$ and the alkylidene complexes $Ta(CH_2R)_3(CHR)$ [R = $C(CH_3)_3$].

Coordination Properties

Dialkylamides. The coordination properties of a transition-metal dialkylamide are largely determined by the steric requirements of the specific dialkylamide and further by its ability to form both σ and π bonds with the metal. Even the smallest dialkylamido ligand, NMe_2, is sterically demanding and gives rise to discrete monomeric four-coordinated metal complexes, $M(NMe_2)_4$, where M = Ti, V, and Mo. The tetrakis-(dimethylamide) of Zr(IV) does show a tendency to polymerize in solution, and it is fairly certain that the dimethylamides of Zr(IV) and Hf(IV) do not contain four-coordinated metals in the crystalline state. Whether or not this polymerization leads to five- or six-coordinated metals is not yet known. However, the ability of second- and third-row transition metals to coordinate more than four $^-NMe_2$ ligands has been confirmed by single-crystal x-ray diffraction studies for both $Nb(NMe_2)_5$ and $W(NMe_2)_6$. For $Nb(NMe_2)_5$ and $Nb(piperidide)_5$ the NbN_5 moiety approaches a square-pyramidal structure (absolute C_{2v} symmetry).[49] Although $Ta(NMe_2)_5$ is isomorphous with $Nb(NMe_2)_5$, the closely related diethylamide $Ta(NEt_2)_5$ has been found[50] to adopt a TaN_5 trigonal-bipyramidal structure. The change in MN_5 structure on going from NMe_2 to NEt_2 probably arises because the D_{3h} structure is favored on steric grounds.[51] With higher homologues NR_2 (R = Et, n-Pr, n-Bu, etc.) the predominant products from eq 1 involving MCl_5 (M = Nb and Ta) are $Nb(NR_2)_4$[19,20] and $Ta(NR_2)_3NR$,[21] respectively. This implies a greater stability of covalent Nb(IV) relative to Ta(IV) and a greater tendency of the 5d element to form a stable imido double bond, Ta=NR, and of course reflects the importance of steric considerations.

The structure of $W(NMe_2)_6$, shown in Figure 1, contains a regular WN_6 octahedron.[33] The $W-NC_2$ units are all planar and so arranged to give three mutually perpendicular planes involving *trans*-$C_2N-W-NC_2$ units. Thus the $W(NC_2)_6$ moiety belongs to the symmetry point group T_h. In this configuration tungsten attains an 18-electron valence shell as a result of forming six N–W σ bonds and three N–W π-bonds. The latter are completely delocalized over the WN_6 moiety, leading to an average W–N bond order of 1.5; cf. $W(CO)_6$. There is also a triply degenerate, essentially nonbonding molecular orbital arising from the remaining six $^-NMe_2$ π electrons. The recently reported[52] photoelectron spectrum of $W(NMe_2)_6$ supports this bonding scheme. $W(NMe_2)_6$ is clearly a very sterically congested molecule, and it is not surprising that $W(NR_2)_6$ compounds have not been isolated for higher homologues, e.g., for NMeEt and NEt_2. For the latter, either reduced tungsten species such as $W_2(NR_2)_6$[30–32] or imido compounds $W(NR_2)_2(NR)_2$[53] have been obtained.
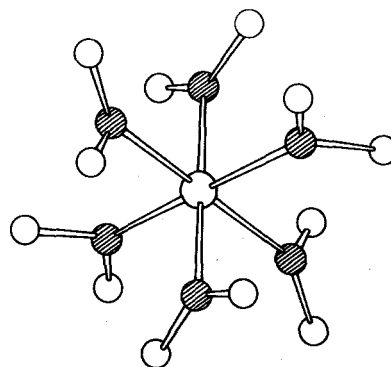
Figure 1. Molecular structure of $W(NMe_2)_6$. The molecule has T_h symmetry. W–N, 2.03 Å; N–C, 1.51 Å; C–N–C angle, 104.9°.

