ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 26

TRANSITION-METAL ALKOXIDES

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I. Introduction

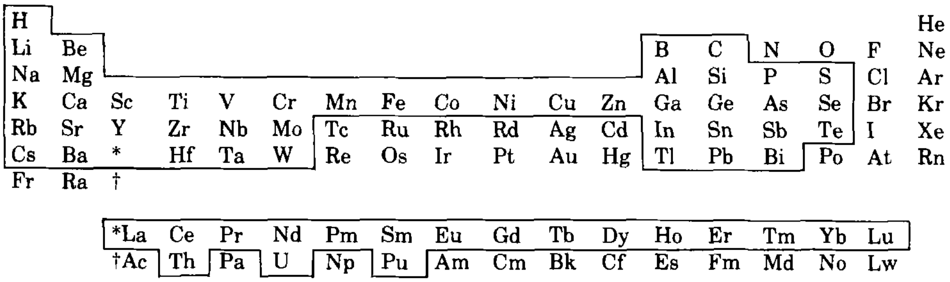
After an early doubtful claim by Demarcay (*1*) in 1875, titanium tetraethoxide was synthesized in 1924 by Bischoff and Adkins (*2*), employing the reaction of titanium tetrachloride with sodium ethoxide in excess ethanol. This was followed by the classical work of Jennings, Wardlaw, and Way (*3*) in 1936, showing that the reaction of titanium tetrachloride with ethanol only resulted in a crystalline compound, $TiCl_2(OEt)_2 \cdot 2EtOH$. Thereafter, progress in the field of alkoxide chemistry of transition metals was slow until 1950, and the only alkoxides of transition metals that appear to have been reported until then

ISBN 0-12-023626-5

were those of tungsten(V) (*4*), vanadyl(III) (*5*), tantalum(V) (*6*), chromium(III) (*7*), iron(III) (*7*), manganese(II) (*8*), and cobalt(III) (*8*).

With the publication of the work on zirconium ethoxide by Bradley and Wardlaw (*9*) in 1950, the knowledge of this interesting class of compounds has grown at a rapid pace, as evinced by the publication of a number of review articles on alkoxides of metals in general (*10*, *11*) and transition metals in particular (*12*). A survey of the rapidly growing literature (about 1200 references) up to 1975 in a recent book *Metal Alkoxides* (*13*) indicates that the alkoxide chemistry of the elements that are placed within the borders in the periodic table had already been studied in some detail by that time. A closer scrutiny reveals that among the transition elements the main focus of attention was on the earlier transition metals (particularly in the d^0 state), except for some work on alkoxides of $3d^{5-9}$ elements, which were investigated mainly from the points of view of their magnetochemistry and electronic spectra (*14*). In contrast to the soluble and volatile alkoxides of earlier transition metals, almost all of the alkoxides of later 3d elements, with the exception of iron(III) alkoxides (*15*) and chromium tetra-*t*-alkoxides (*16*), were found to be insoluble in organic solvents and nonvolatile. There appears to be a surge, particularly since publication of *Metal Alkoxides* (*13*), in research activity in a number of laboratories on the alkoxy derivatives of later transition metals [$3d^{5-9}$ (*17*), Mo, W, Re, Ru, Rh, Pd, and Pt], including the synthesis of a number of soluble and volatile bimetallic alkoxides of later 3d metals. Sterically demanding alcohols have also received special attention for enhancing the kinetic stability of transition-metal alkoxides in general.

Because the literature up to 1975 has already been reviewed (*13*), this chapter is in general limited to the progress made since then in the alkoxide chemistry of 3d, 4d, and 5d metals [4f (*18*) and 5f metals are also excluded], referring to the essential background literature relevant to new advances only.



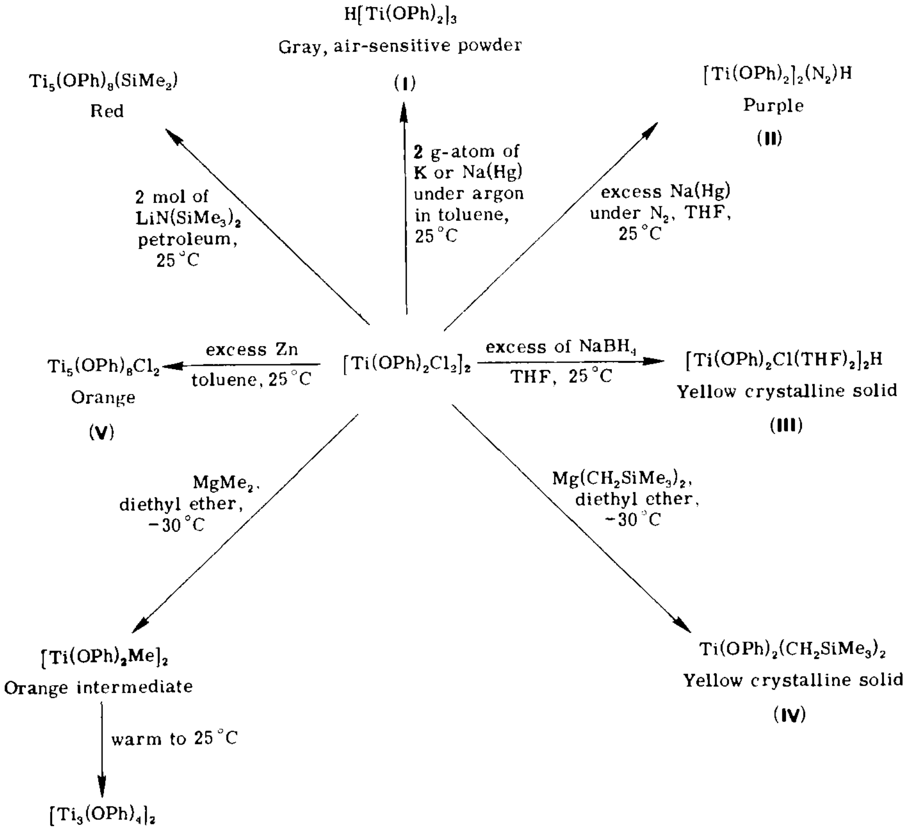
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Rd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	†															

*La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

II. Alkoxy and Allied Derivatives of 3d Metals

A. TITANIUM

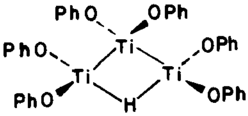
The most significant contribution in this area has been a detailed study (*19*) of titanium diphenoxide dichloride, which has been shown to have the same dimeric structure in solution as in the solid state (*20*). Interest in this compound was renewed by the observation (*21*) that the phenoxide ion can be η-bonded to a metal atom (Ru or Rh) through ring carbon atoms (*21*) rather than through the oxygen atom. Van Tamelen (*22*) reported that the reduction of various alkoxide complexes of titanium, including $Ti(OPh)_2Cl_2$, with sodium naphthalide or potassium under nitrogen gave appreciable quantities of ammonia via an intermediate for which the stoichiometry $Na_3Ti_4N_4(OR)_{10}$ has been



SCHEME 1

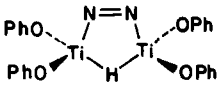
proposed. Although the expectation of the workers (*19*)—to synthesize π-bonded products—was not fulfilled, the results of the reactions of $Ti(OPh)_2Cl_2$ with a number of reducing agents can be summarized, as shown in Scheme 1.

The following tentative structures have been suggested for some of the products in Scheme 1.



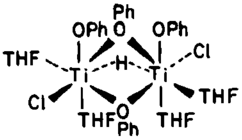
(I)

$H[Ti(OPh)_2]_3(I)$



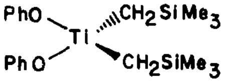
(II)

$[Ti(OPh)_2]_2(N_2)H$



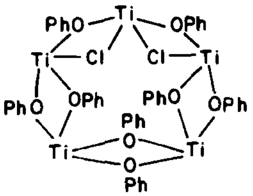
(III)

$[Ti(OPh)_2Cl(THF)_2]_2H$



(IV)

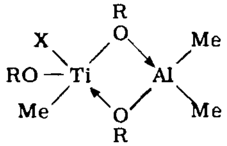
$Ti(OPh)_2(CH_2SiMe_3)_2$



(V)

$Ti_5(OPh)_8Cl_2$

An interesting migration of one methyl group from aluminum to titanium, without reduction of titanium, has been reported (*23*) in the reactions of titanium complexes, $XTi(OR)_3$ [X = η^5-cyclopentadienyl (Cp); R = Et, *i*Pr] with aluminum trimethyl to give bimetallic complexes with alkoxy bridges:

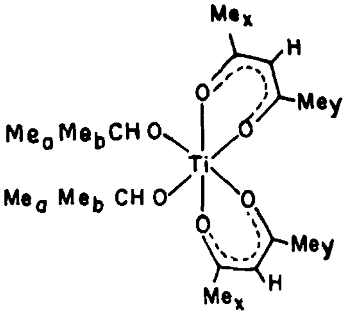


Following the preparation (*24*) of $Ti(OR_f)_4$ and $Zr(OR_f)_4$ by the reactions of anhydrous chlorides with 2,2,2-trifluoroethanol (R_fOH) in the presence of anhydrous ammonia, the preparation of $(Cp)Ti(OR_f)_3$ by the reaction of $(Cp)TiCl_3$ with $LiOR_f$, has been reported (*25*). The reaction of $(Cp)TiCl_3$ with R_fOH itself gave $(Cp)TiCl(OR_f)_2$, which on methylation with LiMe gave $(Cp)(Me)Ti(OR_f)_2$. Synthesis of a series of derivatives $TiX_{4-n}(OR_f)_n$ ($n = 2$ or 3 for X = Cl; $n = 1$ or 2 for X = (O-*i*Pr) and their adducts with RCN (R = Me, Et) and R_fOH has been reported (*26*).

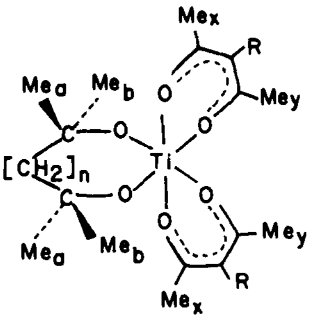
Following a study of the insertion reactions of $Ti(OR)_4$ (*27*) and $(Et_2N)Ti(OR)_3$ (*28*), complexes of the type $CpTi(OR)_{3-n}[N(Ph)COOR]_n$ (R = Et, *i*Pr, *t*Bu; $n = 1, 2,$ or 3) have been synthesized (*29*) by reactions of $CpTi(OR)_3$ with PhNCO.

A number of mixed isocyanatotitanium derivatives, $Ti(O\text{-}i Pr)_{4-n}(NCO)_n \cdot mX$ ($n = 1, 2, 3,$ or 4; X = $MeCO_2$-*i*Pr or MeCN; $m = 0, 1,$ or 2) were prepared (*30*) by the reactions of $Ti(O\text{-}i Pr)_4$ with acetyl isocyanate or by the reactions of $Ti(O\text{-}i Pr)_{4-n}Br_n$ with AgNCO in acetonitrile. Insertion reactions in these complexes were also studied with isopropanol, which yielded the corresponding carbamates. Similarly, the reactions of $M(OR)_4$ (M = Ti, Zr; R = Et, *i*Pr) with pyruvonitrile have been reported (*31*) to yield products of the type $M(OR)_{4-n}(CN)_n \cdot m$MeCOOR ($m = 0, 0.5,$ and 1 when $n = 1, 2,$ and 3, respectively; $m = 1.5$ for Ti and 2 for Zr when $n = 4$). The reactions of metal tetracyanides with isopropanol were also found to yield $Ti(O\text{-}i Pr)_2(CN)_2 i PrOH$ and $Zr_2(CN)_5(O\text{-}i PR)_3 2 i PrOH$.

A variable-temperature NMR study (*32*) of titanium chelates (**I–IV**)



(I)



(II)-(IV)

(II), $n = 1$, R = H; (III), $n = 0$, R = H; (IV), $n = 1$, R = COMe

indicated that distereoisomerism is possible in the diisopropoxy compound (I), but the NMR spectrum indicates the presence of only the cis isomer, as reported previously by Bradley and Holloway (*33*) for titanium and by Saxena *et al.* for zirconium (*34*). For derivatives (I) to (III) a low-temperature NMR study showed anisochronous geminal methyl groups (Me_a and Me_b) and acetylacetonatomethyls (Me_x and Me_y), indicating that metal-centered rearrangement is slow on the NMR time scale. Study of the 3-acetylpentane-2,4-dionato(triac) complex (**IV**) provided information on the problem of bond rupture versus twisting.

Continuing their earlier studies on similar compounds, Bickley and Serpone (*35*) have investigated the configurational rearrangements in *cis*-$Ti(acac)_2XY$ [acac = anion of 2,4-pentanedione, X = Cl or Br, and Y = iC_3H_7O or 2,6-$(iC_3H_7)_2C_6H_3O$]. When Y = O-iC_3H_7, the isopropyl methyl NMR resonance remains a sharp doublet even at −63°C, but diastereotopic splitting was observed when Y = 2,6-$(iC_3H_7)_2C_6H_3O$. It has been suggested on the basis of previous results (*36*) that rearrangements probably occur via twist processes.

Substitution of an OR group by a Cl ligand by the action of HCl on quasi-tetrahedral biscyclopentadienyltitanium complexes of the type (Cp)(Cp')Ti(OR)(OR') has been shown (*37*) to be a stereospecific process that occurs with retention of configuration at titanium. The ligand-exchange reactions of (Cp)(Cp')Ti(OR)Cl with KCNS and of (Cp)(Cp')Ti(OR)NCS with HBr at the chiral titanium atom have also been studied (*38*); both reactions are selective, but only the latter is stereospecific, involving retention at the titanium atom.

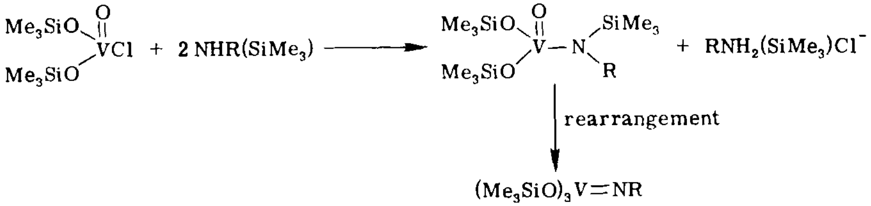
In a number of publications Paul and co-workers (*39*) have investigated the complexation reactions of a number of chloride alkoxides of titanium with ligands such as phthalimide, succinimide, α,α′-dipyridyl, 1,10-phenanthroline, acetonitrile, pyridines, triphenylarsine oxide, dimethylformamide, triphenylphosphine oxide and 2-, 3-, and 4-picoline *N*-oxides and hexamethylphosphoramide.

A number of titanium(IV) and zirconium(IV) complexes of Schiff bases and related ligands have been prepared by reactions with titanium and zirconium isopropoxides in different stoichiometric ratios. They have been characterized by Tandon and co-workers (*40*), using IR and NMR spectroscopy.

B. VANADIUM

Phenylvanadyl complexes, $PhVO(O\text{-}iPr)_2$ and $PhVOCl(O\text{-}iPr)$, have been synthesized (*41*) by stirring $VO(O\text{-}iPr)_2Cl$ with PhLi and $VO(O\text{-}iPr)Cl_2$ with Ph_2Hg in pentane at −50 and −10°C, respectively. Similar attempts to prepare $PhVO(OCH_2CF_3)_2$ have, however, been reported to be unsuccessful.

The novel complexes $(Me_3SiO)_3V{=}NR$ (R = *t*-butyl or 1-adamantyl) have been synthesized (*42*) by the following reactions.



$(Me_3SiO)_2V(O)Cl + 2\,NHR(SiMe_3) \longrightarrow (Me_3SiO)_2V(O){-}N(SiMe_3)R + RNH_2(SiMe_3)Cl^- \xrightarrow{\text{rearrangement}} (Me_3SiO)_3V{=}NR$

R = *t*-butyl or 1-adamantyl

The structure of the adamantyl derivatives has been determined by X-ray crystallography and is represented in Fig. 1; the V—N bond length is extremely short 1.614(2) Å and the V—N—C angle is nearly linear 175.8(2)°, indicating a considerable triple-bond character in V=NR.

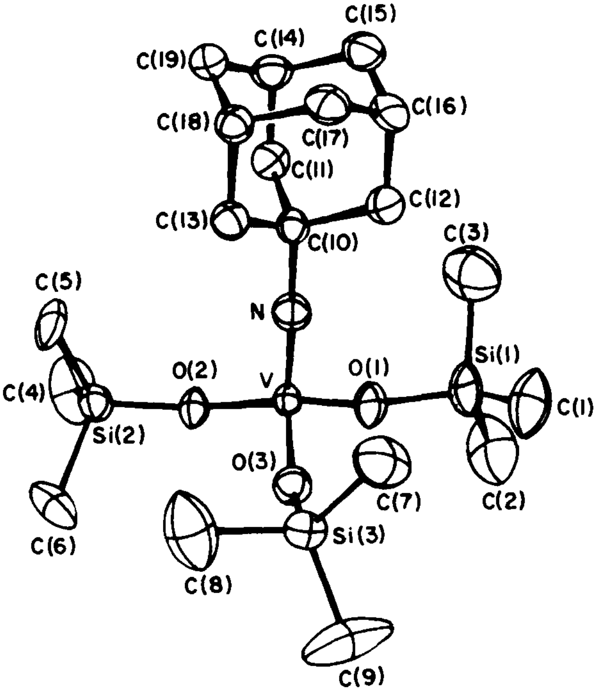


FIG. 1. Structure of $(Me_3SiO)_3V{=}N$(adamantyl).

C. CHROMIUM

Although a number of novel routes involving rather inaccessible starting materials (*43*, *44*) have been employed, the literature on the synthesis of even simple alkoxides of chromium in its most common +3 oxidation state is full of contradictions, and even simple derivatives like $Cr(O\text{-}i\text{Pr})_3$ and $Cr(O\text{-}t\text{Bu})_3$ have not been described until recently. The claim (*7*) for the preparation of $Cr(OEt)_3$ by the simple metathetic reaction between $CrCl_3$ and NaOEt in ethanol could not be confirmed by Brown, Cunningham, and Glass (*45*), who had earlier described (*44*) the synthesis of $Cr(OMe)_3$ and $Cr(OEt)_3$ by photolytic decarboxylation of tricarbonylarenechromiums. These workers (*45*) were, however, able to confirm partially the preparation of the two alkoxides by photolysis of alcoholic solutions of ammonium chromate, which were reported in 1964 by von Hornduff and Kappler (*43*). However, attempts to prepare $Cr(O\text{-}i\text{Pr})_3$ and $Cr(O\text{-}t\text{Bu})_3$ by both of these methods resulted in products with very low carbon and hydrogen analyses, which was ascribed to the instability of these branched alkoxides (*45*). After attempting a number of routes, the best method reported for preparation of $Cr(OPh)_3$ was the irradiation of tricarbonylbenzenechromium in the presence of phenol under oxygen.

In a publication dealing with magnetism and electronic spectra of methoxides and ethoxides of later 3d metals, Adams *et al.* (*14*) used the more plausible (in view of the ease of separation of products) route employing metathesis between LiOMe and $CrCl_3$. $Cr(OEt)_3$ was, however, prepared by these workers also using the method of von Hornduff and Kappler (*43*).

The preparation of primary alkoxides of chromium(III) has been carried out (*46*) successfully using the simple reactions of the $CrCl_3 \cdot 3THF$ adduct (solubility of which in organic solvents provides a distinct advantage) with lithium alkoxides:

$$CrCl_3 \cdot 3THF + 3LiOR \xrightarrow[C_6H_6]{ROH} Cr(OR)_3 + 3LiCl$$
$$R = Me, Et, n\text{Bu}$$

$Cr(O\text{-}i\text{Pr})_3$ and $Cr(O\text{-}t\text{Bu})_3$ could not be prepared by this method; instead, hydrolyzed products were obtained. These latter, branched alkoxides also could not be prepared by the alcoholysis or transesterification reactions of lower alkoxides, even under forcing conditions. $Cr(OPh)_3$ could, however, be synthesized by refluxing $Cr(OEt)_3$ with excess phenol in benzene, removing the ethanol azeotropically with the solvent. This $Cr(OPh)_3$ was found to undergo reaction with excess isopropanol (but not with *t*-butanol), and, on repeating the reaction a number of times, almost pure $Cr(O\text{-}iPr)_3$ could be prepared for the first time as a green, insoluble solid. Interestingly, it was finally possible to synthesize $Cr(O\text{-}tBu)_3$ by the simple reaction of $CrCl_3 \cdot 3THF$ with 3 mol of LiO-*t*Bu (avoiding excess of *t*-butanol) in THF:

$$CrCl_3 \cdot 3THF + 3LiO\text{-}tBu \xrightarrow{THF} Cr(O\text{-}tBu)_3 + 3LiCl$$

$Cr(O\text{-}tBu)_3$, obtained as a soluble product in this reaction, gave volatile $Cr(O\text{-}tBu)_4$, which could be distilled under reduced pressure. The spectrum of this distilled liquid shows bands at 13,870 and 15,700 cm^{-1} and a shoulder at 25,300 cm^{-1}, which can be understood on the basis of a distorted octahedral environment for chromium in $Cr(O\text{-}tBu)_4$, the special stability of which has been explained (*47*) on the basis of two singly occupied lower e_g shells in a tetrahedral environment for chromium. On treatment of $Cr(O\text{-}tBu)_4$ with methanol, ethanol, and isopropanol, $Cr(OMe)_3$, $Cr(OEt)_3$, and $Cr(O\text{-}iPr)_3$ were obtained.