The planarity of the $M-NC_2$ units and the somewhat short M–N bond lengths observed for $Nb(NMe_2)_5$ and $W(NMe_2)_6$ provide an indication of the importance of nitrogen to metal π bonding. Further evidence for nitrogen to metal π bonding is seen in the properties of the paramagnetic monomeric compounds $V(NMe_2)_4$[54–56] and $Nb(NEt_2)_4$[20] and the diamagnetic monomeric compounds $Mo(NR_2)_4$,[29] where R = Me and Et. The d^1 metal ions [V(IV) and Nb(IV)] show ESR spectra indicative of an orbital singlet ground state and axial symmetry, $g_\| < g_\perp$, which is consistent with the unpaired electron residing in the $d_{x^2-y^2}$ orbital (b_1) in a field of D_{2d} symmetry. The diamagnetic monomeric nature of $Mo(NMe_2)_4$ is particularly striking since it is clearly incompatible with a d^2 ion in a regular tetrahedral field. However, this diamagnetism can be readily understood by a consideration of the consequences of N–Mo π bonding. If we assume that the $Mo-NC_2$ units are planar, then the highest symmetry for the $Mo(NC_2)_4$ moiety is D_{2d}. There are in fact two such arrangements. These differ with respect to the transformation properties of the $^-NMe_2$ π bonding orbitals: one configuration leads to $A_1 + B_2 + E$ and the other to $A_2 + B_2 + E$. In D_{2d} symmetry the metal valence orbitals transform as $A_1(s,p_z,d_{z^2})$, $B_1(d_{x^2-y^2})$, $B_2(d_{xy})$, $E(p_x,p_y)$, and $E(d_{xz},d_{yz})$. Thus in one D_{2d} configuration molybdenum can form four σ bonds ($A_1 + B_2 + E$) and four π bonds ($A_1 + B_2 + E$), leaving the $d_{x^2-y^2}$ of B_1 symmetry completely nonbonding and containing both electrons. In this manner molybdenum attains an 18-valence shell of electrons. In a directly analogous manner, the bonding in $M(NR_2)_4$ where M = V and Nb can be considered to give rise to a nonbonding $b_1{}^1$ orbital ground state. It is unfortunate that at this time there are no detailed x-ray structural data on these interesting monomeric $M(NMe_2)_4$ compounds.

The dimethylamides and diethylamides of Ti(III),[57–59] V(III),[57] and Cr(III)[22,24] appear to exist in a dimeric form in solution. They are, however, relatively unstable. They are readily oxidized and also undergo valence disproportionation under vacuum at relatively mild temperatures to yield the volatile stable quadrivalent metal dialkylamides as indicated by eq 2.

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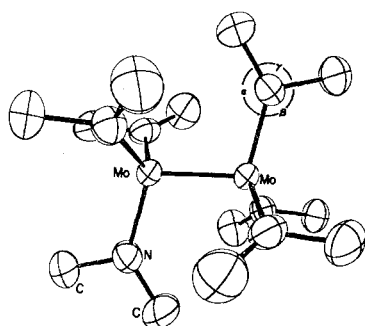
Figure 2. Molecular structure of $Mo_2(NMe_2)_6$. The molecule has S_6 symmetry. Mo–Mo, 2.142 (2) Å; Mo–N, 1.98 (1) Å; N–C, 1.48 (2) Å; Mo–Mo–N angle, 103.7 (3)°; α, 133 (1)°; β, 116 (1)°; $\gamma = 110$ (1)°.

$$(R_2N)_2M \overset{\displaystyle R_2 \atop \displaystyle N}{\underset{\displaystyle N \atop \displaystyle R_2}{}} M(NR_2)_2 \longrightarrow [M(NR_2)_2]_n + M(NR_2)_4 \quad (2)$$
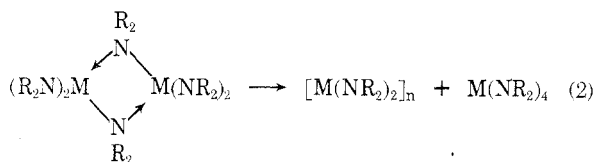
Similar behavior has been observed for chromium(III) alkyls[60] and tertiary alkoxides[61] in which chromium cannot attain six-coordination due to the steric requirements of bulky ligands. There is no doubt that four-coordinated Cr(IV) is stabilized by bulky ligands in nonaqueous systems.

In sharp contrast to the unstable Cr(III) dialkylamides, the dialkylamides of Mo(III)[26-28] and W(III)[30-32](NMe_2, NMeEt, and NEt_2) are volatile diamagnetic dimeric compounds of considerable thermal stability. Dimerization occurs by metal–metal triple bond formation in the absence of bridging $^-NR_2$ ligands. The structures of $M_2(NMe_2)_6$, where M = Mo[27,28] and W,[30,31] are virtually identical; the structure of $Mo_2(NMe_2)_6$ is shown in Figure 2. The $M_2(NC_2)_6$ skeletons have virtual S_6 symmetry, differing little from D_{3d}. The M–M distances are very short, 2.214 (2) Å, M = Mo, 2.294 (1) Å, M = W, and the M_2N_6 moiety is staggered (D_{3d}). These observations together with the observed diamagnetism form the basis for the claim that there exists an M–M triple bond. The M–NC_2 units are all planar, and the M–N distances are somewhat short. This again suggests the existence of N–M π bonding, and it is perhaps this interaction which accounts for the significantly longer Mo–Mo distance in $Mo_2(NMe_2)_6$ (2.214 (2) Å) relative to that in $Mo_2(CH_2SiMe_3)_6$ (2.167 Å) since N–Mo π bonding populates what are effectively δ and δ^* orbitals with respect ot M–M bonding. In the S_6 ground state the $M_2(NMe_2)_6$ molecules have six proximal and six distal methyl groups with respect to the triple bond. This distinction between proximal and distal methyl groups is apparent in the variable-temperature ^1H NMR spectra. At room temperature and above a single resonance is observed, but below −30° two resonances appear in the integral ratio 1:1 separated by 2 ppm. This clearly indicates the temperature-dependent rate of proximal and distal methyl exchange and the large diamagnetic anisotropy associated with the M–M triple bond.[62]

It has not been possible to substitute four very ster-
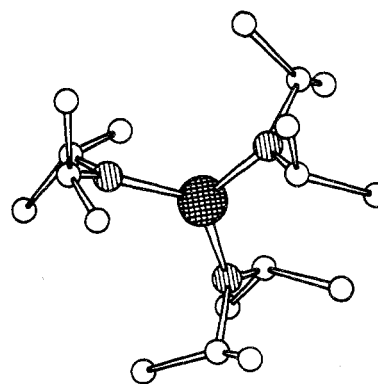
Figure 3. Molecular structure of $Cr[N(CHMe_2)_2]_3$. Cr–N, 1.841 (9), 1.884 (8), 1.882 (9) Å; N–C, 1.516 (12), 1.484 (11), 1.491 (13), 1.468 (11), 1.473 (11), 1.465 (10) Å; N–Cr–N angles, 120.7 (4), 118.6 (4), 120.7 (4)°; Cr–N–C angles, 115.9 (4), 129.4 (5), 122.3 (4), 123.2 (5), 128.0 (4), 115.9 (5)°.

ically demanding diisopropylamido groups around a first-row transition metal. However, the use of this extremely bulky group did allow us to isolate[23] a discrete three-coordinated Cr(III) compound, $Cr(N-i-Pr_2)_3$, which, being a coordinatively unsaturated molecule, was extremely reactive (see later) but was thermodynamically stable with respect to disproportionation of the type previously described by eq 2. The structure of this interesting molecule deduced[63] from x-ray studies is shown in Figure 3. The CrN_3 moiety is planar, as are the $CrNC_2$ units. The $Cr(NC_2)_3$ moiety adopts a propeller arrangement, D_3 molecular symmetry, with Θ, the dihedral angle between the NC_2 planes and the Cr–N_3 plane, equal to 71°. This configuration probably arises from a compromise of steric and electronic factors. N to Cr π bonding is maximized from $\Theta = 0°$, which is clearly the most unfavorable geometry from steric considerations. This situation is akin to that observed for triarylcarbonium ions[64] and triarylboranes.[65]

The characterization of three-coordinated Cr(III) leads us to speculate on whether the use of appropriately bulky NR_2^- ligands will allow the isolation of three-coordinated Mo(III) and W(III) compounds. This possibility has not yet been fully investigated, although from a small amount of sublimate obtained from the reaction between $MoCl_3$ and $LiNSi_2Me_6$, a base peak MoL_3^+ together with cluster species $M_2l_3^+$ and $M_3L_3^+$ (L = NSi_2Me_6) was observed[66] in the mass spectrum.

Bis(trimethylsilylamido) Compounds. Burger and Wannagat[38,39] originally reported the preparation of a number of binary metal compounds with the very bulky "silazane" ligand $N(SiMe_3)_2$, e.g., ML_3 (M = Al, Ga, Cr, and Fe), ML_2 (M = Be, Mn, Co, Ni, Zn, Cd, and Hg), ML (M = Li, Na, and Cu). It is reasonably certain that the ML_2 compounds contain two-coordinated metals and that in ML_3 compounds the metals are three-coordinated. More recently Bradley and co-workers[40-42] have isolated some additional three-coordinated species of the transition metals (M = Sc, Ti, and V) and of the lanthanides[43] (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb, and Lu) and YL_3. Single-crystal x-ray analysis has shown that the three-coordinated compounds exhibit

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either trigonal-planar MN_3 units akin to that observed[67] for $Cr(N\text{-}i\text{-}Pr_2)_3$ (M = Ti, V, Cr, Fe, Al, In)[68,69] or pyramidal MN_3 (Sc, Eu, Yb).[70] In the pyramidal molecules the metal atoms are displaced by approximately 0.3–0.4 Å from the N_3 plane. The reason for this structural difference is not yet clear, but it does appear that the more covalently bonded compounds have the trigonal-planar configuration. Moreover dipole moment measurements suggest that in solution the lanthanide disilylamides are planar. The isomorphous series ML_3 (M = Ti, V, Cr, and Fe) is of a particular interest for ligand field studies (d^1, d^2, d^3, and d^5 configurations), and detailed spectroscopic and magnetic studies have been carried out showing a substantial crystal-field stabilization of the d electrons occurs.[71] However, the silylamido ligand is not high in the nephelauxetic series, and the Fe(III) compound is high spin.