The spectra of primary and secondary alkoxides of chromium(III) are similar and may be interpreted (*46*) on the basis of an octahedral environment for chromium (see Table I).

Primary alkoxides of chromium(III) do not appear to undergo alcoholysis reactions, even under forcing conditions with other (tertiary, secondary, as well as other primary) alcohols. This is rather unusual in view of the usually strong lability of the alkoxy groups exhibited in

TABLE I

ELECTRONIC VISIBLE SPECTRA OF SOME CHROMIUM(III) ALKOXIDES

Product	$^4A_{2g} \rightarrow {}^4T_{2g}$(10 Dq) ($cm^{-1}$)	$^4A_{2g} \rightarrow {}^4T_{1g}$ (cm^{-1})	*B* (cm^{-1})
$Cr(OMe)_3$[a]	17,610	24,150	612
$Cr(OEt)_3$[a]	17,000	23,470	600
$Cr(O\text{-}tBu)_3$[a]	17,060	23,700	610
$Cr(OPh)_3$	16,900	23,920	615
$Cr(OMe)_3$[b]	17,240	23,800	609
$Cr(OEt)_3$[b]	16,370	23,470	654
$Cr(O\text{-}iPr)_3$[b]	15,880	22,940	720
$Cr(OMe)_3$[c]	17,180	24,150	613
$Cr(O\text{-}iPr)_3$[c]	16,180	23,280	728

[a] Prepared from LiCl method.

[b] Prepared from $Cr(OPh)_3$.

[c] Prepared from $Cr(O\text{-}tBu)_4$.

alkoxides of most of the metals studied; the main factor hindering such facile interchange has generally been explained on the basis of steric requirements (*13*). The special inertness of Cr(III) primary alkoxides to alcoholysis may, therefore, be ascribed to the special stability of octahedral chromium(III) (with three singly occupied lower energy t_{2g} levels). The Jahn–Teller effect does not appear to be able to disturb the regularity of this octahedral species, which is consequently unable to react both by dissociative as well as associative mechanisms.

Although primary alkoxides of chromium(III) do not undergo alcoholysis reactions, $Cr(O\text{-}i Pr)_3$ could be converted to $Cr(OMe)_3$ or $Cr(OEt)_3$ by refluxing with excess MeOH or EtOH. $Cr(O\text{-}iPr)_3$, however, does not undergo alcoholysis reactions with tertiary or other secondary alcohols, even under forcing conditions. As reported earlier, $Cr(O\text{-}tBu)_4$ on treatment with MeOH, EtOH, or *i*PrOH readily gives the corresponding Cr(III) alkoxides; this may be easily understood on the basis of greater stability and insolubility of the octahedral species.

In view of the general inertness of the primary alkoxides of chromium(III), a more detailed investigation of their substitution reactions has been carried out, and it has been shown that although these are inert to other simple alcohols they undergo interchange with chelating ligands such as ethanolamine (*46*), β-diketones (*46, 48*) and carboxylic acids (*46*). A wide variety of derivatives synthesized in such reactions has been characterized by detailed spectral and magnetochemical studies (*46*).

$$Cr(OEt)_3 + xHOCH_2CH_2NH_2 \xrightarrow{\text{benzene}} Cr(OEt)_{3-x}(OCH_2CH_2NH_2)_x + xEtOH$$

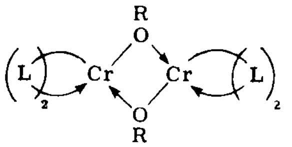
(These are slow reactions that give products insoluble in organic solvents.)

$$Cr(OR)_3 + x\beta\text{-dkH} \xrightarrow{\text{benzene}} Cr(OR)_{3-x}(\beta\text{-dk})_x + xROH$$

$$Cr(OR)_3 + xR'COOH \xrightarrow{\text{benzene}} Cr(OR)_{3-x}(OOCR')_x + xROH$$

R = Me, Et; β-dkH = acetylacetone, benzoylacetone, 2-theonyltrifluoroacetone;
$R' = C_7H_{15}, C_{13}H_{27}, C_{15}H_{31}, C_{21}H_{43}$; $x = 1, 2$, or 3

The reactions in the latter two cases (i.e., with β-diketones and carboxylic acids) are slow in the beginning, and the products $Cr(OR)_2(\beta\text{-dk})$ and $Cr(OR)_2(OOCR')$ are insoluble and polymeric; products $Cr(OR)(\beta\text{-dk})_2$ and $Cr(OR)(OOCR')_2$ are all soluble in organic solvents, in which they depict dimeric behavior, probably with an octahedral configuration of the type



Only a few mixed methoxide 3-chloro- or 3-bromoacetylacetonates of chromium(III) could be prepared (*49*, *50*) by the reactions of the β-diketonates with methanol, but the derivatives of simple (unhalogenated) β-diketones could not be prepared by this method. The simple method of treating the alkoxides with β-diketones appears to have general applicability, and a wide variety of allied mixed derivatives could also be prepared by this route, as exemplified (*46*) by the reactions

$$\mathrm{Cr(OEt)}_x(\beta\text{-dk})_{3-x} + x\beta\text{-dk}'\mathrm{H} \longrightarrow \mathrm{Cr}(\beta\text{-dk}')_x(\beta\text{-dk})_{3-x} + x\mathrm{EtOH}$$

β-dk and β-dk$'$ = acetylacetone or benzoylacetone; $x = 1, 2$

The physicochemical properties of a few β-diketonate derivatives of chromium(III) are listed in Table II.

TABLE II

ELECTRONIC VISIBLE SPECTRA OF ALKOXY β-DIKETONATES OF CHROMIUM(III)

Compound[a]	${}^4A_{2g} \to {}^4T_{2g}(F)$ (cm^{-1})	${}^4A_{2g} \to {}^4T_{1g}(F)$ (cm^{-1})	B (cm^{-1})	μ_{eff} (BM)[b]
$\mathrm{Cr(acac)_3}$	17,825	23,981	594	3.88
$\mathrm{Cr(OEt)(acac)_2}$	17,007	24,875	850	3.81
$\mathrm{Cr(OEt)_2(acac)}$	17,067	23,585	604	3.78
$\mathrm{Cr(bza)_3}$	17,452	22,833	491	3.85
$\mathrm{Cr(OEt)(bza)_2}$	17,421	23,474	592	3.81
$\mathrm{Cr(OEt)_2(bza)}$	17,064	23,809	609	3.79
$\mathrm{Cr(tta)_3}$	17,182	23,640	596	3.84
$\mathrm{Cr(OEt)(tta)_2}$	16,835	24,390	775	3.80
$\mathrm{Cr(OEt)_2(tta)}$	16,234	23,753	811	3.77
$\mathrm{Cr(OMe)(acac)_2}$	16,949	25,125	926	3.68
$\mathrm{Cr(O\text{-}\mathit{i}Pr)(acac)_2}$	16,780	23,100	529	—

[a] Abbreviations: acac, acetylacetone; bza, benzoylacetone; tta, 2-theonyltrifluoroacetone.

[b] BM, Bohr magneton.

Like the alkoxides of earlier transition elements, for example, titanium (*26, 29*), chromium(III) alkoxides (methoxide and ethoxide) have been shown to react exothermally with isocyanates in stoichiometric ratios in benzene, giving the insertion products as shown in the reaction (*51*)

$$Cr(OR)_3 + nR'NCO \longrightarrow (RO)_{3-n}Cr[N(R')COOR]_n$$

$$R = Me \text{ and } Et;\ R' = Ph \text{ and } Naph;\ n = 1\text{–}3$$

All the insertion products are colored solids, sparingly soluble in common organic solvents, and highly sensitive to moisture; on hydrolysis they yield urethanes HN(R')COOR.

A detailed physicochemical study of the compounds with the formulas $Cr_2(O\text{-}i\text{Pr})_6(NO)_2$, $Cr(O\text{-}i\text{Pr})_3(NO)L$ (L = ammonia, pyridine, or 2,4-lutidine), and $Cr(O\text{-}t\text{Bu})_3NO$ has been carried out (*52*). These products have been obtained (*53*) by the reactions of the monomeric compound $Cr(N\text{-}i\text{Pr}_2)_3NO$ with alcohols in hydrocarbon solvents. The bulky and relatively nonacidic *t*-butanol reacts slowly to give a red solid $Cr(O\text{-}t\text{Bu})_3NO$, which has been shown (*54*) to be monomeric. The reaction of isopropanol under similar conditions, however, yields a brick-red crystalline dimeric compound $Cr_2(O\text{-}i\text{Pr})_6(NO)_2$, whereas less sterically demanding and more acidic methyl and ethyl alcohols react to give the polymeric alkoxides $[Cr(OR)_3]_n$.

The diamagnetic crystalline compound $Cr_2(O\text{-}i\text{Pr})_6(NO)_2$ is air sensitive. It is appreciably soluble and quite stable in organic solvents, in which it is dimeric. It is thermally quite stable and can be sublimed at 90–100°C (10^{-4} cm Hg). $Cr_2(O\text{-}i\text{Pr})_6(NO)_2$ shows a single IR band at 720 cm^{-1} due to NO.

In both $Cr(O\text{-}t\text{Bu})_3(NO)$ and $Cr_2(O\text{-}i\text{Pr})_6(NO)_2$ the metal atom appears either in a local trigonal–pyramidal or –bipyramidal ligand field that splits metal orbitals into three sets: a(d_{z^2}), e($d_{x^2-y^2}$, d_{xy}), and e(d_{xz}, d_{yz}). The latter e set is little involved in a metal–ligand σ bond and thus lies lowest in energy. The formal oxidation state of the metal is +2, and, irrespective of the formalism used to count valence electrons, the electronic ground-state configuration is (d_{xz}, d_{yz}).

On the basis of physicochemical properties (mol wt measurements, mass, IR, and NMR spectra), the structure of $Cr_2(O\text{-}i\text{Pr})_6(NO)_2$ could be represented schematically as in Fig. 2, in which each chromium atom is in a trigonal bipyramidal environment with a crystallographically imposed inversion center and a virtual C_{2h} symmetry. The σ_h plane contains the two chromium atoms, the two bridging oxygen atoms, and the two nitrosyl ligands.

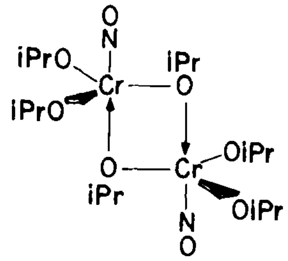
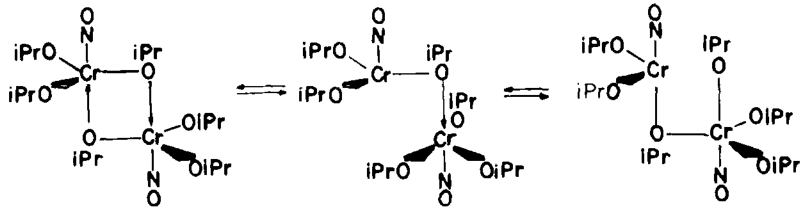


FIG. 2. Schematic representation of the molecular structure of $Cr_2(O\text{-}i Pr)_6(NO)_2$.

The relatively low position of a single intense IR band at 1720 cm^{-1} for ν NO indicates a higher component of metal d → NO π^* bonding. The NMR spectrum of the derivative in toluene below 0°C shows two septets in the integral ratio of 2:1, which are assignable to the terminal and bridging methyne protons and three partially overlapping doublets assignable to the isopropyl methyl groups, indicating the diastereotopic nature of the methyl groups of the terminal O-*i*Pr ligand [cf. structure of $Mo_2(O\text{-}i Pr)_6(NO)_2$ (*55*)]. These resonances broaden slowly as the temperature is raised and coalesce above 80°C to give a sharp doublet and septet indicative of rapid (NMR time scale) bridge ⇄ terminal O-*i*Pr ligand exchange.

The formation (*52*) of bimetallic $CrMo(O\text{-}i Pr)_6(NO)_2$ in equilibrium with the simple moieties on mixing equimolecular amounts of $Cr_2(O\text{-}i Pr)_6(NO)_2$ and $Mo_2(O\text{-}i Pr)_6(NO)_2$ indicated that the interchange of O-*i*Pr groups is intramolecular. A study of variable temperature PMR spectra of the bridge ⇄ terminal equilibrium indicated the following threshold mechanism for the interchange process.



This mechanism involves the formation of reactive four-coordinate chromium species, $Cr(O\text{-}i Pr)_3NO$, which should be stabilized compared to the dimer formed by the replacement of O-*i*Pr groups by the bulkier O-*t*Bu groups. Conversely, decreasing the ramification of the alkoxy ligands or increasing the size of the central metal atom should favor the formation of six-coordinated species.

Formation of a number of extremely oxygen-sensitive (some pyrophoric) alkoxides of chromium(II) by alcoholysis of $Cr[N(SiMe_3)_2]_2LL'$ (LL′ = ether, THF, or py) has been described (*56*). Solubility of these alkoxides has been reported to be influenced by drying conditions. Thoroughly dried aliphatic products are quite insoluble and exhibit coordination-polymer characteristics. Alkoxides from sterically demanding alcohols and phenols (e.g., 2,6-di-*t*-butylphenol) are less associated and exhibit in general higher solubility; these latter products tend to form adducts with donor ligands.

Hydrocarbon solutions of chromocene have been shown (*57*) to react rapidly with alcohols (Me, Et, and *i*Pr) to give polymeric chromium(II) alkoxides $[Cr(OR)_2]_n$. The more sterically demanding and less acidic *t*-butanol and R'_3SiOH (R′ = Me and Ph) react more slowly and lead to products of empirical formulas CpCrO-*t*Bu and $CpCrOSiR_3$, respectively. The *t*-butoxide complex, characterized by a number of physical techniques, including single-crystal X-ray crystallography, is dinuclear $Cp_2Cr_2(O\text{-}t Bu)_2$ with a nonplanar $(Cr\text{-}\mu O)_2$ moiety and a Cr—Cr distance of 2.65(2) Å. The Patterson map is quite complex, as expected, with four unique chromium atoms per asymmetric unit. This prompted the investigators to examine the possibility of the existence of two essentially identical and crystallographically related molecules, only one of which is illustrated in Fig. 3. It is reactive toward a number of

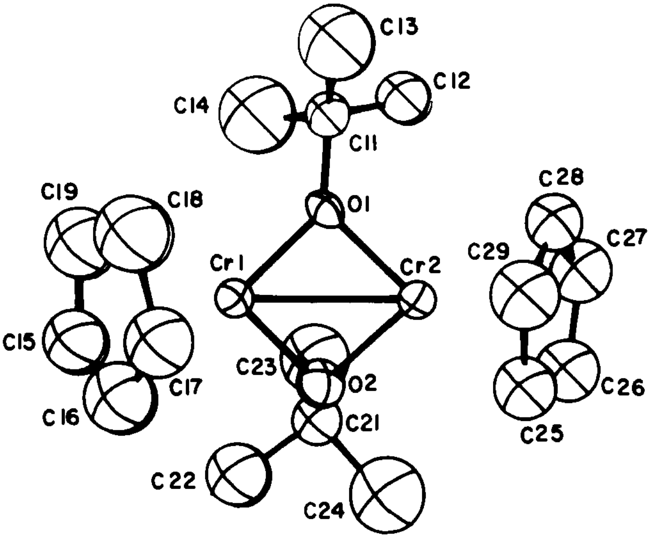


FIG. 3. X-Ray structural view of $Cp_2Cr_2(O\text{-}t Bu)_2$.

small, unsaturatd molecules, including acetylenes, CO, CO_2, nitric oxide, and nitrous oxide. The reaction between CO_2 and $Cp_2Cr_2(O\text{-}t\text{Bu})_2$ in THF leads to chromocene and $Cr_2(O_2CO\text{-}t\text{Bu})_4(THF)_2$, which has been structurally characterized by single-crystal X-ray crystallography. $Cr_2(O_2CO\text{-}t\text{Bu})_4(THF)_2$ has the dichromium acetate structure with a Cr—Cr distance of 2.367(3) Å and axially coordinated THF molecules. The principal crystallographic data for $Cp_2Cr_2(O\text{-}t\text{Bu})_2$ are space group $P2_{1/n}$, $a = 15.102(4)$, $b = 18.712(4)$, $c = 14.413(3)$ Å, $\beta = 104.40(2)°$, $V = 3945(2)$ Å^3, and $Z = 8$. The principal crystallographic data for $Cr_2(O_2CO\text{-}t\text{Bu})_4(THF)_2$ are space group $P2_{1/c}$, $a = 10.011(1)$, $b = 9.852(2)$, $c = 19.477(3)$ Å, $\beta = 104.74(1)°$, $V = 1857(1)$ Å^3, and $Z = 2$.

D. MANGANESE

A series of air-sensitive alkoxides of manganese(II) also have been prepared (*58*) in a manner similar to those of chromium(II), by the alcoholysis of the adducts of $Mn[N(SiMe_3)_2]_2$:

$$Mn[N(SiMe_3)_2]_2 \cdot (L)_n + 2ROH \rightarrow Mn(OR)_2 + 2HN(SiMe_3)_2 + nL$$

L = tetrahydrofuran, pyridine, or *t*-butyl cyanide; $n = 0$, 1, or 2; R = Me, Et, *i*Pr, *n*Bu, *s*Bu, *t*Bu, 1-pentyl, 2-pentyl, neopentyl, 2-hexyl, triethylmethyl, 1-octyl, 1-nonyl, 1-decyl, 1-adamantyl, benzyl, 2,6-di-*t*-butylphenyl, 2,4,6-tri-*t*-butylphenyl, etc.

The products, characterized by elemental analyses, reflectance spectroscopy, and chemical behavior, range from amorphous coordination polymers and gelatinous fibers to (probably monomeric) crystals.

The manganese(II) alkoxides are all extremely air sensitive, especially when wet and incompletely dried. With traces of oxygen they all change their color, eventually becoming brown or black. Some of them are pyrophoric and burn (or explode) in oxygen.

Abel, Farrow, and Towle (*59*) have studied the reactions of bromopentacarbonylmanganese, $MnBr(CO)_5$, with a number of alcohols (Et, *i*Pr, *n*Bu) and triethylamine:

$$3MnBr(CO)_5 + 3ROH + 3NEt_3 \rightarrow [Mn(OR)(CO)_3]_3 + 6CO + 3NEt_3HBr$$

According to these workers other alcohols did not appear to undergo reactions (which is rather difficult to understand). However, taking advantage of trimethyltin as a leaving group (*60*) in metathetical reactions, they were earlier successful in synthesizing similar compounds by the reactions

$$3MnBr(CO)_5 + 3Me_3Sn(OR) \rightarrow [Mn(OR)(CO)_3]_3 + 6CO + 3Me_3SnBr$$

$$R = Me, Et, nPr, iPr, nBu, C_6H_{11}, CH_2CH{=}CH_2, CH_2Ph$$

All the products were trimeric, except in the case of the benzyl (CH_2Ph) product, in which a tetrameric derivative, $[Mn(OCH_2Ph)(CO)_3]_4$, was the major component. This tetrameric product showed only three metal–carbonyl bands in the IR spectrum, whereas its NMR spectrum showed that all of the benzyl groups had identical environments. On the basis of these observations, the symmetrical structure shown in Fig. 4 was suggested for the tetrameric product.

The trimeric products, on the other hand, exhibited nine clearly defined Mn—CO stretching modes in their IR spectra, and ^1H- and ^{13}C-NMR sprectra showed two different types of alkyl group environments. These observations suggested (*61*) a remarkably unsymmetrical structure.