The isolation of discrete three-coordinated lanthanide ions provides a prime example of the role of steric hindrance in determining coordination number. Typical coordination numbers for these large ions are 8, 9, and 10 though 6, 7, and 12 are also known.[72] Owing to the strong nucleophilic nature of the $^-N(SiMe_3)_2$ anion, the nitrogen–lanthanide bond might be expected to be considerably more covalent than other ligand–lanthanide bonds, which are generally considered to be of rather ionic nature. Consequently, the effect of the ligand field on the f orbital levels should be unusually great. The trigonal symmetry of these molecules will yield a very small axial ligand field (z) and a large ligand field in the perpendicular plane (xy), defining the C_3 axis to be coincident with the z axis. The combination of high molecular symmetry and a large ligand field splitting should result in the observation of a few, well-separated maxima corresponding with a particular $^{2S+1}L_J$ excited state in their electronic absorption spectra, instead of the broad envelope which is often observed (particularly in aqueous solution spectra). This is indeed the situation. The spectra of these compounds also show intense absorption bands at ca. >25,000 cm^{-1} which are probably associated with ligand to lanthanide charge transfer. Consistent with this formulation is the observation that for Eu, Yb, and Sm, whose dipositive states are particularly stable, this band is shifted to lower energy, e.g., for Eu this band commences at ca. 16,000 cm^{-1}.

Attempts to synthesize ML_4 compounds have not yet succeeded, and $MClL_3$ compounds (M = Ti, Th) were obtained instead.[73,74] The NMR spectra showed that in the titanium compound the silylamide ligands are locked into a conformation in which the two $SiMe_3$ groups on each ligand are nonequivalent due to restricted rotation about the Ti–N bond, but in the thorium compound there is free rotation on the NMR time scale.

Additional unusual compounds have been obtained with the silylamide groups augmented by other neutral donor ligands. For example, the three-coordinated Mn(II) compound $Mn[N(SiMe_3)_2]_2$ (THF) has been characterized[75] by x-ray single-crystal analysis and electron spin resonance studies. By contrast, the chromium(II) bis(silylamide) took up two molecules of tetrahydrofuran, giving $Cr[N(SiMe_3)_2]_2(THF)_2$ with a trans square-planar configuration.[76] Not surprisingly both the chromium(II) and manganese(II) were in the high spin state. Some interesting compounds were also obtained using triphenylphosphine as the additional ligand. From the reaction of $CoCl_2[P(C_6H_5)_3]_2$ a very reactive green crystalline three-coordinated Co(II) complex was isolated, $Co[N(SiMe_3)_2]_2[P(C_6H_5)_3]$, while under comparable conditions the analogous nickel(II) salt gave a reactive yellow crystalline three-coordinated Ni(I) complex, $Ni[N(SiMe_3)_2][P(C_6H_5)_3]_2$.[77] In the latter case there must be a fine balance between electronic and steric factors, resulting in this unique type of compound. No doubt the phosphine is a better π-acceptor ligand than the silylamide and helps to stabilize the lower valency nickel. A number of other alkylarylphosphines also promote the formation of the three-coordinated nickel silylamide–bis(phosphine). Presumably steric hindrance of the bulky ligands prevents the formation of square-planar metal bis-(silylamide)–bis(phosphine) complexes. However, a relatively stable orange crystalline Co(I) complex, $Co[N(SiMe_3)_2][P(C_6H_5)_3]_2$, has recently been synthesized[78] starting from $CoCl[P(C_6H_5)_3]_3$.

Another example of a phosphine-stabilized low-coordinated metal silylamide is the gold(I) compound $Au[N(SiMe_3)_2](PMe_3)$.[79] We have also prepared[78] the diamagnetic Cu(I) complex $Cu[N(SiMe_3)_2][P(C_6H_5)_3]_2$, giving a series d^8, d^9, d^{10}.