Phenyldimethylphosphine reacts with $(EtO)_3Mn_2(CO)_9$ to displace one carbonyl group producing $(EtO)_3Mn_3(CO)_8(PMe_2Ph)$, which also shows two different alkoxy-group environments and eight IR bands in the carbonyl stretching region. Its structure as determined by X-ray diffraction (*61*) is illustrated in Fig. 5a, and from this the structure of the parent trimeric alkoxotricarbonyls of manganese is deduced to be that given in Fig. 5b.

The structure in Fig. 5b is in accordance with the observations of two different types of alkoxyl groups and the large number of active CO

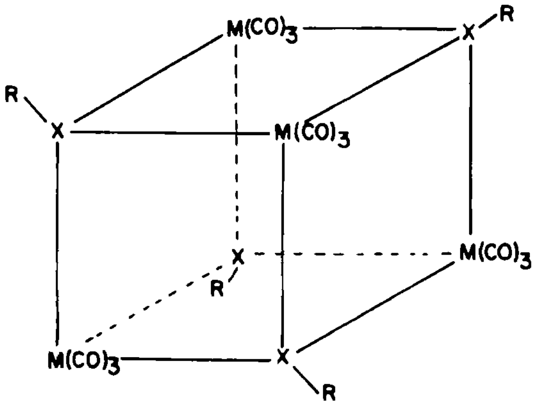


FIG. 4. Cube-shaped structure of the tetrameric alkoxo tricarbonyls of manganese.

stretching modes. The three manganese atoms form a scalene triangle in which only one of the sides (Mn^1—Mn^3) is construed as a metal–metal bond.

Interaction of $Mn_3(OEt)_3(CO)_9$ with phenol brings about (*59*) replacement of only one ethoxide group. Of the three alkoxide groups in the type of structure in Fig. 5b, the formally five-electron-donor face-bridging alkoxide groups have no nucleophilic character, but the edge-bridging oxygen atom formally still has one lone pair of electrons available for reaction.

Reactions of $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$ have been studied (*62*) with BX_3 (X = F, Cl, Br, I), and the halide complexes $Mn_3(CO)_9(\mu_3\text{-}OEt)_2(\mu_2\text{-}X)$ have been isolated; the Cl and Br products have also been prepared from the reactions of anhydrous HX. The crystal and molecular structures of $Mn_3(CO)_9(\mu\text{-}OEt)_2(\mu_2\text{-}X)$ (X = F, I) and $Mn_3(CO)_8(PMe_2Ph)(\mu_3\text{-}OEt)_2(\mu_2\text{-}OEt)$ have been determined by X-ray diffraction. The complexes have a similar structure, consisting of three manganese atoms at the corners of a scalene triangular cluster with two face-bridging OEt ligands and one edge-bridging X or OEt ligand. The remaining ligands are arranged symmetrically around the plane defined by manganese atoms.

Ultraviolet irradiation of fac-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with excess triisopropyl phosphate results in elimination of both isopropyl chloride and carbon monoxide to give an isopropoxymanganese complex $[(NC)_2C{=}CP(O)(OCHMe_2)_2Mn$

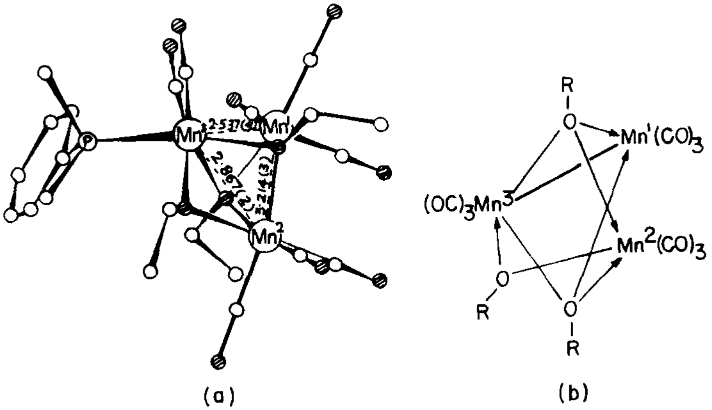


FIG. 5. (a) Structure of the complex $Mn_3(OEt)_3(CO)_8(PMe_2Ph)$. ○, C; ▨, O. (b) Representation of the structure of $[Mn(OR)(CO)_3]_3$, showing the unique nature of each $Mn(CO)_3$ group and the noble gas formalism for each Mn atom.

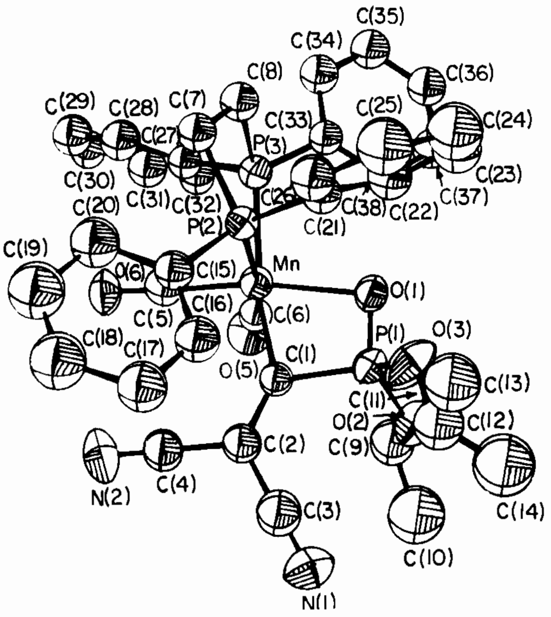


FIG. 6. Ortep drawing of the structure of $(NC)_2C{=}CP(O)(O\text{-}i\text{Pr})_2Mn(CO)_2(Ph_2PCH_2CH_2PPh_2)$.

$(CO)_2$(dppe)], the crystal structure of which has been determined by X rays (*63*) and is represented in Fig. 6.

E. IRON

A series of complexes of iron(II) aryloxides and alkoxides with 2,2′-bipyridine (L) with the formulas $Fe(OC_6H_4X)_2L_n$ and $Fe(OR)_2L_n$ have been prepared (*64*) by the reaction of diethylbis(2,2′-bipyridine)iron(II) with *p*-substituted phenols (X = H, Me, Ph, Cl, CN, NO_2) and alcohols (R = Me, Et, *i*Pr, H_2CPh). Interaction of these complexes with acyl and alkyl halides leads to the formation of corresponding esters and ethers. When treated with organic acetates, these complexes yield the corresponding acetates via an alkoxo exchange reaction.

F. COBALT

Alkoxy derivatives of cobalt appear to have received comparatively much less attention. Adams *et al.* (*14*) reported in 1966 the preparation for the first time of cobalt(II) methoxide by the reaction of anhydrous cobalt chloride with lithium methoxide in methanol. On the basis of spectral and magnetic measurements an octahedral geometry was suggested for this compound. Kakos and Winter (*65*) in the following year prepared a series of derivatives Co(OMe)X (X = Cl, Br, or I) and examined their magnetic and spectral properties.

A detailed study of the alcoholates of cobalt(II) has been carried out (*66*). $CoCl_2$ dissolves in a number of alcohols, and from the clear blue solutions thus obtained alcoholates with the general formula $CoCl_2 \cdot 2ROH$ (R = Me, Et, *i*Pr, *n*Bu, *i*Bu and *s*Bu) and $CoCl_2 \cdot t\text{BuOH}$ could be isolated by removing the excess alcohol under reduced pressure (1 mm) at 20–25°C, either from solution or from the crystallized alcoholate (after decanting the excess alcohol). Magnetic measurements and electronic spectra of the alcoholates suggest an octahedral environment for cobalt(II) in the methanolate complex and tetrahedral geometry for all other alcoholates.

Cobalt alkoxides have been synthesized (*67*) by the reactions of cobalt chloride with 2 mol of lithium alkoxide in the respective alcohol and benzene:

$$CoCl_2 + 2LiOR \xrightarrow[C_6H_6]{ROH} Co(OR)_2 + 2LiCl$$

$$R = Me, Et, \text{ or } i\text{Pr}$$

The purple-colored alkoxides are insoluble in organic solvents and are nonvolatile.

Cobalt isopropoxide interchanges its alkoxy groups readily with primary alcohols at room temperature:

$$Co(O\text{-}i\text{Pr})_2 + \underset{\text{(excess)}}{2ROH} \rightarrow Co(OR)_2 + 2i\text{PrOH}$$

$$R = Me, n\text{Bu}$$

However, it does not react with other secondary and tertiary alcohols. Similarly, the primary alkoxides do not react with any alcohol, even under forcing conditions.

The visible spectra of cobalt(II) alkoxides show a multiple band with maximum in the range $18{,}235 \pm 285\ cm^{-1}$ and a shoulder on the higher frequency side at $20{,}170 \pm 450\ cm^{-1}$. The observed spectra indicate an octahedral geometry for cobalt in these alkoxides.

G. NICKEL

A number of alcoholate complexes of nickel chloride, $NiCl_2 \cdot xROH$, have been described (*68*). The alcoholates of the primary alcohols ROH ($R = CH_3, C_2H_5, C_4H_9, C_6H_{13}$, and C_8H_{17}) have been prepared from solutions of $NiCl_2$ in the respective alcohols. $NiCl_2$ is insoluble in secondary and tertiary alcohols, but their adducts were prepared by an alcohol-interchange technique:

$$NiCl_2 \cdot CH_3OH + R'OH \rightarrow NiCl_2 \cdot R'OH + CH_3OH$$

$$R' = i\text{-}C_3H_7,\ t\text{-}C_4H_9,\ \text{or}\ t\text{-}C_5H_{11}$$

All of the monoalcoholates (primary, secondary, and tertiary) exhibit three bands in their electronic spectra at around 7500 ± 500 ($^3A_{2g} \rightarrow {}^3T_{2g}$), 12,500 ± 1000 [$^3A_{2g} \rightarrow {}^3T_{1g}(F)$], and 22,000 ± 500 cm^{-1} [$^3A_{2g} \rightarrow {}^3T_{1g}(P)$], indicating a pseudooctahedral geometry for the complexes.

Following the method of Adams *et al.* (*14*), a number of alkoxides of nickel(II) have been synthesized (*17, 69*) by the reactions of anhydrous nickel chloride with lithium alkoxides in 1:2 stoichiometric ratios:

$$NiCl_2 + 2LiOR \xrightarrow[\text{1,4-dioxane}]{\text{ROH or}} Ni(OR)_2 + 2LiCl$$

$$R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ i\text{-}C_3H_7,\ s\text{-}C_4H_9,\ t\text{-}C_4H_9,\ t\text{-}C_5H_{11},\ \text{or}\ t\text{-}C_6H_{13}$$

As mentioned earlier, nickel chloride is soluble in primary alcohols (with the formation of adducts), whereas it is insoluble in secondary and tertiary alcohols. The reactions of nickel chloride suspended in the latter alcohols (and dioxane) with the corresponding lithium alkoxides are much slower and do not appear to proceed to completion easily. Because this might be due to insolubility of nickel chloride in secondary and teritary alcohols, addition of a little pyridine, which tends to solubilize nickel chloride, has been attempted and has been found to facilitate the reactions considerably. All of these alkoxides of nickel are nonvolatile, colored solids, which are insoluble in common organic solvents. The primary alkoxides are light green in color, whereas the secondary and tertiary alkoxides are blue to violet. The latter alkoxides are particularly sensitive to moisture, in the presence of which they are hydrolyzed with a sharp color change from violet (blue) to green. All of the secondary and tertiary alkoxides are unstable toward heat and tend to decompose at around 90–100°C.

The spectra and magnetic moments of these alkoxides also show interesting differences. The spectra of the primary alkoxides exhibit three well-defined spin-allowed bands at 8750 ± 250 (ν_1; $^3A_{2g} \rightarrow {}^3T_{2g}$), 14,810 ± 115 [$\nu_2$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$], and 24,980 ± 125 cm^{-1} [ν_3; $^3A_{2g} \rightarrow {}^3T_{1g}(P)$], which are characteristic of an octahedral environment for nickel in these primary alkoxides. On the other hand, the spectra of secondary and tertiary alkoxides of nickel indicate a tetrahedral geometry with well-defined spin-allowed transitions at 7580 ± 100 (ν_2; $^3T_1 \rightarrow {}^3A_2$) and 15,850 ± 70 cm^{-1} [ν_3; $^3T_1 \rightarrow {}^3T_1(P)$].

The magnetic moments of the primary alkoxides of nickel(II) fall in the range 3.45 ± 0.04 BM (Bohr magnetons), and those of secondary as well as tertiary alkoxides are found in the range 3.65 ± 0.05 BM at room temperature; these observations also are in accord with their octahedral and tetrahedral configurations, respectively.

Like the primary alkoxides of chromium(III), the primary alkoxides of nickel also do not undergo alcoholysis reactions with other alcohols, even under forcing conditions. The secondary and tertiary alkoxides, however, undergo alcoholysis reactions with primary alcohols even at room temperature, but these also do not appear to react with other secondary and tertiary alcohols. Similar trends are observed in the transesterification reactions of the different alkoxides with alkyl esters.

It is interesting to observe that, although nickel methoxide does not undergo alcoholysis reactions, these undergo insertion reactions with phenyl and naphthyl isocyanates with evolution of heat (*70*):

$$\mathrm{Ni(OR)_2} + x\mathrm{R'NCO} \rightarrow \mathrm{(RO)_{2-x}Ni[N(R')COOR]_x}$$

$$\mathrm{R} = \mathrm{Me\ and\ }i\mathrm{Pr};\ \mathrm{R'} = \mathrm{Ph\ and\ Naph};\ x = 1, 2$$

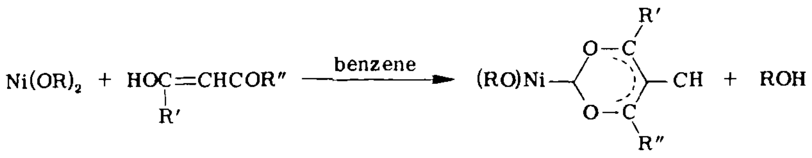
Nickel alkoxides also undergo reactions with alkanolamines, β-diketones, and carboxylic acids, and interesting products have been obtained. The reactions with alkanolamines (*71*) in different stoichiometric ratios in benzene can be represented by the reactions

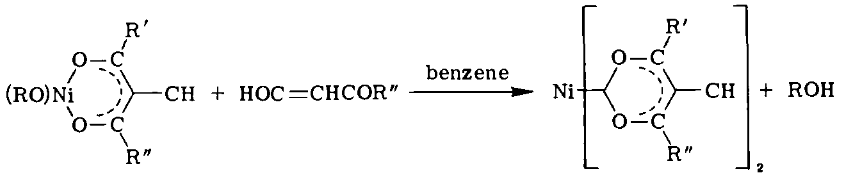
$$\mathrm{Ni(OR)_2} + n\mathrm{Hetha} \rightarrow \mathrm{Ni(OR)_{2-n}(etha)_n} + n\mathrm{ROH}$$

$$\mathrm{Ni(OR)_2} + \mathrm{H_2etha'} \rightarrow \mathrm{Ni(etha')} + 2\mathrm{ROH}$$

$$\mathrm{R} = \mathrm{Me\ or\ }i\mathrm{Pr};\ \mathrm{etha} = \mathrm{ethanolamine\ with\ }n = 1\mathrm{\ or\ }2;\ \mathrm{etha'} = \mathrm{di\text{-}\ or\ triethanolamine}$$

Nickel alkoxides have been shown to interact slowly with β-diketones:





$R = CH_3, i\text{-}C_3H_7; R', R'' = CH_3, C_6H_5, CF_3, \text{ or } C_4H_3S$

It is interesting to record that the monoalkoxide mono-β-diketonates (even the methoxide) undergo alcoholysis reactions with other alcohols (primary, secondary, and tertiary), as illustrated by the following typical reactions.

$$\mathrm{Ni(O\text{-}}i\mathrm{Pr)(\beta\text{-}dk)} + \underset{\text{(excess)}}{\mathrm{ROH}} \xrightarrow{\text{r.t.}} \mathrm{Ni(OR)(\beta\text{-}dk)} + i\mathrm{PrOH}$$

$$R = \mathrm{Me \text{ or } Et}$$

$$\mathrm{Ni(OMe)(\beta\text{-}dk)} + \mathrm{ROH} \xrightarrow[\text{reflux}]{\text{benzene}} \mathrm{Ni(OR)(\beta\text{-}dk)} + \mathrm{MeOH}$$

$$R = \mathrm{Et}, i\mathrm{Pr}, \text{ or } t\mathrm{Bu}$$

$$\mathrm{Ni(O\text{-}}i\mathrm{Pr)(\beta\text{-}dk)} + t\mathrm{BuOH} \xrightarrow[\text{reflux}]{\text{benzene}} \mathrm{Ni(O\text{-}}t\mathrm{Bu)(\beta\text{-}dk)} + i\mathrm{PrOH}$$

The mixed alkoxide β-diketonates also undergo exchange reactions with other β-diketones, resulting in the synthesis of a variety of mixed β-diketonates:

$$\mathrm{Ni(OR)(\beta\text{-}dk)} + \mathrm{H\beta\text{-}dk'} \xrightarrow{\text{benzene}} \mathrm{Ni(\beta\text{-}dk)(\beta\text{-}dk')} + \mathrm{ROH}$$

$$R = \mathrm{Me \text{ or } }i\mathrm{Pr}, \text{ and } \beta\text{-dk or } \beta\text{-dk}' = \text{acac, bzac, dbzm, or tta}$$

All of these products are colored solids and are soluble in benzene, from which they can all be recrystallized. All the bis-β-diketonate derivatives are trimeric. Among the monoalkoxide derivatives, the isopropoxide and tertiary butoxide mono-β-diketonates are trimeric, but the methoxide and ethoxide analogs are tetrameric.

Nickel bisacetylacetonate also forms monoadducts with a number of alcohols: $\mathrm{Ni(acac)_2 \cdot ROH}$ (R = Me, Et, *i*Pr, *n*Bu, *s*Bu or *t*Am). These alcoholates can be recrystallized from benzene, in which they show dimeric association.

On the basis of infrared, electronic reflectance, and electron-spin resonance spectra as well as magnetic measurements, all of these derivatives have been shown (*70, 72*) to have distorted octahedral structures.

The reactions of nickel alkoxides with carboxylic acids can also be represented (*73*) by the reactions

$$\mathrm{Ni(OR)_2 + \mathit{n}R'COOH \xrightarrow{benzene} Ni(OR)_{2-\mathit{n}}(OOCR')_\mathit{n} + \mathit{n}ROH}$$

$$\mathrm{R = CH_3 \text{ or } \mathit{i}\text{-}C_3H_7;\ R' = C_{13}H_{27}, C_{15}H_{31}, \text{ or } C_{17}H_{35};\ \mathit{n} = 1 \text{ or } 2}$$

The progress of the reaction can be conveniently followed by estimating the alcohol liberated in the reaction and collected azeotropically with benzene. The reactions are quite facile and can be completed in a short period. Unlike the parent alkoxides, all of the colored mono- as well as disubstituted products obtained are highly soluble in benzene and other organic solvents. Monomethoxide monocarboxylates do not undergo alcoholysis reactions. The isopropoxide analogs, on the other hand, undergo facile interchange with methanol or ethanol at ambient temperature, but the complete interchange of isopropoxide by tertiary butoxide groups, requires refluxing for a long time with continuous fractionation of isopropanol produced in the reaction.

All of these carboxylate derivatives are nonvolatile colored solids, soluble in benzene but insoluble in alcohols. All of the alkoxide monocarboxylate derivatives have been shown to be tetrameric, whereas the dicarboxylates are trimeric in refluxing benzene. The IR spectra of these derivatives appear to suggest a bidentate nature of the carboxylate moieties in them. Electron-reflectance spectra and magnetic measurements indicate an octahedral environment for nickel in all these derivatives.