2,5-Dimethylpyrrole Compounds. It seemed desirable to investigate other bulky uninegative N-donor ligands besides $N\text{-}i\text{-}Pr_2$ and $N(SiMe_3)_2$, particularly bearing in mind the greater versatility of the silylamido ligand. Although both of these ligands are bulky, they should differ considerably in electronic behavior. Thus the diisopropylamido group can be both a σ-donor and π-donor ligand, whereas the bis(trimethylsilylamido) group is potentially a σ donor, a weaker π donor due to N_π–Si_π interactions, and possibly a weak π acceptor using the vacant π-antibonding NSi_2 orbital. (It is probably this difference which has allowed the isolation of stable silylamido but no dialkylamido compounds of the later transition elements.) It occurred to us that the 2,5-dimethylpyrrolyl group might to a certain degree mimic the silylamido ligand rather than the diisopropylamido group, and accordingly the lithio derivative was used[80] in reactions with nickel(I) and nickel(II)

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chloride–triphenylphosphine complexes. We isolated $Ni(NC_6H_8)[P(C_6H_5)_3]_2$ as lime-green reactive crystals. This Ni(I) compound was paramagnetic and gave an ESR signal corresponding to an axially symmetric d^9 species. The Ni(II) complex $Ni(NC_6H_8)_2[P(C_6H_5)_3]$ was a purple diamagnetic crystalline compound which was relatively stable and gave a parent molecular ion in the mass spectrum. It therefore seems likely that the bulky 2,5-dimethylpyrrole ligand will also have considerable scope in stabilizing unusual coordination numbers and unusual valency states for the transition metals.

Reactions

Transition-metal dialkylamides are reactive toward protic substrates, readily eliminating amine according to eq 3.[81]

$$M(NR_2)_n + nHL \rightarrow ML_n + nHNR_2 \qquad (3)$$

$$L = halogen, OH, OR, SR, etc.$$

Alcoholysis reactions of this type have often been employed in the synthesis of metal alkoxides when other procedures are inapplicable, as is the case, for example, in the synthesis of $V(OR)_4$[18] and $M(OR)_3$ where M = Mo[26] and W.[32] Reaction 3 is, however, sometimes accompanied by a change in the valency of the metal. For example, $Cr(NEt_2)_4$ reacts[25] with primary and secondary alcohols according to eq 4. Only tertiary alcohols and trialkylsilanols,[61] which are not susceptible to this type of oxidation, and the sterically demanding 3,3-dimethyl-2-butanol[82] are known to give chromium(IV) alkoxides.

$$2Cr(NEt_2)_4 + 7RR'CHOH$$
$$\rightarrow 2Cr(OCHR'R)_3 + RR'CO + 8HNEt_2 \qquad (4)$$
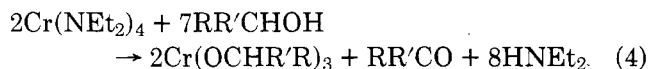
$$R' = H \text{ or alkyl}$$

Cyclopentadiene has been found to react with $M(NMe_2)_4$, where M = Ti, Zr, and Hf, to give partially substituted complexes $(\eta^5\text{-}C_5H_5)M(NMe_2)_3$ and $(\eta^5\text{-}C_5H_5)_2M(NMe_2)_2$. With $V(NMe_2)_4$[57] and $Cr(NEt_2)_4$[25] partially substituted species were not isolated, but reaction proceeded further with reduction of the metal and formation of the sandwich compounds $(\eta^5\text{-}C_5H_5)_2M$.

The scope of eq 3 has been very systematically explored by Lappert and co-workers with special reference to the reactivity of the $Sn\text{-}NR_2$ bond but with some extension to reactions of $M(NR_2)_4$ where M = Ti, Zr, and Hf.[83-86] Some interesting tetrakis(Schiff base) complexes, TiL_4[87] and ZrL_4,[88] have been made.

Another general class of reaction is the so-called insertion reaction which may be represented by eq 5.

$$L_xM(NR_2)_y + yA{=}BC \rightarrow L_xM[AB(CNR_2)]_y \qquad (5)$$
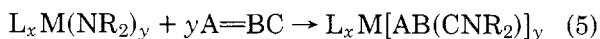
N,N-dialkyldithiocarbamates of the early transition
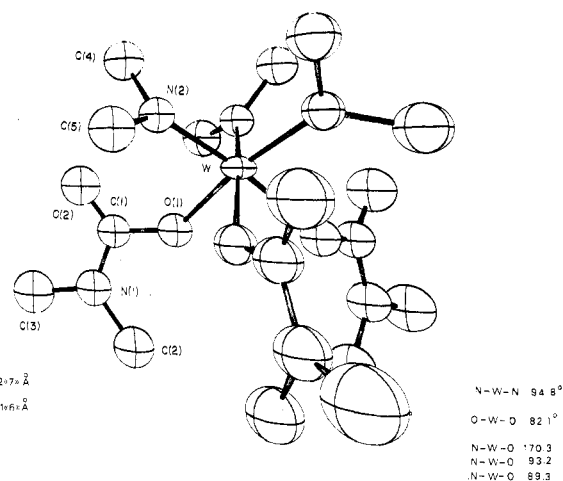