H. COPPER

The general applicability of the lithium alkoxides (cf. *14, 74*) in the synthesis of copper(II) alkoxides has been shown (*75*):

$$\mathrm{CuCl_2 + 2LiOR \xrightarrow{ROH} Cu(OR)_2 + 2LiCl}$$

$$\mathrm{R = Me, Et, \mathit{i}Pr, \mathit{t}Bu}$$

Synthesis of a few more alkoxides of copper has been described (*67*) by the alcohol-interchange reactions

$$\mathrm{Cu(OR)_2 + \underset{(excess)}{2R'OH} \xrightarrow{benzene} Cu(OR')_2 + 2ROH}$$

$$\mathrm{R = Me, Et \text{ or } \mathit{n}Bu;\ R' = Me, Et, \mathit{i}Pr, \mathit{n}Bu, \mathit{s}Bu, \mathit{t}Bu, \text{ or } \mathit{t}Am}$$

Alcohol-interchange reactions of copper(II) alkoxides reveal some novel features compared to those of alkoxides of chromium(III) (*17, 46*), cobalt(II) (*17, 66*), and nickel(II) (*17, 69*). Compared to the novel nature of alcoholysis reactions of these latter alkoxides, copper(II) alkoxides undergo facile alcohol-interchange reactions. Copper(II) alkoxides in this respect show resemblance to alkoxides of earlier transition metals like titanium and vanadium, which also undergo very facile alcoholysis reactions.

It has been observed that the primary alkoxides of copper(II) interchange their alkoxide groups quantitatively with tertiary, secondary, or other primary alcohols under refluxing conditions only, whereas the secondary and tertiary alkoxides undergo a more facile alcohol-interchange reaction with primary alcohols, even at room temperature with slight evolution of heat. It has been found that the secondary and tertiary alkoxides of copper(II) do not appear to undergo alcohol-interchange reactions with other secondary and tertiary alcohols. Although it is difficult to sort out the effects of various factors like thermodynamic and kinetic stabilities as well as the role of crystal field stability in different plausible geometries (apparently the main factor in alcoholysis trends of nickel alkoxides), the alcohol-interchange reactions of copper(II) alkoxides appear to be governed mainly by steric factors. As in a number of other metals, the alkoxy interchange reactions are sterically less hindered when esters are used in place of alcohols as reactants. For example, it has been reported (*67*) that copper(II) isopropoxide, which hardly undergoes interchange with *t*-butanol can be converted to *t*-butoxide by treating with *t*-butyl acetate:

$$\mathrm{Cu(O\text{-}\mathit{i}Pr)_2 + 2CH_3COO\text{-}\mathit{t}Bu \rightleftharpoons Cu(O\text{-}\mathit{t}Bu)_2 + 2CH_3COO\text{-}\mathit{i}Pr}$$

The alcoholysis reactions of copper(II) alkoxides thus follow the following order of relative lability, which is similar to that already reported in the alkoxides of a number of earlier transition metals (*13*): primary alkoxides $\gg$ secondary alkoxides $\sim$ teritary alkoxides.

Brubaker and Wicholas (*74*) reported subnormal magnetic moments for $Cu(OMe)_2$ (1.12 BM) and $Cu(OEt)_2$ (1.18 BM) and suggested a highly polymeric structure for these with tetragonally distorted copper atoms. Adams *et al.* (*14, 76*) measured the magnetic susceptibility of $Cu(OMe)_2$ over the range 80–350 K. They favored a linear-chain model for polymeric $Cu(OMe)_2$ analogous to that of $CuCl_2$.

Singh (*67*) has measured the magnetic susceptibilities of typical primary, secondary, and tertiary alkoxides of copper and has found that (a) for $Cu(OBu)_2$ it increases from 0.64 at 88.5 to 1.18 at 298.7 K; (b) for $Cu(O\text{-}iPr)_2$ it increases from 0.98 at 88.0 to 1.50 at 297.1 K; and

(c) for $Cu(O\text{-}tAm)_2$ it increases from 1.37 at 87.5 to 1.83 at 297 K. These data indicate the presence of antiferromagnetic exchange interaction, which, as expected, decreases with increasing ramification of the alkyl group. The J values calculated employing the Ising model also follow a trend in the same direction as shown from the following values of J.

$\lvert J\rvert Cu(O\text{-}nBu)_2$	$\lvert J\rvert Cu(O\text{-}iPr)_2$	$\lvert J\rvert Cu(O\text{-}tAm)_2$
129 cm^{-1}	81 cm^{-1}	43 cm^{-1}

The visible spectra of $Cu(OMe)_2$, $Cu(OEt)_2$, and $Cu(O\text{-}nBu)_2$ are similar and show absorption bands at 15,500 ± 75 and 19,100 ± 300 cm^{-1}, which point to a distorted octahedral environment around copper. However, the spectra of branched alkoxides of copper, $Cu(O\text{-}iPr)_2$, $Cu(O\text{-}sBu)_2$, $Cu(O\text{-}tBu)_2$, and $Cu(O\text{-}tAm)_2$, are characterized by a very broad absorption in the visible region at approximately 15,000 cm^{-1} that appears to tail in the near-infrared region. This band may be assigned to a $^2E_g \rightarrow {}^2T_{2g}$ transition, which would indicate a six-coordinated tetragonal geometry for copper in these branched alkoxides.

Copper(II) complexes with unsubstituted phenoxide groups have not been reported as yet, and it may be that these have not been isolated because they would be unstable toward reductive elimination to phenoxy radicals, which would then couple to give diphenoquinone or 1,4-phenylene ethers (*77*) in the presence of copper. In view of this, it is interesting to report that coordinated diphenoxo derivatives of copper(II) have been obtained by the reactions

$$CuCl_2(bipy) + 2NaOPh \xrightarrow{THF} Cu(OPh)_2(bipy) + 2NaCl$$

(brown complex
moderately soluble
in THF)

$$CuCl_2(en) + 2Na(OPh)\cdot PhOH \xrightarrow{THF} Cu(OPh)_2(en)\cdot PhOH + 2NaCl$$

(green complex)
sparingly soluble
in THF)

The bisphenoxo derivative of copper(II), $Cu(OPh)_2(en)_2 \cdot 2PhOH$ has been shown (*78*) by X-ray diffraction to be a centrosymmetric phenoxo-bridged dimer with terminal phenoxo and ethylenediamine groups and hydrogen bonded phenol molecules. The crystals are monoclinic (space group $P2_{1/n}$, and the unit cell has dimensions a = 19.000(3), b = 10.930(9), c = 8.968(5) Å, β = 89.90(2)°, V = 1862.4 Å^3, and Z = 4. The copper atoms are five-coordinate, and the coordination geometry is that of a distorted square pyramid. The Cu—Cu distance is 3.215 Å, and the compound has a nearly normal magnetic moment at room temperature. The X-ray crystal structure of CuO-*t*Bu prepared by the reaction of CuCl with LiO-*t*Bu in THF showed it to be a tetrameric compound, $[CuO\text{-}tBu]_4$ (*79*). The crystals are triclinic (space group $P\bar{1}$) with $a = 11.890$, $b = 11.284(2)$, $c = 10.047(9)$ Å; $\alpha = 90.54(3)$, $\beta = 106.39(5)$, and $\gamma = 113.86(4)°$; *d*(calculated) = 1.55 for $Z = 8$. Four of the formula units form a planar ring containing four Cu and four O atoms. The tertrameric units persist even in the vapor phase.

Treatment of Cu(O-*t*Bu) with di-*t*-butyl peroxide gave $Cu(O\text{-}tBu)_2$ as a yellow-green solid (*80*). Cu(O-*t*Bu) has been shown to be an excellent metalation reagent, as illustrated by the following facile reaction at room temperature.

$$\underset{80\ \text{mmol}}{PhC{\equiv}CH} + \underset{4\ \text{mmol}}{Cu(O\text{-}tBu)} \rightarrow \underset{97\%}{PhC{\equiv}CCu} + \underset{97\%}{tBuOH}$$

The coupling of 1,3-dinitrobenzene with aryl iodides by Cu(O-*t*Bu) and pyridine provides (*81*) a convenient route for 2,6-dinitrobiphenyls and is an improvement on the earlier methods (*82*).

Secondary and primary alkoxides and the phenoxide of copper(I) have been synthesized (*83*) by the heterogeneous reaction of alcohols with methylcopper(I). The reactions of copper(I) alkoxides with aryl halides yield alkyl aryl ethers under particularly mild conditions. Thermal decomposition of primary alkoxides of copper(I) generates intermediate alkoxy radicals, whereas that of secondary alkoxides appears to take place either by a free-radical mechanism or through an intermediate formation of copper(I) hydride.

Copper(I) alkoxides, $ROCu(PPh_3)_2$ (R = Et, $PhCH_2$), react with CO_2 to give products corresponding in composition to $ROCO_2Cu(PPh_3)_2$ (*84*). Hydrolysis or thermolysis of these (alkylcarbonato)copper(I) complexes gives a binuclear carbonatocopper(I) complex, $(Ph_3P)_2CuOCO_2Cu(PPh_3)_2$.

Continuing their earlier investigations (*84a,b*) on the condensation of 5,5,5-trifluoro-4-hydroxy-4(trifluoromethyl)-2-pentanone (hexafluorodiacetone alcohol) with diamines in the presence of metal ions, Willis *et al.* (*84c*) have determined the structure of a dinuclear iminoalkoxy compound of copper(II).

III. Alkoxy and Allied Derivatives of 4d and 5d Metals

Except for some earlier work on alkoxy derivatives of zirconium, niobium, and tantalum, and a more recent surge in penetrating investigations of the alkoxy derivatives of molybdenum and tungsten, the chemistry of 4d and 5d metal alkoxides appears to have received comparatively little attention. These are, therefore, dealt with together, which is also convenient because pairs of these elements show more similarities in their chemistry compared to those of the corresponding 3d metals.

A. Zirconium and Hafnium

A series of *N*-methylaminoalkoxides of zirconium, $Zr(O\text{-}i\text{Pr})_{4-n}(OCHR'CH_2NR''R''')$ ($R' = R'' = H$, $R''' = Me$, $R' = H$, $R'' = R''' = Me$, $R' = R'' = R''' = Me$, $n = 1\text{–}4$), have been synthesized (*35*) by the reactions of $Zr(O\text{-}i\text{Pr})_4 \cdot i\text{PrOH}$ with aminoalcohols. Similar to zirconium isopropoxides (*86*), these aminoalkoxides, $Zr(OCHR'CH_2NR''R''')_4$, have also been shown to undergo insertion reactions with PhNCO to give products of the type $Zr(NPhCOOCHR'CH_2NR''R''')_4$.

A series of mixed derivatives of zirconium with possible coordination numbers 5, 6, 7, and 8 have been synthesized (*87*) by the reactions of zirconium isopropoxide with a number of aliphatic and aromatic hydroxy esters: $HOC_6H_{10}R$, HOCHPhR, and HOCMePhR ($R = CH_2COOEt$).

Conductometric titration of $ZrCl_4$ with KOPh in nitrobenzene indicates (*88*) the formation of a number of chloride phenoxides and a tetraphenoxide of zirconium.

The compounds $MCl(OC_6H_3t\text{Bu}_2\text{-}2,6)_3$ (M = Zr, Hf) have been synthesized by the reactions of the metal tetrachlorides with $LiO(C_6H_3t\text{Bu}_2\text{-}2,6)$ in diethyl ether (*88a*). The hafnium has been structurally characterized to show a sterically congested, mononuclear molecule in which several distortions of the aryloxo ligands have taken place.

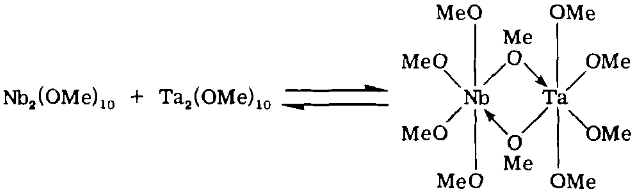
B. Niobium and Tantalum

A detailed variable-temperature ^{13}C-NMR study of $Nb(OEt)_5$ and $Ti(OR)_4$ (R = Et, Pr, Bu, *i*Bu, *i*Pr, *t*Bu, neopentyl) has been carried out (*89*), and the data have been interpreted in terms of the degree of association and equilibria among the oligomeric entities.

A crystal and molecular structure study (*90*) of niobium pentamethoxide showed a structure with two conformers in the unit cell that is pronouncedly pseudo-body-centered and that contains two crystallographically different centrosymmetric dimeric molecules with different conformations. Both forms consist of two approximately octahedral units with a shared edge, which are differentiated by a cis or trans arrangement of the equatorial methyl groups with respect to the equatorial plane.

A detailed study of the coordination ability of about 40 potential nitrogen-, oxygen-, phosphorus-, and sulfur-donor ligands has been made by Hubert-Pfalzgraf (*91*) and has been actually discussed in terms of frontier orbitals, pK_a values, charge distribution, and Gutmann's donor numbers (D_n) of the ligands.

A very interesting mixed $NbTa(OCH_3)_{10}$ has been isolated (*92*) as a crystalline compound, and it has been characterized by proton NMR, IR, and mass spectrometry. In solution it is in dynamic random equilibrium with the symmetric dimers $Nb_2(OCH_3)_{10}$ and $Ta_2(OCH_3)_{10}$:



NbX_5 and TaX_5 (X = Cl, Br) have been shown (*93*) to react with oxygen-donor ligands in anhydrous alcohol to yield halide alkoxide complexes of the type $M(OR)_3X_2L$ [M = Nb, Ta; R = Me, Et; X = Cl, Br; L = Ph_3PO, Ph_3AsO, Ph_2SO and $(Me_2N)_3PO$].

$M(OPh)_nBr_{5-n}$ (M = Nb, Ta) have been prepared (*94*) by stepwise phenolysis of MBr_5 in CCl_4.

Chelates of niobium and tantalum phenoxides and chloride phenoxides with benzoin (HL) with the formulas $M(OPh)_4L$, $MCl(OPh)_3L$ and $MCl_2(OPh)_2L$ have been prepared (*95*) by refluxing $M(OPh)_5$, $MCl_2(OPh)_3$, and $MCl_3(OPh)_2$ with benzoin in a 1:1 molar ratio in benzene.

Crystalline high-melting-point salts $[M(OPh)_4]SbCl_6$ have been synthesized (*96*) by the reactions of $M(OPh)_4Cl$ (M = Nb, Ta) with $SbCl_5$ in CH_2Cl_2.

A series of mixed alkoxide cyanides of niobium and tantalum, $M(OR)_{5-n}(CN)_n \cdot xCH_3COOR$ (M = Nb, Ta; R = Et, *i*Pr; $n = 1$–5, $x = 0.5$–2.5) have been prepared (*97*) by the reactions of the pentaalkoxides with pyruvonitrile in the required molar ratios in cyclohexane. The reactions of $Nb(CN)_5 \cdot 2CH_3COO$-*i*Pr and $Ta(CN)_5 \cdot 2.5CH_3COO$-*i*Pr with refluxing isopropanol yield products, $M(O\text{-}i\text{Pr})_2(CN)_3CH_3$-COO-*i*Pr, similar to those obtained in the reactions of $M(O\text{-}i\text{Pr})_5$ with CH_3COCN in 1:3 molar-ratio reactions.

A number of niobium(V) oxyalkoxide derivatives, $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$, $NbO(OCH_2CF_3)_2(OCH{=}CF_2)(CF_3CH_2OH)_{0.5}$, $[NbO(OEt)_3]_2$, $[NbOCl_2(OCH_3) \cdot CH_3OH]_2$, and $NbO(OCH_3)(OC_6H_4CHO)$, have been synthesized (*98*) by direct alkoxylation of niobium oxychloride. The molecular constitution of the solutions of $[NbO(OEt)_3]_2$ and $[NbO(OCH_2CF_3)_3 \cdot MeCN]_2$ in nonpolar solvents was tentatively interpreted as a dynamic equilibrium between various μ-alkoxo and μ-oxo isomers, the latter being favored by dilution. In polar media dimeric units are retained for $[NbO(OEt)_3]_2$, whereas the trifluoroethoxide derivative splits into monomeric species.

C. MOLYBDENUM AND TUNGSTEN

1. *Higher Alkoxides and Halide Alkoxides of Molybdenum and Tungsten*

The preparation of $W(OPh)_6$ by the reaction of WCl_6 with PhOH has been reported (*99*). Hexamethoxides of molybdenum and tungsten as well as uranium have been synthesized (*99a*) by the reactions of their hexafluorides with excess of tetramethylsilicate; the last stage of the reaction is slow in the case of tungsten, yielding mainly $WF(OMe)_5$, which can be converted into $W(OMe)_6$ by treatment with a methanol solution of NaOMe.

Reactions of $MoOCl_4$ in CH_2Cl_2 with solid $NaOC(CF_3)_3$ have been investigated in different molar ratios, and derivatives $MoOCl[OC(CF_3)_3]_3$ and $MoO[OC(CF_3)_3]_4$ have been isolated (*100*). Both products are volatile and may be sublimed at temperatures as low as 60°C. The cell dimensions of $MoOCl[OC(CF_3)_3]_3$ are a = 6.82, b = 20.86, and c = 17.22 Å (primitive orthorhombic), and those for $MoO[OC(CF_3)_3]_4$ are a = 13.305, b = 13.946, and c = 13.570 Å (face-centered orthorhomic).

2. *Alkoxides of Molybdenum and Tungsten in 3- and 4-Oxidation States*

A series of alkoxides of molybdenum and tungsten with the general formulas $M(OR)_3$ and $M(OR)_4$ have been described. The derivatives $M(OR)_3$ are of special interest because they represent the first known examples in which association occurs not through alkoxy bridges but by the formation of metal–metal triple bonds (*101–104*).

a. Alkoxides of Molybdenum(III). Alkane solutions of $Mo_2(NMe_2)_6$ react (*102–104*) smoothly with the alcohols and silanols ROH [R = Me, Et, *n*Pr, *i*Pr, *t*Bu, CH_2CMe_3, CMe_2Ph, $C(CF_3)_3$, $SiMe_3$, and $SiEt_3$] and pinacol, $Me_2C(OH)C(OH)Me_2$. The ease of alcoholysis decreases with the ramification of the alkyl group, so much so that even under refluxing conditions with Et_3COH partial substitution occurs yielding $Mo_2(NMe_2)_2(OCEt_3)_4$. Stripping the solvent in these reactions gives crude samples of $[Mo(OR)_3]_x$ compounds or their amine adducts. Dinuclear compounds $Mo_2(OR)_6$ (R = *i*Pr, CH_2CMe_3, *t*Bu, $SiMe_3$, and $SiEt_3$) and $Mo_2(O_2C_2Me_4)_3$ have been obtained by vacuum sublimation (100–160°C, 10^{-4} cm Hg). These $Mo_2(OR)_6$ compounds are crystalline solids that are soluble in alkanes, benzene, toluene, and THF, with the exception of R = CMe_2Ph and $C(CF_3)_3$ and the pinacolate derivative. Their colors, which vary from pale yellow to red, depending on the nature of the R group, arise from a tailing of strong UV absorption into the visible region of the spectrum: they show no λ_{max} in the visible region of the spectrum. The molecular weight of $Mo_2(O\text{-}t\text{Bu})_6$ in benzene corresponds to the dimeric formula. They are diamagnetic both in the solid state and in solution. In the mass spectrometer they show strong parent ions $Mo_2(OR)_6^+$ together with many other Mo_2-containing ions; indeed, the virtual absence of mononuclear ions is quite striking. ^1H- and ^{13}C-NMR spectra in the temperature range 90 to −90°C of the compounds in toluene-d_8 show one type of OR ligand. However, in the case of R = CH_2CMe_3 both proton and ^{13}C signals are lost in the baseline at low temperatures.

The structure of $Mo_2(OCH_2CMe_3)_6$ is shown in Fig. 7, and some of the important structural parameters are given in Table III. The structure is similar to those of $Mo_2(NMe_2)_6$ (*105*) and $Mo_2(CH_2SiMe_3)_6$

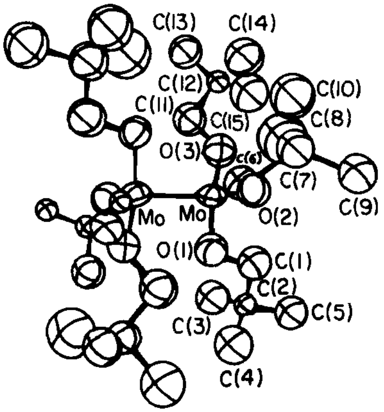


FIG. 7. Ortep stereoscopic view of the $Mo_2(OCH_2CMe_3)_6$ molecule.

(*106*). The central Mo_2X_6 moiety (X = O, N, C) virtually has D_{3d} symmetry, and the Mo—Mo distances are in the range 2.167–2.222 Å.

The bonding in $Mo_2(OCH_2CMe_3)_6$ and related $Mo_2(OR)_6$ compounds appears to involve four σ bonds (three to oxygen atoms and one to the other molybdenum atom), using approximately tetrahedral orbitals (may be sp^3, sd^3, or any intermediate combination) on each Mo atom. Then, taking the Mo—Mo σ bond as the z axis, two metal σ bonds can be formed employing d_{xz}, d_{yz}, and/or p_x, p_y orbitals on each atom. The Mo≡Mo bond so formed would readily account for the short Mo≡Mo distance (2.222 Å), which is about 1 Å less than that in a Mo—Mo bond, and the diamagnetic nature of the compound.

The importance of steric factors in determining the characteristics of this series of $Mo(OR)_3$ alkoxides can be demonstrated (*104*) by the fact that dimers $(RO)_3Mo{\equiv}Mo(OR)_3$ with Mo≡Mo bonds are formed only in the cases of highly ramified R groups. Even the neopentyl (H_2CCMe_3) derivative appears to be on the border. In hydrocarbon solvents $Mo_2(OCH_2CMe_3)_6$ undergoes a slow and irreversible reaction, leading to the formation of a brick-red precipitate, which appears to be a polymeric compound of the composition $[Mo(OCH_2CMe_3)_3]_n$. The reaction of $Mo_2(NMe_2)_6$ with EtOH yields a black compound that is highly soluble in hydrocarbons; analyses and molecular-weight determina-

TABLE III

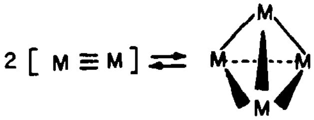
INTERATOMIC DISTANCES AND ANGLES FOR MOLECULES IN FIGURE 7[a]

Molecule	Interatomic distance (Å)	Molecule	Interatomic distance (Å)
Mo—Mo′	2.222(2)	C(2)—C(5)	1.57(1)
Mo—O(1)	1.905(6)	C(6)—C(7)	1.57(1)
Mo—O(2)	1.867(6)	C(7)—C(8)	1.58(1)
Mo—O(3)	1.855(6)	C(7)—C(9)	1.54(1)
Molecule	**Bond angle (deg)**	**Molecule**	**Bond angle (deg)**
Mo′—Mo—O(1)	98.3(2)	C(3)—C(2)—C(4)	108.1(10)
Mo′—Mo—O(2)	105.5(2)	C(3)—C(2)—C(5)	111.0(10)
O(1)—Mo—O(2)	115.9(3)	C(6)—C(7)—C(8)	103.5(8)
Mo—O(1)—C(1)	114.5(7)	C(8)—C(7)—C(9)	109.0(8)
Mo—O(2)—C(6)	135.1(6)	C(8)—C(7)—C(10)	111.4(9)

[a] Primed atoms are symmetry related to the corresponding unprimed atoms.

tions indicate a tetrameric formula $[Mo(OEt)_3]_4$. In the mass spectrometer the ion of the highest mass corresponded to $[Mo_4(OEt)_{12}]^+$ although other multinuclear species, for example, $[Mo_3(OEt)_9]^+$ and $[Mo_2(OEt)_6]^+$, were very prominent and mononuclear moieties like $Mo(OEt)_5{}^+$ also were observed. This ethoxide is diamagnetic and gives a very complex ^1H-NMR spectrum due to overlapping of several ethyl resonances. In the ^{13}C-NMR spectrum in benzene-d_6, eight methylene carbon signals were observed in the intensity ratio 1 : 1 : 1 : 1 : 2 : 2 : 2 : 2, which appears to be consistent with the tetrameric formula. In contrast to this, the corresponding reaction of $Mo_2(NMe_2)_6$ with MeOH leads to a nonvolatile hydrocarbon-insoluble brown paramagnetic polymeric alkoxide $[Mo(OMe)_3]_n$. The IR spectrum of the methoxide indicates a predominance of the bridging OMe ligands, and the polymerization probably occurs by the formation of MoO_6 units [cf. $Cr(OMe)_3$ (*45*)]. A notable difference in the chemistry of Cr(III) and Mo(III) is that Cr(III) will, though somewhat reluctantly, form tetrahedral complexes as in the salts $LiCr(CH_2SiMe_3)_4$ (*107*) and $LiCr(O\text{-}t\text{Bu})_4$ (*108*), whereas molybdenum prefers to adopt a $L_3Mo{\equiv}MoL_3$ structure at the expense of forming a fourth Mo—L bond.

In trying to explain the slow polymerization of $Mo_2(OCH_2CMe_3)_6$, Chisholm *et al.* (*104*) have cited the "aging" phenomenon of $Al(O\text{-}i\text{Pr})_3$ (*109*). The latter has, however, been shown to involve a change from a tetrahedral to an octahedral aluminum atom (*110*), but the same may not be applicable in the case of molybdenum neopentyloxide, in which a reorganization of the following type has been suggested by Chisholm *et al.* (*104*).



$Mo_2(O\text{-}i\text{Pr})_6$ reacts with Cl_2, Br_2, and I_2 in carbon tetrachloride solutions to yield tetrahalide products with the composition $Mo_2(O\text{-}i\text{Pr})_6X_4$, which are orange (X = Cl or Br) and brown (X = I) crystalline solids. X-Ray studies of the chloro and bromo compounds show that both of these contain contral $Mo_2O_6X_4$ units that have virtual D_{2h} symmetry (*111a*).

A black, air-sensitive hydrocarbon-soluble solid of empirical composition $MoF(O\text{-}t\text{Bu})_2$ is obtained (*111*) by the addition of PF_3 (2 equivalents) to a hydrocarbon solution of $(t\text{BuO})_3Mo{\equiv}Mo(O\text{-}t\text{Bu})_3$.

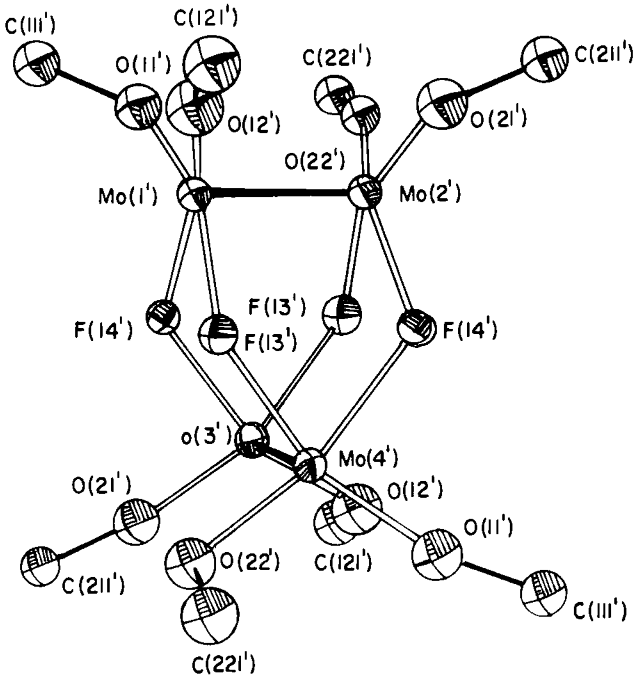


FIG. 8. Ortep view of the central $Mo_4(\mu\text{-}F)_4(OC)_8$ skeleton of the $Mo_4(\mu\text{-}F)_4(O\text{-}t\mathrm{Bu})_8$ molecule.

The product is tetrameric with the structure $Mo_4(\mu\text{-}F)_4(O\text{-}t\mathrm{Bu})_8$, which is shown in Fig. 8.

An interesting derivative with the suggested formulation $(t\mathrm{BuO})_2(\mathrm{Et})\mathrm{Mo{\equiv}Mo}(O\text{-}t\mathrm{Bu})_3$ has been synthesized (*112*) by the reaction of $Mo_2Et_2(NMe_2)_4$ [obtained (*113*) by the reaction of $Mo_2Cl_2(NMe_2)_4$ with LiEt] with *t*-butanol in benzene at room temperature:

$$\mathrm{Mo_2Et_2(NMe_2)_4} + \underset{\text{(excess)}}{4t\text{-BuOH}} \rightarrow \underset{\substack{\text{burgundy-red}\\ \text{solid}}}{\mathrm{Mo_2Et(O\text{-}}t\mathrm{Bu)_5}} + 4\mathrm{NHMe_2} + \mathrm{C_2H_6}$$

The alkylation of $Mo_2(O\text{-}i\mathrm{Pr})_6$ with $LiCH_2SiMe_3$ in pentane results (*113a*) in a high (75%) yield of $Mo_2(CH_2SiMe_3)_6$. The corresponding reactions of $Mo_2(O\text{-}i\mathrm{Pr})_8$ gives an almost equimolar mixture of $Mo_2(CH_2SiMe_3)_6$. The corresponding reaction of $Mo_2(O\text{-}i\mathrm{Pr})_8$ gives an almost equimolar mixture of $Mo_2(CH_2SiMe_3)_6$ and $Mo(CH_2SiMe_3)_3({=}CSiMe_3)$.

b. Alkoxides of Molybdenum(IV). A series of molybdenum(IV) alkoxides have been prepared (*114*) by the reaction

$$\mathrm{Mo(NMe_2)_4 + 4ROH \rightarrow M(OR)_4 + 4NHMe_2}$$

$$\mathrm{R = Me, Et,}\ i\mathrm{Pr,}\ t\mathrm{Bu\ and\ CH_2CMe_3}$$

The corresponding reactions involving trialkylsilanols R_3SiOH (R = Me and Et) yield an amine adduct:

$$\mathrm{Mo(NMe_2)_4 + 4R_3SiOH \rightarrow Mo(OSiR_3)_4 \cdot (HNMe_2)_2 + 2NMe_2H}$$

The properties of the alkoxides depend upon the steric requirements of the alkoxy group, as illustrated by a few properties of these derivatives, which are given in Table IV.

Of all the derivatives given in Table IV, only $[\mathrm{Mo(O\text{-}}i\mathrm{Pr)_4]_2}$ is diamagnetic. It is a fluxional molecule on the NMR time scale, and the low-temperature-limiting (^{1}H and ^{13}C)-NMR spectra correspond to a structure of the type $(i\mathrm{PrO})_3\mathrm{Mo}(\mu\text{-O-}i\mathrm{Pr})_2 \cdot \mathrm{Mo(O\text{-}}i\mathrm{Pr})_3$. X-Ray crystallography (*115*) has shown (Fig. 9) that the molecule has a rigorous crystallographic center of inversion and approximately C_{2h} symmetry, with the configuration of oxygen atoms around each molybdenum a slightly distorted trigonal bipyramid. The observed Mo—Mo distance of 2.523(1) Å could be explained on the basis of a double metal–metal bond or coupling of one pair of electrons through the bridge system.

The Mo—Mo distance in the oxide alkoxide derivative, $\mathrm{Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6}$ ($\mathrm{R = H_2C \cdot CMe_3}$ or $\mathrm{HCMe_2}$) has been shown (*115a*) to be 2.535 Å, which is comparable with Mo—Mo distance (2.524 Å) in $\mathrm{Zn_2Mo_3O_8}$.

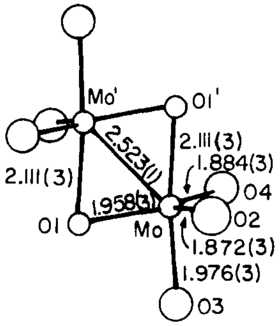


FIG. 9. Skeleton of the structure of $\mathrm{Mo_2(O\text{-}}i\mathrm{Pr)_8}$, showing relevant internuclear distances and bond angles.

TABLE IV

CHARACTERIZATION DATA FOR ALKOXIDES AND TRIALKYLSILOXIDES OF MOLYBDENUM(IV)

Compound[a]	Color	Volatility[b] (°C, 10^{-4} torr)	UV–vis λ_{max}, [nm(ε)][c]	μ_{eff}[d] (BM) $T = 313$ K	Mol wt[e] (calc)	Mass-spectrum parent peak (m/e)
$Mo(O\text{-}t\text{Bu})_4$	Green–brown	70–75	600(40)	1.38	450 ± 20 (388)	388
$Mo(O\text{-}i\text{Pr})_4$	Blue	70–90	640(700)	Diamagnetic	600 ± 30 (332.28)	664
$Mo(OCH_2CMe_3)_4$	Blue-green	150–170	640(320)	0.70	740 ± 30 (444)	888
$Mo(OEt)_4$	Dark green	70–90	700(340)	0.31	860 ± 30 (276)	828
$Mo(OSiMe_3)_4 \cdot 2HNMe_2$	Yellow	100–120	955(2.0) 915(2.0) 390(35)	2.63	551 ± 20 (542)	542
$Mo(OSiEt_3)_4 \cdot 2HNMe_2$	Orange–brown	76 (dec.)	1185(10) 1150(10) 885(20) 730(30) 480(40)	2.20	(711.2)	620

[a] $Mo(OMe)_4$ is purple, nonvolatile, and insoluble in hydrocarbon solvents.

[b] May be sublimed readily at these temperatures.

[c] In cyclohexane.

[d] Determined in toluene by the Evans method.

[e] Determined cryoscopically in benzene.

The reactions of $Mo_2(O\text{-}t\text{Bu})_6$ (*115b*) and $Mo_2(O\text{-}i\text{Pr})_6$ (*115c*) with molecular oxygen yield derivatives with the formulas $MoO_2(OR)_6$. Only in the latter case could an intermediate product with the composition $Mo_6O_{10}(O\text{-}i\text{Pr})_{12}$ be isolated, and it has been shown to contain a serpentine chain of molybdenum atoms with both six- and five-coordinated molybdenums. The average oxidation state for molybdenum is 5.33, which leaves four electrons free for metal–metal bonding. These are apparently used to form two localized single Mo—Mo bonds with length 2.585 Å. An interesting feature not observed previously in metal-alkoxide structures is the presence of "semibridging" OR groups with an M · · · O distance of 2.88 Å, which is too long for a regular bridging bond but much too short to be viewed as nonbonding.

c. Alkoxides of Tungsten(III and IV). The reactions of $W_2(NMe_2)_6$ with alcohols lead to the formation of tungsten alkoxides (*101, 116*). The nature of the products, however, appears to be much more dependent, compared to those in the corresponding reactions of $Mo_2(NMe_2)_6$ (*103–105*), on the nature of the alcohol.

The reactions of $W_2(NMe_2)_6$ with *t*BuOH and Me_3SiOH yield (*116*) the crystalline compounds $W_2(O\text{-}t\text{Bu})_6$ and $W_2(OSiMe_3)_6(NHMe_2)_2$, re-

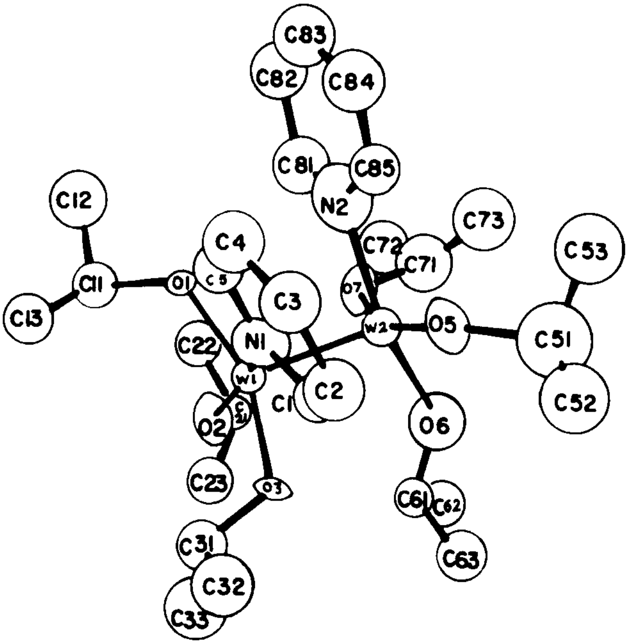


FIG. 10. Structure of the $W_2(O\text{-}i\text{Pr})_6 \cdot (\text{py})_2$ molecule.

spectively. These tungsten compounds, unlike their molybdenum analogs, cannot be sublimed *in vacuo;* they are thermally unstable and the mode of their thermal decomposition *in vacuo* appears to be autocatalytic and not stoichiometric.

The reaction between $W_2(NMe_2)_6$ and the less bulky alcohols *i*PrOH and Me_3CCH_2OH leads to polynuclear products instead of the binuclear products $(RO)_3Mo{\equiv}Mo(OR)_3$ obtained in the corresponding reactions of $Mo_2(NMe_2)_6$. When the reaction of $W_2(NMe_2)_6$ with isopropanol is carried out in pyridine solution, a black, crystalline product, $W_2(O\text{-}i\text{Pr})_6(\text{py})_2$, is obtained that has (Fig. 10) two $W(O\text{-}i\text{Pr})_3 \cdot \text{py}$ units linked by a W≡W bond with a length of 2.332(1) Å. Low-temperature ^{13}C-NMR spectra support the conclusion that this structure is present in solution also.

A detailed study of the reaction of $W_2(NMe_2)_6$ with excess isopropanol has revealed a much more fascinating (*117, 118*) story, involving oxidation of tungsten from the +3 to the +4 state and the final formation of an interesting derivative $W_4(\mu\text{-H})_2(O\text{-}i\text{Pr})_{14}$. Although the mechanism of the reaction has not been fully investigated, the initial step appears to be a normal alcoholysis reaction, common to all metal dimethylamides, leading to the formation of $W_2(O\text{-}i\text{Pr})_6$, which undergoes an oxidative addition of H and *i*PrO across the tungsten–tungsten triple bond to give a solvated $W_2(\mu\text{-H})(O\text{-}i\text{Pr})_7$ species. Solvation again probably involves coordination of excess isopropanol, and evidence has been adduced that $W_4(\mu\text{-H})_2(O\text{-}i\text{Pr})_{14}$ forms dinuclear fragments in the presence of donor molecules such as pyridine, dioxane, and isopropanol.

The compound $[W_2(\mu\text{-H})(O\text{-}i\text{Pr})_7]_2$ has been investigated by IR, NMR, and mass spectroscopy and by a single-crystal X-ray study (see Fig. 11).

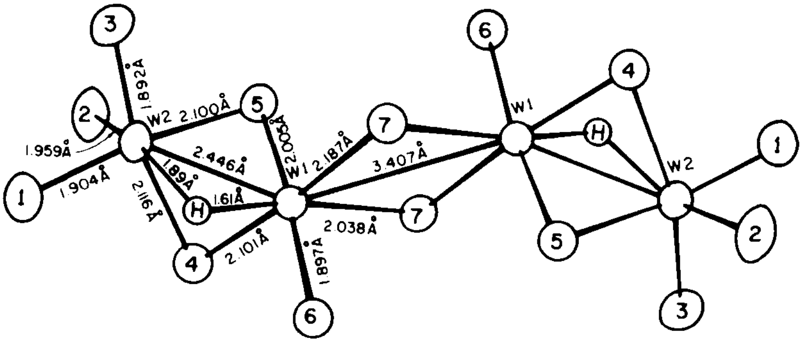


FIG. 11. A view of the $W_4(\mu\text{-H})_2O_{14}$ skeleton, showing the bridging hydrogen atoms and emphasizing the essentially octahedral coordination of each tungsten atom.

Finally, the reactions of $W_2(NMe_2)_6$ with methanol and ethanol ($\gg$6 equivalents) in hydrocarbon solvents at ambient temperatures yield (*119*) dark green or brown crystals of empirical formula $W(OR)_4$. These compounds are diamagnetic, air sensitive, and hydrocarbon soluble. The structure of $[W(OEt)_4]_4$ as represented in Fig. 12 has a striking resemblance to that reported for $[Ti(OEt)_4]_4$, with the change that the presence of d^2 tungsten atoms brings them closer to each other than the d^0 titanium atoms in Fig. 12; Ti—Ti distances are shown (in parentheses) with W—W distances.