Figure 4. Molecular structure of $W(NMe_2)_3(O_2CNMe_2)_3$. The molecule has C_3 symmetry. W–N (2), 1.922 (7) Å; W–O (1), 2.041 (6) Å; N–W–N angle, 94.8°; O–W–O angle, 82.1°; N–W–O angles, 170.3, 93.2, 89.3°.

W-N(2) 1.922(7) Å
W-O(1) 2.04 1(6) Å

N-W-N 94.8°
O-W-O 82.1°
N-W-O 170.3
N-W-O 93.2
N-W-O 89.3

elements were first made[89,90] by the insertion of carbon disulfide into $M\text{-}NR_2$ bonds. One limit of this reaction arises from the susceptibility of the dithiocarbamato ligand toward oxidation. Thus the dialkylamides of Cr(IV),[25] Nb(V),[90] and W(VI)[53] react with CS_2 to give dithiocarbamato complexes of Cr(III), Nb(IV), and W(IV), respectively. Tetraalkylthiuram disulfides were formed as the oxidized organic products. A notable exception to the general insertion of CS_2 into $M\text{-}NR_2$ bonds is found in the monomeric three-coordinate compound $Cr(N\text{-}i\text{-}Pr_2)_3$ which does not react with CS_2, but does react with CO_2.[91]

Similar insertion reactions occur with COS and CO_2. The N,N-dialkylcarbamato ligand, $^-O_2CNR_2$, is much less susceptible to oxidation, and, carbamato compounds of Nb(V)[92] and W(VI)[93] have been isolated. It is particularly interesting to note that the reaction between $W(NMe_2)_6$ and CO_2 leads to a partially inserted product $W(NMe_2)_3(O_2CNMe_2)_3$,[93] even in the presence of excess CO_2. The structure of this tungsten compound, shown in Figure 4, together with the observations outlined below provide the basis for some mechanistic insight into the reactivity of transition metal dialkylamides.

The high chemical reactivity of transition-metal dialkylamides might lead one to believe that the M–N bonds are weak and have a tendency toward ionic character, $M^+NR_2^-$. However, the physical properties of these compounds, which show considerable thermal stability and volatility, strong infrared and Raman-active bands, short metal–nitrogen bond distances, and planar nitrogens, suggest otherwise.[81] Furthermore, based on thermochemical studies, Bradley and Hillyer[94] estimated the value of $\bar{D}(Ti\text{-}N)$ of $\sim$73 kcal/mol in $Ti(NEt_2)_4$. Nevertheless the reactivity in solution could be due to the facile initial ionic dissociation 6.

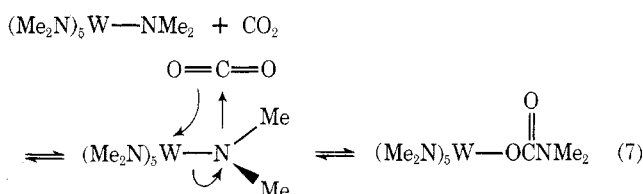$$M(NMe_2)_n \rightleftharpoons [M(NMe_2)_{n-1}]^+NMe_2^- \qquad (6)$$
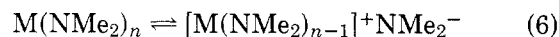
Such a step could form the basis for proton-exchange reactions of type 3 and insertion reactions of type 5. In

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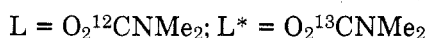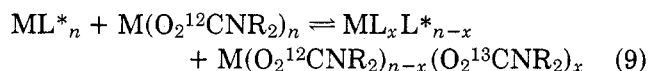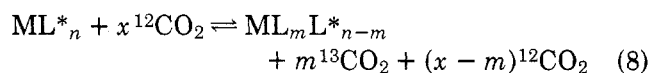(88) D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *Chem. Commun.*, 368 (1970).