Cotton and Fang (*119a*) have carried out a calculation depicting that the lengthening of the two W—W bonds in the eight-electron cluster $W_4(OEt)_{16}$ results from a second-order Jahn–Teller distortion, caused by removal of two electrons from the C_{2h} rhombohedral M_4 geometry, thus accommodating ten cluster electrons in effectively five M—M bonds.

d. Adduct Formation and Other Reactions of $Mo_2(OR)_6$ and $W_2(OR)_6$. Red or purple crystalline adducts $Mo_2(OR)_6 \cdot 2NHMe_2$ have been isolated (*104*) by treating $Mo_2(OR)_6$ (R = Me_3Si and Me_3CCH_2) with dimethylamine, and it has been shown that in hydrocarbon solvents the following equilibrium lies well to the right when L = NH_3, $MeNH_2$, Me_2NH, Me_3N, or Me_2PhP.

$$Mo_2(OR)_6 + 2L \rightleftharpoons Mo_2(OR)_6L_2$$

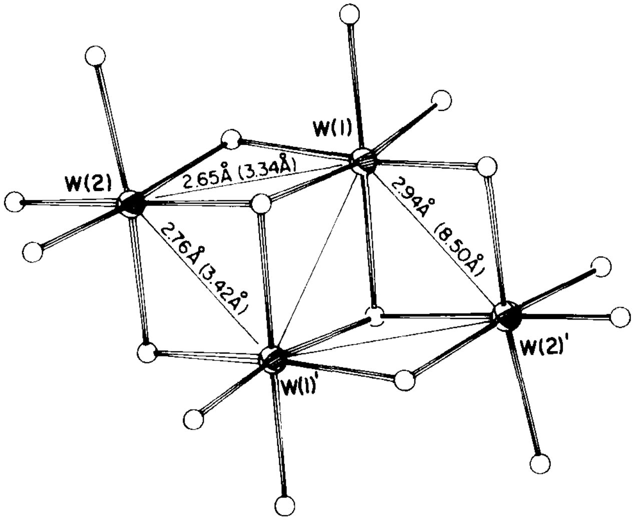


FIG. 12. Ortep view of the central W_4O_{16} unit of the $W_4(OEt)_{16}$ molecule.

In view of the fact that the related dialkylamides (*105*) and alkyls (*106*) Mo_2L_6 ($L = NR_2$, R) do not show this type of affinity for Lewis bases like ammonia, it was conjectured (*105*) that the exceptional behavior of some $Mo_2(OR)_6$ compounds could be due to the preferential ability of these alkoxy groups to form derivatives with alkoxy bridges, endowing the adduct with a structure of the type $L(RO)_2Mo(\mu\text{-}OR)_2Mo(OR)_2L$. However, determination (*120*) of crystal structure by X rays showed that the molecule $Mo_2(OSiMe_3)_6 \cdot 2NHMe_2$ has a nonbridged structure, $(Me_3SiO)_3(Me_2NH)Mo{\equiv}Mo(Me_2NH)(OSiMe_3)_3$, with an Mo≡Mo distance of 2.242(1) Å, a mean Mo—O distance (average of six) of 1.95 ± 0.02 Å, and a mean Mo—N distance (average of two) of 2.282 ± 0.004 Å (Fig. 13). The rotational conformation is intermediate between eclipsed and staggered, but closer to the latter. This structure, therefore, provides the first proven example of a molecule having two four-coordinated metal atoms triply bonded to each other, without any bridging groups (see Fig. 13).

In contrast to the adduct $Mo_2(OSiMe_3)_6 \cdot 2NMe_2H$, in which the original Mo≡Mo bond is retained and there is no bridging ligand, the reaction of a solution of $Mo_2(O\text{-}t Bu)_6$ in hydrocarbon with CO at room temperature and 1-atm pressure appears to give an intermediate monocarbonyl adduct $Mo_2(O\text{-}t Bu)_6(\mu CO)$, in which the CO ligand bridges a Mo=Mo double bond. The overall reaction can be represented as (*121*)

$$2Mo_2(O\text{-}t Bu)_6 + 6CO \rightleftarrows Mo(CO)_6 + 3Mo(O\text{-}t Bu)_4 \ldots \qquad (1)$$

As mentioned previously, the reaction proceeds via slow and reversible formation of a bridged adduct, $Mo_2(O\text{-}t Bu)_6(CO)$. Dark purple crystals of the compound could be isolated by exposing near-saturated alkane

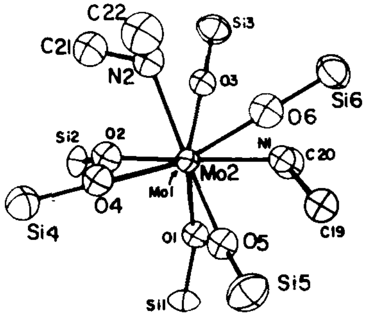


FIG. 13. Ortep view of the $Mo_2(OSi)_6(NC_2)_2$ portion of $Mo_2(OSiMe_3)_6(NHMe_2)_2$, looking directly down the Mo—Mo bond with Mo(1) eclipsed by Mo(2).

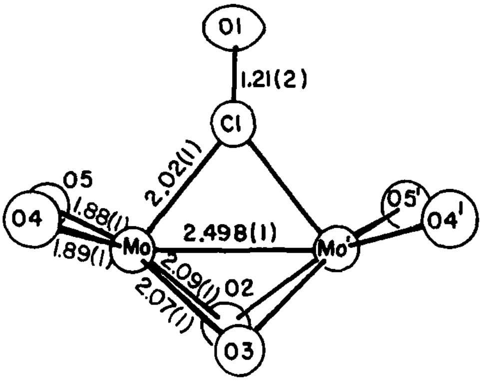


FIG. 14. A view of the $Mo_2O_6(CO)$ skeleton of the $Mo_2(O\text{-}t\mathrm{Bu})_6(CO)$ molecule, with relevant internuclear distances.

solutions of $Mo_2(O\text{-}t\mathrm{Bu})_6$ to two equivalents of CO at room temperature and then cooling the solution to about −15°C. $Mo_2(O\text{-}t\mathrm{Bu})_6(CO)$ is thermally unstable, liberating CO and forming $Mo_2(O\text{-}t\mathrm{Bu})_6$ when heated under vacuum:

$$Mo_2(O\text{-}t\mathrm{Bu})_6 + CO \rightleftharpoons Mo_2(O\text{-}t\mathrm{Bu})_6(CO)\ .\ .\ . \qquad (2)$$

The structure of this interesting compound, as revealed by X-ray studies, is illustrated in Fig. 14.

TABLE V

PERTINENT STRUCTURAL DATA FOR THE $Mo(O\text{-}t\mathrm{Bu})_2(CO)_2(py)_2$ MOLECULE[a]

Molecule	Bond distance (Å)	Molecule	Bond distance (Å)
Mo—C(1)	1.94	Mo—O(3)	1.94
Mo—C(2)	1.95	Mo—O(4)	1.95
C(1)—O(1)	1.16	Mo—N(1)	2.34
C(2)—O(2)	1.17	Mo—N(2)	2.36

Molecule	Angle (deg)	Molecule	Angle (deg)
C(1)—Mo—C(20	72	O(3)—Mo—O(4)	156
N(1)—Mo—N(2)	85	C(3)—O(3)—Mo	140
C(1)—Mo—N(1)	101	C(4)—O(4)—Mo	141
C(2)—Mo—N(2)	102	Mo—C(1)—O(1)	173
		Mo—C(2)—O(2)	174

[a] All distances and angles quoted are significant to ±1 in the last digit quoted.

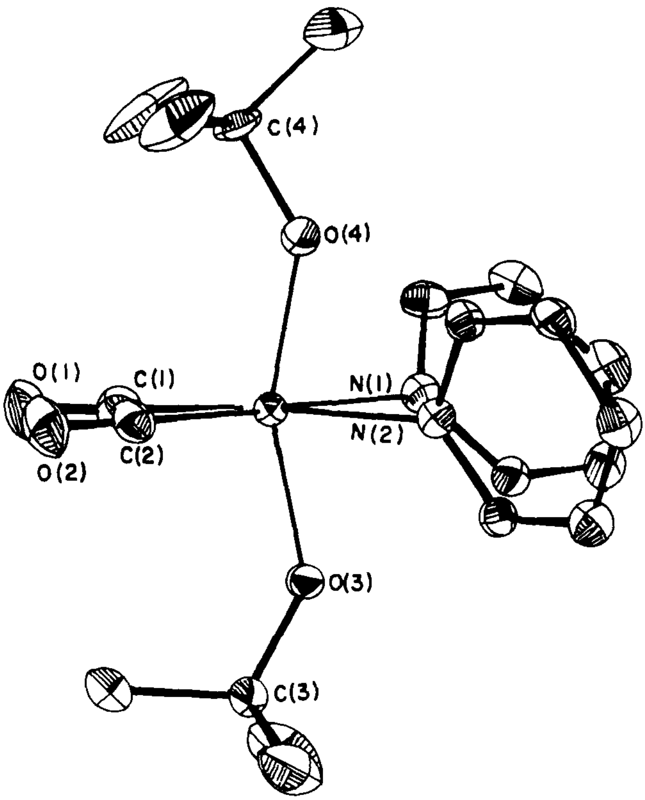


FIG. 15. Ortep view of the $Mo(O\text{-}t\mathrm{Bu})_2(CO)_2(py)_2$ molecule, showing the atomic numbering scheme used in Table V.

In an attempt to trap alkoxide–carbonyl compounds of molybdenum in a reduced oxidation state in reaction (1), mild carbonylation (room temperature and 1-atm pressure of CO) of $Mo_2(O\text{-}t\mathrm{Bu})_6$ was carried out (*122*) in a hexane–pyridine solvent mixture. The structure of a green, air-sensitive crystalline compound with the composition $Mo(O\text{-}t\mathrm{Bu})_2(py)_2(CO)_2$ is represented in Fig. 15 (see also Table V).

Although analogous carboxylation of $(i\mathrm{PrO})_3M{\equiv}M(O\text{-}i\mathrm{Pr})_3$ also yields $Mo(CO)_6$, the reaction probably follows a different stoichiometry from that indicated by reaction (1), because molybdenum(IV) isopropoxide $[Mo_2(O\text{-}i\mathrm{Pr})_8]$ is binuclear, with a Mo=Mo double bond (*114*), and itself reacts with CO to give a black crystalline substance of empirical formula $Mo(O\text{-}i\mathrm{Pr})_3CO$. The derivative is unstable in solution, slowly reacting to form $Mo(CO)_6$; in the presence of added CO this reaction is fast. Although X-ray structural determination has not been possible so far, the molecule appears to be tetrameric.

In view of the known catalytic activity of molybdenum oxide compounds, the reactions of molybdenum alkoxides were studied with alkynes (*123*). $Mo_2(O\text{-}i Pr)_6$ in hydrocarbon solutions reacts rapidly with alkynes RC_2R' ($R = R' = H$; $R = Me$, $R' = H$, $R = R' = Me$) at room temperature, but products could not be identified with certainty. However, in the presence of added pyridine (>2 equivalents), crystalline solids with the composition $Mo_2(O\text{-}i Pr)_6(py)_2(RC_2R')$ were isolated from a hexane solution. The crystal and molecular structures of the ethyne adduct are shown in Fig. 16.

The acetylene bridges the two molybdenum atoms in a crosswise manner. The C—C distance, 1.368(6) Å, is longer than in ethylene [1.337(3) Å] and is, in fact, among the longest known for $M_2(\mu\text{-}C_2R_2)$ compounds. The Mo—C distances are, however, short [2.09 Å (average)]. These values may be compared with C—C = 1.337(5) Å and Mo—C = 2.18 Å (average) associated with the $Mo_2(\mu\text{-}C_2H_2)$ unit in $Cp_2Mo_2(CO)_4(C_2H_2)$ (*124*). The compound $Mo_2(OCH_2CMe_3)_6(HNMe_2)_2$ reacts in hydrocarbon solvents with HC≡CH (1 equivalent) to give a similar derivative, $Mo_2(OCH_2CMe_3)_6(HNMe_2)_2(C_2H_2)$.

Hydrocarbon solutions of $Mo_2(OR)_6$ compounds (R = *i*Pr, *t*Bu) react with dimethylcyanamide, Me_2NCN, to give intensely purple solutions

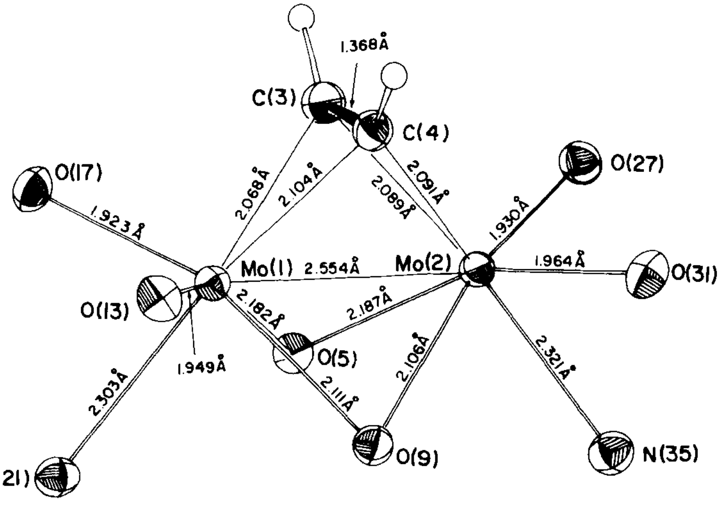


FIG. 16. Ortep view of the central skeleton of the $Mo_2(O\text{-}i Pr)_6(py)_2(C_2H_2)$ molecule, showing the relevant internuclear distances.

from which dark, air- and moisture-sensitive crystals corresponding in analysis to $Mo_2(OR)_6 \cdot NCNMe_2$ are obtained (*125*). Formation of these adducts is reversible, and the Me_2NCN ligand is readily lost when these compounds are heated *in vacuo;* only $Mo_2(OR)_6$ compounds sublime. On the basis of IR and ^{1}H-NMR studies, it has been proposed that the ligand Me_2NCN acts as a four-electron donor and spans the Mo—Mo bond in a manner similar to that reported in the $Cp_2Mo_2(CO)_4 \cdot NCNMe_2$ derivative (*126*). The cyanamide ligand can be considered to form an N σ bond to one molybdenum atom and a CN π bond to the other. It has been further suggested that in the ground state (solid structure) the alkoxy groups are not eclipsed but adopt a partially staggered configuration similar to that in $Mo_2(OSiMe_3)_6 \cdot 2NHMe_2$ (*120*). The ground-state structure would, therefore, consist of two enantiomers, which are schematically represented in Fig. 17.

The reactions of $Mo_2(OR)_6$ compounds (R = *i*Pr, *t*Bu, and CH_2CMe_3) with nitric oxide yield (*55*) a novel type of yellow crystalline nitrosyl complex with the empirical formula $Mo(OR)_3NO$. These derivatives show NO stretching frequencies at approximately 1640 cm^{-1}, and they are diamagnetic, dimeric, and fluxional in solution. The compound $[Mo(O\text{-}i\text{Pr})_3NO]_2$ crystallizes in space group $P\bar{1}$ with $Z = 2$ and unit-cell dimensions $a = 10.828(1)$, $b = 15.848(2)$, $c = 9.885(2)$ Å, $\alpha = 90.21(2)$, $\beta = 115.93(2)$, $\gamma = 82.42(1)°$, and $V = 1509.4(5)$ Å^3. There are two crystallographically independent molecules, one centered on the origin, the other at ½, ½, ½, that are essentially identical in structure. Each molybdenum atom is five-coordinated in a trigonal bipyramidal

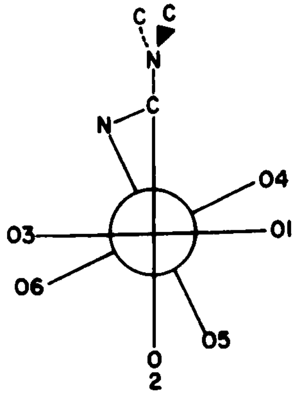


FIG. 17. Schematic representation of the proposed ground-state structure of the $Mo_2(O\text{-}i\text{Pr})_6 \cdot NCNMe_2$ molecule, viewed down the Mo—Mo bond.

manner and attains only a 14-valence-shell electron configuration. The nitrosyl ligands occupy terminal axial positions, and the two bridging O-*i*Pr groups form short bonds in equatorial positions and long bonds in axial positions that are trans to the NO ligands. The Mo—N—O units are essentially linear (178°), and the bond lengths therein are 1.754(7) Å for Mo—N and 1.19(1) Å for N—O. The Mo · · · Mo separation of 3.335(2) Å precludes metal-to-metal bonding; the Mo≡Mo bonds of $Mo_2(OR)_6$ derivatives are thus cleaved by the addition of two NO ligands. The electronic structure in these new nitrosyl metal complexes can be formulated so that the highest filled MO is the e level responsible for Mo to NO π bonding; it is made up of metal d_{xz}, d_{yz}, and NO π^* orbitals. It would be interesting, in view of this, to investigate the possibility of the existence of other similar $MX_3(NO)L$ molecules.

An adduct of the type just discussed of tungsten(III) with composition $W(O\text{-}t\text{Bu})_3(NO)(C_5H_5N)$ has been isolated (*127*) by the direct reaction between $W_2(O\text{-}t\text{Bu})_6$ and NO (2 equivalents) in pyridine as solvent. The compound exists in a slightly distorted trigonal bipyramidal structure (Fig. 18), with the axial positions occupied by nitrosyl and pyridine ligands. The tungsten atom is displaced 0.34 Å toward the nitrosyl ligand from the equatorial plane of the three alkoxy oxygen atoms. The nitrosyl ligand is coordinated linearly, and the W—N(1) bond is quite short [1.732(8) Å], which is indicative of some multiple-

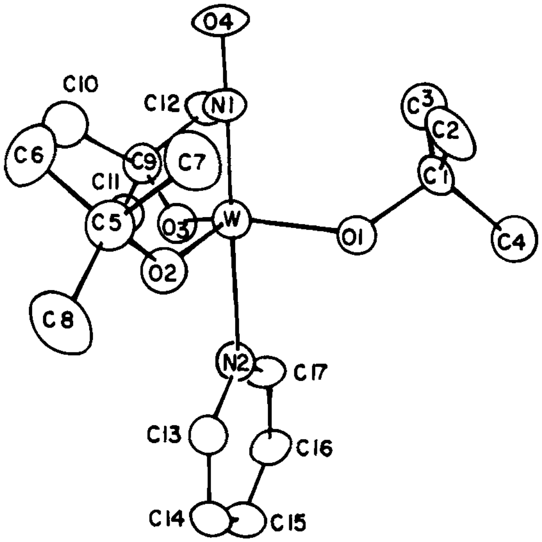


FIG. 18. Ortep view of the $W(O\text{-}t\text{Bu})_3(NO)(C_5H_5N)$ molecule.

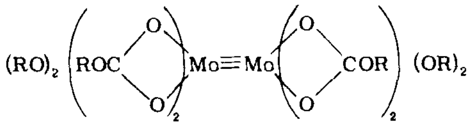
bond character, whereas the tungsten–pyridine bond is considerably longer, W—N(2) = 2.323(7) Å. The W—O distances are in the expected range, that is, 1.876–1.898 Å.

Pyridine as well as similar adducts with other donor ligands (NH_3 and NMe_3) have also been isolated as soluble products by the addition of the ligands to the insoluble products, $W(O\text{-}t\text{Bu})_3NO$, obtained by the reaction between $W_2(O\text{-}t\text{Bu})_6$ and nitric oxide (2 equivalents) in hydrocarbon solvents.

$Mo_2(OR)_6$ compounds (R = Me_3Si, *i*Pr, *t*Bu, and Me_3CCH_2) react (*128*) readily and reversibly both in solution and in the solid state with CO_2 (>2 equivalents) to give insertion products according to the equation

$$Mo_2(OR)_6 + 2CO_2 \rightleftharpoons Mo_2(OR)_4(O_2COR)_2$$

The products are moisture- and oxygen-sensitive cream-colored solids that are diamagnetic. These are quite stable in the solid state at room temperature, but decarboxylation and sublimation occur simultaneously at 90°C under 10^{-4} cm Hg, yielding $Mo_2(OR)_6$. The physicochemical properties suggested a structure of the type



which has been confirmed by the structure shown in Fig. 19, revealed by X-ray crystallography. Using the SCF-X_α scattered-wave method, the ground-state electronic structures of $(HO)_3Mo{\equiv}Mo(OH)_3$ and related molecules (*129*) have been calculated. The $\pi(e_u)$ and $\sigma(a_{1g})$ orbitals, which have large amounts of metal character, have been identified as the orbitals primarily responsible for Mo—Mo bonding. Using the transition-state technique to allow for relaxation effects, the photoelectron spectra have been calculated for $Mo_2(OH)_6$ and have been (after applying a constant downshift to correct for inductive effects) found to compare very well for the experimental spectra exhibited by $Mo_2(OCH_2C(CH_3)_3]_6$.