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an attempt to define the mode of reactivity of transition-metal M–NR$_2$ bonds, Chisholm and Extine[53] have studied extensively the reactions of W(NMe$_2$)$_6$. This is an extremely crowded molecule, as is seen in Figure 1, and on the basis of both electronic and steric considerations is expected to be the transition-metal dialkylamide most likely to react via a dissociative mechanism of type 6. However, W(NMe$_2$)$_6$ was found[53,95] to react with alcohols ROH to give W(OR)$_6$ much more slowly than with CO$_2$ to give W(NMe$_2$)$_3$(O$_2$CNMe$_2$)$_3$. Furthermore W(NMe$_2$)$_6$ and HN(CD$_3$)$_2$ did not react to give amine exchange under comparable conditions. Thus it seems that even for W(NMe$_2$)$_6$ a dissociative step (eq 6) is not operative. For reactions represented by eq 3 and 5 mechanisms involving initial protonation (eq 3) and electrophilic attack (eq 5) of the NR$_2$ lone pair with or without concomitant nucleophilic attack at the metal seem most plausible. Thus for the reaction between W(NMe$_2$)$_6$ and CO$_2$ we envisage an initial step, (7), leading to a monodentate carbamato ligand.

$$(Me_2N)_5W\text{---}NMe_2 \ + \ CO_2$$

$$\rightleftharpoons (Me_2N)_5W\text{---}N\overset{Me}{\underset{Me}{\diagdown}} \ \rightleftharpoons \ (Me_2N)_5W\text{---}O\overset{O}{\overset{\|}{C}}NMe_2 \quad (7)$$

The weaker π-donating oxygen atom leads to enhanced N–W π bonding in the trans position. Further insertion occurs via electrophilic attack on one of the electron-rich nitrogens cis to the initial site of insertion, leading ultimately to W(NMe$_2$)$_3$(O$_2$CNMe$_2$)$_3$. The *fac*-WN$_3$O$_3$ geometry allows for maximum N–W π bonding, as evidenced by the very short W–N bond lengths, 1.922 (7) Å, in W(NMe$_2$)$_6$. The nucleophilicity of the dimethylamido lone pairs in W(NMe$_2$)$_3$(O$_2$CNMe$_2$)$_3$ is thus diminished, and further insertion of CO$_2$ is not favored. The reaction between W(NMe$_2$)$_6$ and CO$_2$ provides a prime example of the role of trans influence[96] in determining both the stereochemistry and the mode of reaction in a transition metal complex.

Recently we have found[97] that early transition-metal *N,N*-dialkylcarbamato compounds are labile toward CO$_2$ exchange reactions of the type represented by eq 8 and 9.

$$ML^*_n + x\,^{12}CO_2 \rightleftharpoons ML_mL^*_{n-m}$$
$$+ m\,^{13}CO_2 + (x-m)^{12}CO_2 \quad (8)$$

$$ML^*_n + M(O_2\,^{12}CNR_2)_n \rightleftharpoons ML_xL^*_{n-x}$$
$$+ M(O_2\,^{12}CNR_2)_{n-x}(O_2\,^{13}CNR_2)_x \quad (9)$$

$$L = O_2\,^{12}CNMe_2; \ L^* = O_2\,^{13}CNMe_2$$

Arguments have been presented[97] which support the view that these CO$_2$ exchange reactions proceed via a facile initial deinsertion step (expulsion of CO$_2$) as represented by eq 10. However, this remains to be established unequivocally.
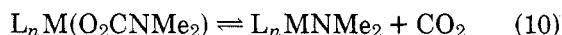
$$L_nM(O_2CNMe_2) \rightleftharpoons L_nMNMe_2 + CO_2 \quad (10)$$
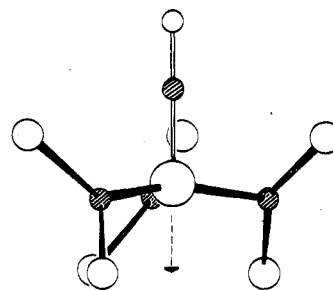
Figure 5. Molecular structure of Cr(NO)[N(SiMe$_3$)$_2$]$_3$. The molecule has C_3 symmetry. Cr–Nn, 1.738 (20) Å; Cr–Ns, 1.790 (10) Å; N–Si, 1.701 (12), 1.739 (13) Å; N–O, 1.191 (28) Å; Ns–Cr–Nn angle, 99.0°. The CrNSi$_2$ group is planar to within 0.05 Å and makes a dihedral angle of ca. 35° with the ONnCrNs plane.

Finally it should be noted that many other insertion reactions (e.g., involving cyanides, isocyanides, acetylenes, ketones, etc.) have been observed by Lappert and co-workers, especially for insertion reactions involving Sn–NR$_2$ bonds.[98–100] It seems likely that many of these insertion reactions could be extended to transition-metal dialkylamides.