D. RHENIUM

With the exception of a volatile brown hexamethoxide (*99a*) and the triple-alkoxo-bridged carbonyl anions (*130*) $[(CO)_3Re(\mu\text{-}OR)_3Re$-

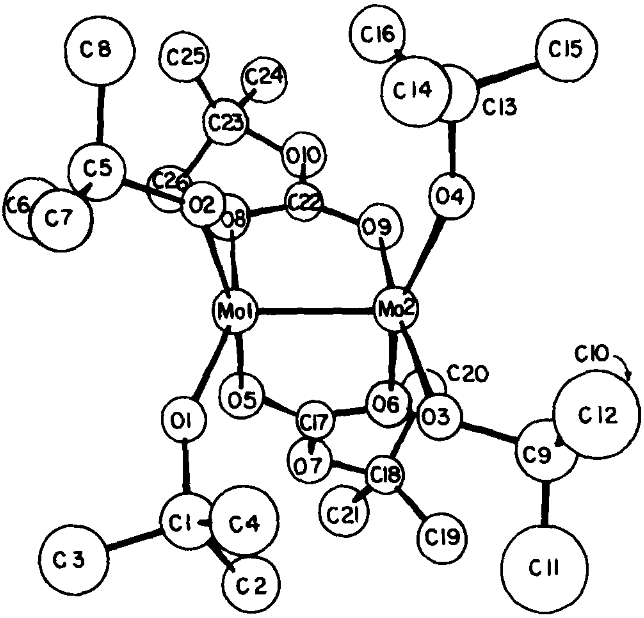


FIG. 19. Ortep drawing of the $Mo_2(O_2COCMe_3)_2(OCMe_3)_4$ molecule.

$(CO)_3]^-$ (R = Et, *i*Pr), other alkoxo species of rhenium have only one alkoxo group and contain either tertiary phosphine ligands (*131*), as in $ReO(OEt)Cl_2(PPh_3)_3$, or methyl and acetate groups in the insoluble $[ReMe(OMe)(O_2CMe)]_n$ (*132*).

Interaction (*133, 134*) of $ReOCl_4$ with methanol in the presence of amines gives the unusual alkoxo compound $(MeO)_2(O)Re(\mu\text{-}O)(\mu\text{-}OMe)_2ReO(OMe)_2$ (**I**), whereas LiO-*t*Bu gives $ReO(O\text{-}t\text{Bu})_4$ (**II**), and LiO-*i*Pr gives an unusual dimeric species, $Li[ReO(O\text{-}i\text{Pr})_5]LiCl(THF)_2$ (**III**). The interaction with phenol in the presence of trimethylphosphine leads to the compound *trans*-$(Me_3P)_2Re(OPh)_4$ (**IV**), whereas with lithium bis(trimethylsilylamide) a unique tetracoordinate rhenium(V) compound $ReO[N(SiMe_3)_3]_3$ is obtained.

The crystal structures of **I** (Fig. 20), **II**, and **IV** have been determined by X-ray crystallography. Compound **I** is monoclinic, space group $P2_{1/n}$, $a = 12.142(1)$, $b = 15.369(1)$, $c = 7.311(1)$ Å, $\beta = 90.22(1)°$, and $Z = 4$. Compound **II** is triclinic, space group $P\bar{1}$, $a = 14.602(5)$, $b = 13.363(3)$, $c = 9.244(6)$ Å, $\alpha = 98.39(4)$, $\beta = 102.35(5)$, $\gamma = 68.71(2)°$, and $Z = 1$. Compound **IV** is monoclinic, space group $P2_{1/c}$, $a = 10.079(2)$, $b = 10.527(3)$, $c = 14.443(3)$ Å, $\beta = 97.28(2)°$, and $Z = 2$.

The reaction of trimethylsilyl perrhenate, $Me_3SiOReO_3$, with excess

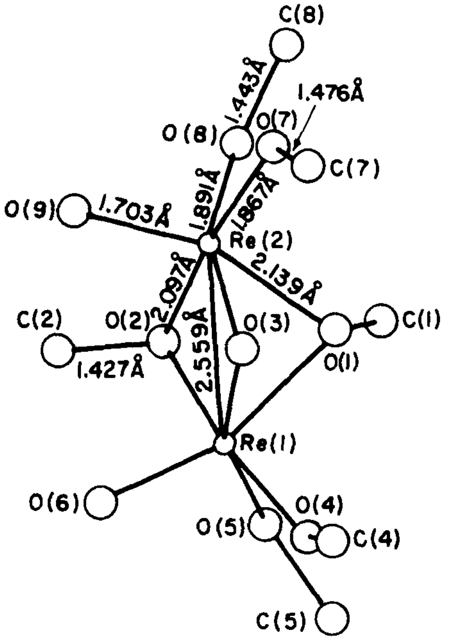
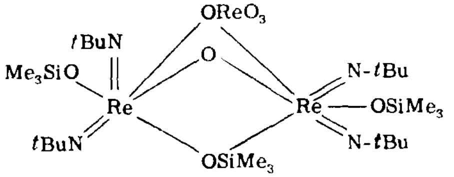


FIG. 20. Molecular structure of $Re_2O_3(OMe)_6$, showing typical internuclear distances.

butyltrimethylsilylamine in hexane gives (*135*) a yellow derivative, $Me_3SiORe(N\text{-}t Bu)_3$ (mp 36–38°C):

$$Me_3SiOReO_3 + 3tBuNHSiMe_3 \rightarrow Me_3SiORe(N\text{-}tBu)_3 + 3Me_3SiOH$$

When an insufficient amount of $tBuNHSiMe_3$ is used in this reaction, a yellow, low-melting-point solid is obtained that corresponds in analysis to $Re_3(N\text{-}tBu)_4O_5(OSiMe_3)_2$, which has been characterized by X-ray crystal-structure study to have a configuration of the type



The trirhenium-cluster alkoxide $Re_3Cl_3(O\text{-}tBu)_6$ has also been synthesized (*136*).

E. RUTHENIUM AND RHODIUM

The interaction of dihydridotetrakis(triphenylphosphine)ruthenium(II) with phenol gives a neutral complex, $RuH(C_6H_5O)(PPh_3)_3$, which may also be obtained with an additional molecule of phenol hydrogen-bonded to the oxygen atom of the phenoxo ligand. The $C_6H_5O^-$ ligand can be considered to be bound as an η^6-phenoxo or, probably more realistically, as an η^5-oxacyclohexadienyl ligand. The π-bonded nature of the phenoxide ion is confirmed by IR, NMR, and X-ray structural data (*21*). A complex of the composition $Rh(OPh)(PPh_3)_3$ (*137*), obtained by the action of phenol on $RhMe(PPh_3)_3$ or $RhPh(PPh_3)_3$, has also been shown to be a π-phenoxo complex.

The crystal structure (Fig. 21) of $Rh(ArO\text{-}\eta^5)(PPh_3)_2$ (Ar = 2,6-$t$$Bu_2-4MeC_6H_2$), obtained by the reaction of ArOH on $Rh[N(SiMe_3)_2](PPh_3)_2$ in toluene at 20°C has been shown (*138*) to involve π-bonded phenoxo ligands with (a) C(2)—C(6) in the same plane [average C—C = 1.38(2) Å], (b) C(1)—O = 1.28 Å, and (c) Rh—C(2) and Rh—C(6) bond lengths in the range 2.19–2.65 Å. The structure of the corresponding titanium complex, $Ti(\eta\text{-}C_5H_5)_2OAr$, by contrast, was depicted as the O-bonded phenoxo ligand.

F. PLATINUM AND PALLADIUM

Transition-metal d^8 complexes containing metal–oxygen bonds have been reported to play an important role as intermediates in synthetic reactions, particularly in some catalytic processes, for example, hydration of nitriles and oxidation of ethylene and alcohols. Until fairly recently, few nonionic hydroxo- or alkoxoplatinum(II) complexes were known. Complexes originally formulated as $Pt(GePh_3)(OR)(PEt_3)_2$ (R = H, Me, Et, iPr) (*139*) are now known to be $Pt(Ph)[Ge(OR)Ph_2](PEt_3)_2$, following a single-crystal X-ray study (*140*) of the hydroxo derivative. Although some nonbridging hydroxo complexes of $5d^8$ and $6d^8$ metals such as Ru^0, Os^0, Rh^I, Ir^I, Pd^{II}, and Pt^{II} had been isolated, only two alkoxo complexes of these soft metals were known until 1976 (*141*); they are $Pt(cyclohexenyl)(Ph_2PCH_2CH_2PPh_2)$ (*142*) and $[Ir(NO)(OR)(PPh_3)_2]^+$ (R = Et or n-Pr) (*143*). A series of mononuclear methoxo complexes, *cis*- and *trans*-$[MR(OMe)(PPh_3)_2]$ (M = Pd or Pt; R = C_6H_5, $CH{=}CCl_2$, $CCl{=}CCl_2$), have been synthesized by metathesis of $MRCl(PPh_3)_2$ with NaOMe. The stability of the M—OR bond appears to be influenced markedly by the identity of the metal (Pt > Pd) and the nature of the trans ligand R. In contrast to mononuclear platinum and palladium complexes, the reaction of NiR-

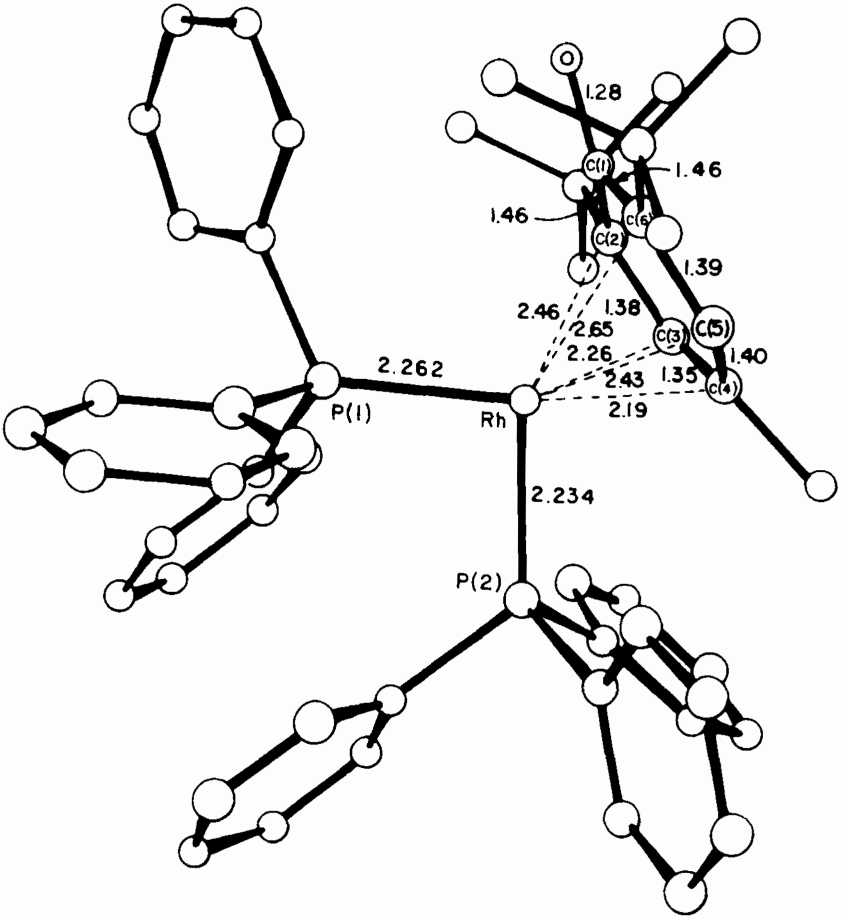
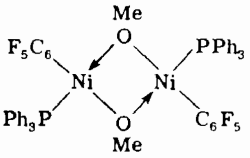
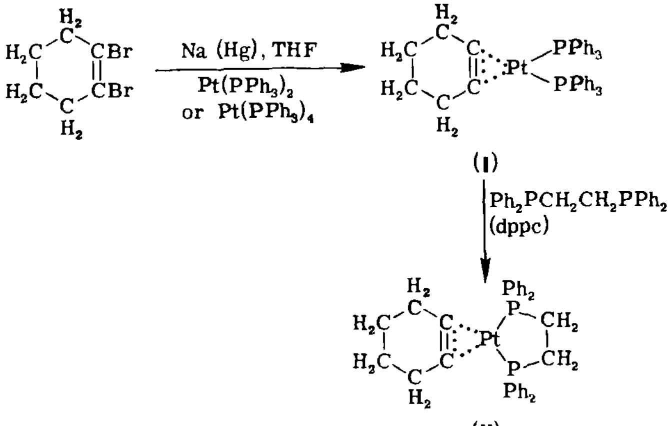


FIG. 21. Perspective view of the molecular structure of [Rh(OAr-η^5)(PPh$_3$)$_2$], showing selected bond lengths.

(Cl)(PPh$_3$)$_2$ (R = C$_6$F$_5$, CCl=CCl$_2$) with NaOMe gives red, crystalline μ-methoxo complexes, [NiR(μ-OMe)(PPh$_3$)]$_2$, with dissociation of 1 mol of PPh$_3$ (*144*).



Cyclohexene–platinum(0) complexes can be prepared as shown here:



(I)

(II)

Compounds **I** and **II** are protonated by water and primary alcohols (*145*), yielding thermally stable crystals of σ-alkoxoplatinum(II) complexes, for example, $Pt(OCH_3)(C_6H_9)(dppe)$. The complexes react readily with CO, bringing about insertion between platinum–oxygen bonds, yielding, for example, $Pt(CO_2CH_3)(C_6H_9)(dppe)$.

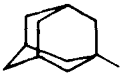
The first moisture-stable mixed methoxy- and chlorobridged dinuclear platinum(II) (*145a*) palladium(II) (*145b*) complexes, $M_2(\mu\text{—Cl})=(\mu\text{—OMe})(t\text{-}Bu_2PCMe_2CH_2)_2$ (M = Pt, Pd), have been isolated by the reactions of the corresponding chloro-bridged dinuclear complexes, $M_2(\mu\text{—Cl})_2(t\text{-}Bu_2PCMe_2CH_2)_2$, suspended in methanol with an equimolar amount of NaOH at 40°C. The corresponding reaction of $(COD)PtCl_2$ (COD=1,5-cyclooctadiene) with 2 equivalents of NaOH in aqueous methanol has been reported (*145c*) to yield the methoxy-bridged dinuclear complex $[Pt(\mu\text{—}OCH_3)(C_8H_{12}OCH_3)]_2$. The methoxy bridges in this last complex are cleared by tertiary phosphines (L) to yield mononuclear methoxy complexes, $(C_8H_{12}OCH_3)Pt(OCH_3)L$.

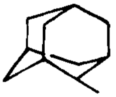
In order to elucidate the factors governing the stability and nature of σ Pt—OR bonds,a series of square-planar complexes, *cis*- and *trans*-$Pt(OMe)(R)L_2$ (R = CH_2CN, CF_3, CH_2CF_3; L_2 = $2PPh_3$, diphosphene), have been prepared as colorless products in high yields by metathesis of $PtCl(R)L_2$ or $[Pt(R)L_2]BF_4$ with NaOMe, slightly above room temperatures in an anhydrous benzene–methanol mixture. The success in preparing these complexes seems to be related to the nature of the alkyl ligand R; a more electronegative R will increase the effective positive charge on the platinum, and consequently the electron density on the OCH_3 group will decrease, increasing the covalency of the Pt—OCH_3 bond. These complexes can be converted to the corresponding hydroxo derivatives by hydrolysis with water. The platinum–oxygen bonds in these complexes undergo facile insertion of CO, COS, CS_2, and SO_2 (*146*).

IV. Alkoxides of Transition Metals with Sterically Hindered and Unsaturated Alcohols

Ever since the pronounced effects of the branching of alkyl groups on the properties of alkoxides of a number of metals, [e.g., titanium, zirconium (*147*), and aluminum (*148*)] were demonstrated (*13*), the preparation of sterically hindered alkoxides of metals has been attracting the attention of the investigators (see *56, 58, 149*).

In view of their sterically demanding and highly symmetrical nature, alkoxides of metals containing adamantyl groups could be expected to exhibit some unusual features. Bochmann *et al.* (*150*) have described the synthesis and properties of 1-adamantoxides, 2-adamantoxides, and 1-adamantylmethoxides of a number of transition metals


1-adamantyl


2-adamantyl

[i.e., Ti(IV), V(IV), Nb(IV and V), Cr(III and IV), Mo(IV), Mn(II), Fe(III), Co(II)] by the reaction

$$\mathrm{Ti(O\text{-}\mathit{i}Pr)_4 + 4ROH \xrightarrow[\text{refluxing}]{\text{benzene}} Ti(OR)_4 + 4\mathit{i}PrOH}$$

$$\mathrm{V(NEt_2)_4 + 4ROH \xrightarrow[\text{r. t., (12–18 h)}]{\text{diethyl ether}} V(OR)_4 + 4NHEt_2}$$

$$\mathrm{Nb(NEt_2)_4 + 4(1\text{-}ado)H \xrightarrow[\text{r. t.}]{\text{diethyl ether}} Nb(1\text{-}ado)_4 + 4NHEt_2}$$

$$\mathrm{Nb(NEt_2)_4 + (1\text{-}ado)H \xrightarrow[\text{refluxing}]{\text{diethyl ether}} Nb(1\text{-}ado)_5}$$

$$\mathrm{Nb(NEt_2)_4 + (2\text{-}ado)H \xrightarrow[\text{r. t.}]{\text{diethyl ether}} Nb(2\text{-}ado)_5}$$

$$\mathrm{Nb(NEt_2)_4 + 4(1\text{-}admeo)H \rightarrow Nb(1\text{-}admeo)_4 \cdot 0.5NEt_2H + 3.5NHEt_2}$$

$$\mathrm{Cr(N\text{-}}i\mathrm{Pr_2)_3 + 3(1\text{-}ado)H \xrightarrow[\text{r. t.}]{\text{diethyl ether}} Cr(1\text{-}ado)_3 + 3NH\text{-}}i\mathrm{Pr_2}$$

$$\mathrm{Cr[N(SiMe_3)_2]_3 + (1\text{-}ado)H \xrightarrow{\text{boiling toluene}} \text{no reaction}}$$

$$\mathrm{Cr(NEt_2)_4 + 4(1\text{-}ado)H \xrightarrow[\text{40–60°C}]{\text{pet. ether}} Cr(1\text{-}ado)_4 + 4NHEt_2}$$

$$\mathrm{Mo(NMe_2)_4 + 4(1\text{-}ado)H \xrightarrow[\text{r. t.}]{\text{diethyl ether}} Mo(1\text{-}ado)_4 \cdot (NHMe_2) + 3NHMe_2}$$

$$\begin{array}{c}\mathrm{Mn[N(SiMe_3)_2]_2 + 2(1\text{-}ado)H} \\ \text{or} \\ \mathrm{2(1\text{-}admeo)H}\end{array} \xrightarrow[\text{diethyl ether}]{\text{light pet.}} \begin{array}{c}\mathrm{Mn(1\text{-}ado)_2 + 2NH(SiMe_3)_2} \\ \text{or} \\ \mathrm{Mn(1\text{-}admeo)_2}\end{array}$$

$$\mathrm{Fe[N(SiMe_3)_2]_3 + 3(1\text{-}ado)H \xrightarrow[\text{refluxing}]{\text{benzene}} Fe(1\text{-}ado)_3 + 3NH(SiMe_3)_2}$$

$$\begin{array}{c}\mathrm{Co[N(SiMe_3)_2]_2 + 2(1\text{-}ado)H} \\ \text{or} \\ \mathrm{2(1\text{-}admeo)H}\end{array} \xrightarrow{\text{benzene}} \begin{array}{c}\mathrm{Co(1\text{-}ado)_2 \quad + 2NH(SiMe_3)_2} \\ \text{or} \\ \mathrm{Co(1\text{-}admeo)_2}\end{array}$$

(1-ado)H = 1-adamantyl alcohol, (1-admeo)H = 1-adamantylmethanol; RO = (1-ado), (2-ado), or (1-admeo)

The alkoxides of tetra- and pentavalent metals are polymeric or monomeric crystalline solids, but those of di- and trivalent metals are polymeric materials. As expected, adamantylmethoxides show characteristics that are somewhat distinct from the adamantoxides; for example, Ti(1-ado)$_4$ and Ti(2-ado)$_4$ are white, crystalline solids with melting points above 350°C and are only moderately soluble in organic solvents, but Ti(1-admeo)$_4$ has a lower melting point, is considerably more soluble in diethyl ether and benzene, and is much more sensitive to hydrolysis.