Dialkylamides of transition metals in lower valency states are extraordinarily sensitive to oxygen. It is possible that peroxo and superoxo compounds are formed initially by addition of molecular oxygen, but the instability of such derivatives poses problems and hazards in characterizing them. Thus under certain conditions the highly reactive chromium tris(diisopropylamide), Cr(N-*i*-Pr$_2$)$_3$, formed[91,101] a 1:1 adduct, Cr(O$_2$)(N-*i*-Pr$_2$)$_3$, which may be a peroxochromium(V) compound. However, at low temperature the uptake of oxygen corresponds to CrO$_3$(N-*i*-Pr$_2$)$_3$, a dangerously explosive compound.[91] With nitric oxide Cr(N-*i*-Pr$_2$)$_3$ reacted[102] to give the diamagnetic Cr(NO)(N-*i*-Pr$_2$)$_3$, which provides a rare example of pseudotetrahedral four-coordinate chromium(II). The stability of the Cr–NO moiety was evident from reaction of Cr(NO)-(N-*i*-Pr$_2$)$_3$ with *tert*-butyl alcohol, which gave CrNO)-(OBu-*t*)(N-*i*-Pr$_2$)$_2$ and Cr(NO)(OBu-*t*)$_3$ without loss of NO.

Reactions of transition-metal disilylamides have been less extensively studied. They are susceptible to hydrolysis and other reactions of type 3. However, they appear less susceptible toward insertion reactions. For example, Cr(NSi$_2$Me$_6$)$_3$ does not react[91] with CO$_2$ and CS$_2$. This observation may well reflect the weaker nucleophilic properties of the $^-$NSi$_2$Me$_6$ ligand. Many of the lower valent transition-metal silylamides are extremely reactive toward molecular oxygen and presumably would show reactivity toward other small unsaturated molecules. For example, Cr(NSi$_2$Me$_6$)$_3$ forms[102] a diamagnetic 1:1 adduct with NO, the structure of which is shown in Figure 5, akin to Cr(NO)-(N-*i*-Pr$_2$)$_3$ described previously.

In attempting to prepare complexes of lanthanide tris(silylamides) we isolated[103] in the course of reactions involving triphenylphosphine oxide and La(NSi$_2$Me$_6$)$_3$

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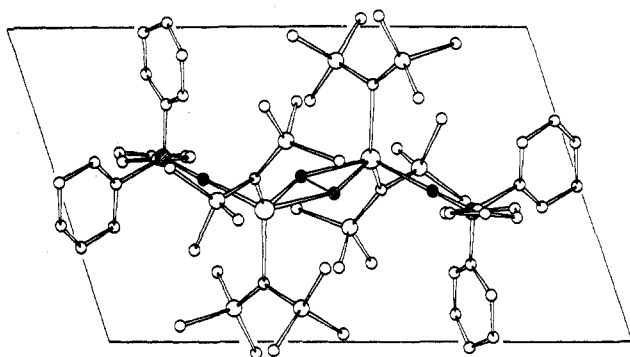
Figure 6. Molecular structure of $La_2(O_2)[N(SiMe_3)_2]_4(OPPh_3)_2$. La–O (peroxide), 2.33, 2.35 Å; La–O (phosphine oxide), 2.44 Å; La–N, 2.39, 2.40 Å; O–O (peroxide), 1.70 Å.

a remarkable new μ-peroxo complex, $O_2La_2(NSi_2Me_6)_4(OPPh_3)_2$, as well as a four-coordinate complex, $La(NSi_2Me_6)_3(OPPh_3)$. The structure of the μ-peroxo compound is shown in Figure 6. The peroxo group acts as a doubly bidentate bridge between the two lanthanum atoms which are each bonded to two silylamido and one phosphine oxide ligand, giving each lanthanum a coordination number of five. This is the first lanthanide peroxy compound to be characterized and apparently the only known example of a peroxy group acting as a doubly bidentate bridging ligand; cf. as a doubly monodentate ligand in $[(NH_3)_5Co–O–O–Co(NH_3)_5]^{4+}$ [104] and as a bidentate nonbridging ligand in $CrO(O_2)_2(C_5H_5N)$. [105]

Conclusions

We expect that further studies of these and related transition-metal–nitrogen complexes should be extremely rewarding from structural, mechanistic, and synthetic standpoints of coordination chemistry.

The importance of ligand steric hindrance in determining the coordination properties of transition-metal complexes cannot be overemphasized. This view has also been well demonstrated by the work of Tolman[106] and Shaw[107] and in the recent elegant designs of reversible binding of molecular oxygen to iron(II) complexes.[108]

To date homogeneous transition-metal catalysis has been restricted to hydrocarbon systems involving the facile formation and rupture of M–H, M–C, C–H, and C–C bonds. An extension to include M–N, C–N, M–O, and C–O bonds seems plausible and could lead to substantial advances in transition-metal catalysis.

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