An X-ray crystallographic study of Mo(1-ado)$_4$(NHMe$_2$) confirms a trigonal bipyramidal structure of the complex, with the amine and one alkoxo group in the axial positions (see Fig. 22). The axial Mo—O distance [1.963(2) Å] is approximately 0.06 Å longer than the equatorial distances [1.888(3)–1.916(2) Å], and Mo—N bond length is 2.321(3) Å. The compound crystallizes in triclinic space group $P1$, with a = 13.500(1), b = 13.168(2), c = 11.646(1) Å, α = 91.034(10), β = 103.835(8), γ = 70.842(10)°, and Z = 2. The structure in Fig. 22 has been solved by Patterson and Fourier methods and refined by least squares to R = 0.041, using 5267 observed diffractometer data.

It may not be out of place to mention here the syntheses (*151*) of per-

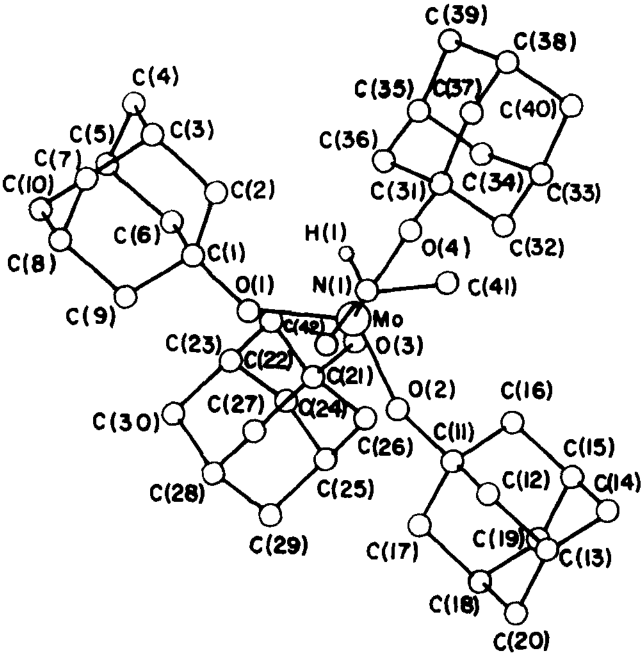
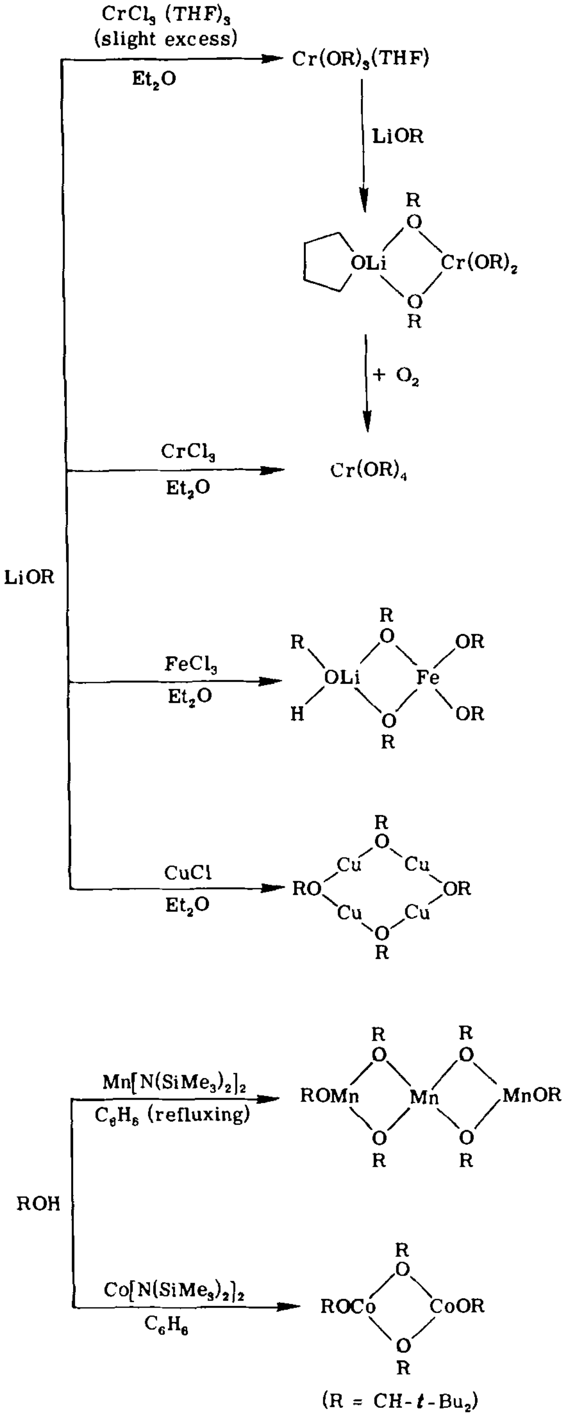


FIG. 22. Structure of $\mathrm{Mo(1\text{-}ado)_4(NHMe_2)}$, showing the atom-numbering system.

1-adamantylmethyls of Ti, V, Cr, Mn, and Zr by the reactions of $\mathrm{Ti(O\text{-}\mathit{i}Pr)_4}$, $\mathrm{V(O\text{-}\mathit{i}Pr)_4}$, $\mathrm{Cr(O\text{-}\mathit{t}Bu)_4}$, $\mathrm{MnBr_2}$, and $\mathrm{ZrCl_4}$ with Li(1-adamantylmethyl) in light petroleum or diethyl ether. The special stability of these peralkyls and their ease of formation can also be understood on the basis of the inertness of the adamantene cage toward structural rearrangements.

In a later publication (*152*) the synthesis and properties of bis(*t*-butyl)methoxides of chromium(III and IV), manganese(II), iron(III), cobalt(II), and copper(I) were described. Bis(*t*-butyl)methanol appears to be sterically even more demanding than 1- or 2-adamantanols; for example, it does not react even in boiling toluene with some first-row transition metal dialkylamides, notably the tris and tetrakis compounds $\mathrm{V(NEt_2)_4}$, $\mathrm{Cr[N(SiMe_3)_2]_3}$, or $\mathrm{Cr(NEt_2)_4}$, although it does react with some bis derivatives, such as $\mathrm{Mn[N(SiMe_3)_2]_2}$. The tris and tetrakis alkoxides have, therefore, been obtained from the metal halide and lithium bis(*t*-butyl)methoxide. Scheme 2 represents the reactions studied.



Royal-blue air-sensitive crystals. Soluble in organic solvents; monomeric. $\mu_{eff} = 3.2$ BM. Dimeric in solid (broad band at 555 cm^{-1}).

Blue or intensely green crystals. Monomeric in benzene; readily oxidized by O_2 or CuCl to $Cr(OR)_4$.

Blue-green crystals stable in air. Absence of absorption in 450–700-cm^{-1} range indicates monomeric nature in solid state.

Air-sensitive yellow crystals; structure similar to $LiCr(OR)_4(THF)$.

Very air-sensitive pale yellow crystals. Decomposes slowly at r.t., particularly in light. More stable than $[CuOMe]_n$ and less stable than Cu(O-*t*Bu).

Pale pink crystals. Air sensitive. Readily soluble in nonpolar solvents; trimeric in benzene. Suggested 3-coordinated structure for terminal metal atoms similar to Mn dialkyls (*153*).

Air sensitive; deep blue; soluble in nonpolar solvents. Dimeric in benzene (cryoscopy). Electronic spectrum in diethyl ether suggests 4-coordinate Co because of coordination of solvent molecules.

SCHEME 2

Electron paramagnetic resonance and electron absorption spectral data of the derivatives in Scheme 2 are given in Table VI. Furthermore, the crystal and molecular structures of the complexes $LiCr(OCH\text{-}t Bu_2)_4 \cdot THF$ (I), $Cr(OCH\text{-}t Bu_2)_4$ (II), and $LiFe(OCH\text{-}t Bu_2)_4 \cdot t Bu_2CHOH$ (III) have been determined by X-ray crystallographic studies and are depicted in Figs. 23–25.

Compound I (Fig. 23) is triclinic, space group $P1$, with a = 19.986(2), b = 11.618(2), c = 11.390(1) Å, α = 117.61(1), β = 76.45(1), γ = 93.11(1)°, and Z = 2. Compound II (Fig. 24) is monoclinic, space group $C_{1/c}$, with a = 20.249(3), b = 10.748(1), c = 20.275(2) Å, β = 116.68(1)°, and Z = 4. Compound III (Fig. 25) is monoclinic, space group $P2_{1/n}$, with a = 18.308(3), b = 22.505(4), c = 11.979(5) Å, β = 94.20(1)°, and Z = 4. The structures were determined using data measured on an automatic diffractometer and were refined by least squares to R values of 0.068 (3396 observed data), 0.067 (2057 data), and 0.061 (4879 data) for I, II, and III, respectively. All structures contain a distorted, tetrahedrally coordinated chromium or iron atom; and in I and III the lithium ion is incorporated into the Mo_4 coordination sphere, bridging two of the four alkoxo oxygen atoms. The transition-metal geometries are discussed in terms of steric and electronic factors.

Among the new alkoxides of transition metals described are the alkenoxides (*154*) [namely, cinnamoxides (*155*), crotyloxides (*156*), methylbutenoxide (*157*), 3-pentene-2-oxides (*158*) and 4-pentene-2-oxides (*159*)], and β-methalloxides (*160*) of titanium, niobium, and tanta-

TABLE VI

ELECTRON PARAMAGNETIC RESONANCE AND ELECTRONIC ABSORPTION SPECTRA OF BIS(t-BUTYL)METHOXIDES

Compound	ESR	Electronic absorption[a] (λ, nm)
$Cr(OCH\text{-}t Bu_2)_3 \cdot THF$	—	700
$LiCr(OCH\text{-}t Bu_2)_4$	$g \approx 3.22$ $g \approx 2.0$[b]	690
$Cr(OCH\text{-}t Bu_2)_4$		716, 567
$Mn(OCH\text{-}t Bu_2)_2$	$g \approx 1.9585$[a]	Absorption rising to charge-transfer band at 300
$LiFe(OCH\text{-}t Bu_2)_4 \cdot Bu_2CHOH$	$g_x = 4.067, 21.3$ $g_y = 6.93$ $g_z = 5.54, 1.65(3)$[b]	Absorption rising to charge-transfer band at 260
$Co(OCH\text{-}t Bu_2)_2$	—	653, 597, 513, 434

[a] In light petroleum, 25°C.

[b] In light petroleum, −160°C.

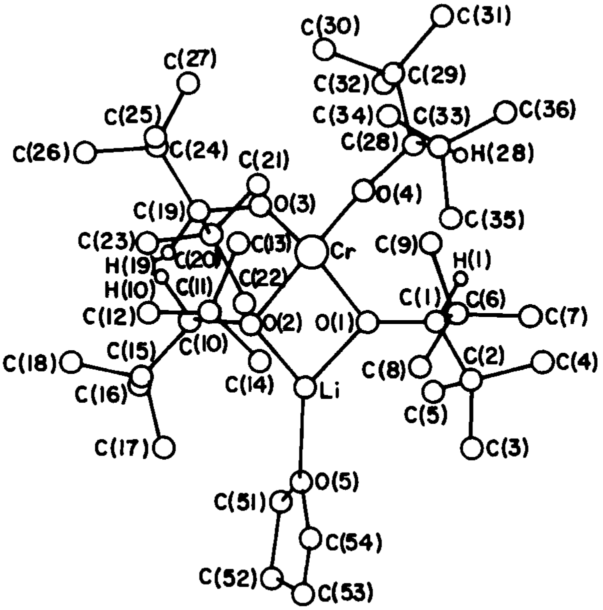


FIG. 23. Structure of LiCr[OCH(CMe$_3$)$_2$]$_4$ · C_4H_8O, showing the atom-numbering system and omitting methyl hydrogens.

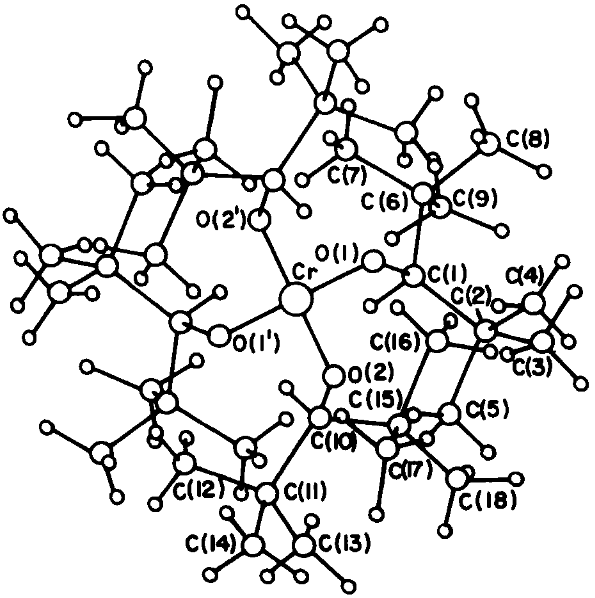


FIG. 24. Structure of Cr[OCH(CMe$_3$)$_2$]$_4$, showing the atom-numbering scheme in the asymmetric units. The smallest circles without numbers represent hydrogen atoms.

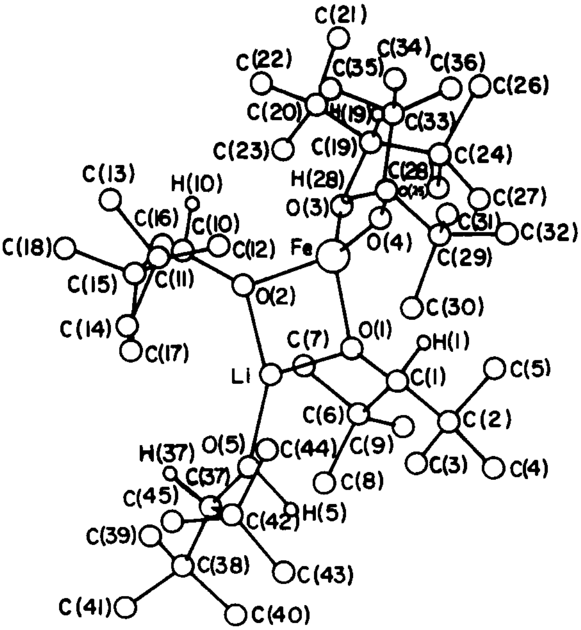
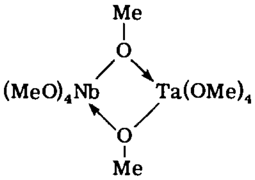


FIG. 25. Structure of LIFe(OCH-tBu$_2$)$_4$ · tBu$_2$CHOH, showing the atom-numbering system and omitting methyl hydrogens.

lum. These alkoxides were generally prepared by the reaction of ethoxides or isopropoxides with the alkenols in benzene, removing the ethanol or isopropanol azeotropically with benzene.

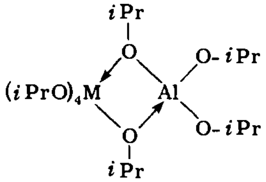
V. Bimetallic Alkoxides of Transition Metals

A large number of bimetallic alkoxides incorporating atoms of two metals within the same molecule were synthesized during the late 1920s by Meerwein and Bersin (*161*), who considered these as "alkoxo salts" similar to hydroxo salts formed by the neutralization of alkali hydroxide with less basic (amphoteric) hydroxides of metals like beryllium, zinc, and aluminum. Isolation of stable volatile derivatives like $NaZr_2(OR)_9$ [not the $Na_2Zr(OR)_6$ expected for an alkoxo salt formulation] by Bartley and Wardlaw (*162*) gave a new orientation to the field. Detailed investigations by Mehrotra and co-workers (*163*), beginning in the late 1960s, particularly on tetraisopropoxyaluminates of a number of metals with the formulation (a) $M[Al(O\text{-}i\text{Pr})_4]_n$ (M = Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Zn, Cd, Ga, In, Sc, lanthanides, Th, Sn, etc.), (b) $(i\mathrm{PrO})_2\mathrm{M}[\mathrm{Al}(\mathrm{O}\text{-}i\mathrm{Pr})_4]_2$ (M = Zr or Hf), and (c) $(i\mathrm{PrO})_3\mathrm{M}[\mathrm{Al}(\mathrm{O}\text{-}i\mathrm{Pr})_4]_2$ (M = Nb or Ta), have shown that the formation of such bimetallic alkoxides could be more easily understood on the basis of a "coordination model" in which alkoxy ligands (OR) bridge atoms of different elements rather than atoms of the same element. The preparation and properties of interesting bimetallic derivatives with the structures

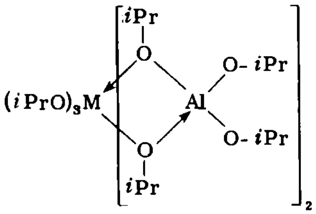


(92)

and



(163)



(M = Nb or Ta)

(163)

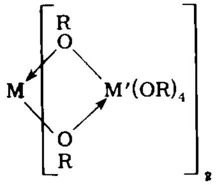
(where M = Nb or Ta) confirm this point of view. Because the literature on bimetallic (earlier termed "double") alkoxides up to 1975 has already been covered (*13, 17, 164, 165*), the following account deals mainly with advances made in these directions since then.

Bimetallic isopropoxides (*166*) and ethoxides (*167*) of niobium and tantalum with magnesium, calcium, strontium, and barium have been synthesized by the reactions of alkaline-earth metals with niobium and tantalum alkoxides in the respective alcohol (*92, 163*).

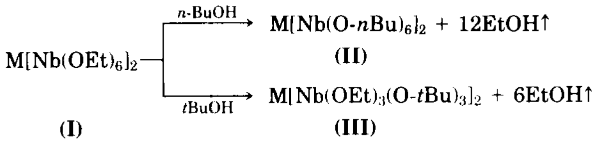
$$\mathrm{M} + 2\mathrm{M'(OR)_5} + 2\mathrm{ROH} \xrightarrow[\mathrm{HgCl_2}]{\mathrm{ROH}} \mathrm{M[M'(OR)_6]_2} + \mathrm{H_2}\uparrow$$

(M = Mg, Ca, Sr, Ba; M' = Nb, Ta, and R = Et or iPr)

All of these bimetallic isopropoxides are colorless solids, and the corresponding ethoxides are viscous liquids, except the barium derivatives (which are foamy solids). Their identity as single entities and not mixtures of the component alkoxides is established by the simple observation that these bimetallic derivatives are volatile (vapor pressure ~1 mm in the temperature range 170–230°C) and soluble in organic solvents like benzene and parent alcohols, whereas the simple alkoxides of alkaline-earth metals are all nonvolatile and insoluble in organic solvents. Comparatively, the solubility of the bimetallic ethoxides is generally higher than that of the corresponding ethoxides. The volatility of these derivatives appears to indicate their covalent character, which is substantiated by their low molar conductances in organic solvents. Based on these observations and their monomeric nature in organic solvents, the following type of simple structure has been assigned to the derivatives



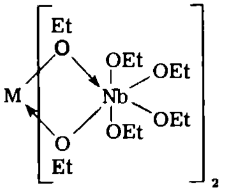
Reactions of bimetallic ethoxide with excess *n*- and *t*-butanol in benzene (with the help of which the ethanol liberated in the reactions was continuously azeotroped out) can be represented by

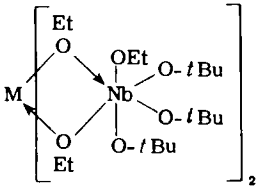


$$\underset{\text{(I)}}{M[Nb(OEt)_6]_2} \xrightarrow{n\text{-BuOH}} \underset{\text{(II)}}{M[Nb(O\text{-}n\text{Bu})_6]_2} + 12EtOH\uparrow$$

$$\underset{\text{(I)}}{M[Nb(OEt)_6]_2} \xrightarrow[t\text{BuOH}]{} \underset{\text{(III)}}{M[Nb(OEt)_3(O\text{-}t\text{Bu})_3]_2} + 6EtOH\uparrow$$

On the basis of PMR spectra, the following types of structures have been suggested for derivatives **I** and **III**.





Bimetallic isopropoxides of alkaline-earth metals with hafnium were synthesized (*168*) by the reactions

$$M + 4Hf(O\text{-}i\text{Pr})_4 \cdot i\text{PrOH} \xrightarrow[\substack{HgCl_2 \\ \text{(catalyst)}}]{i\text{PrOH}} M[Hf_2(O\text{-}i\text{Pr})_9]_2 + H_2\uparrow$$

These products, like the zirconium analogs (*169, 170*), are white, crystalline solids that can be volatilized unchanged under reduced pressure. These are soluble in common organic solvents, in which their molecular weights correspond to their formula weights.

Following the earlier work (*13*) on similar derivatives of lighter alkali metals, apparently covalent (volatile and yielding nonconducting solutions in organic solvents) derivatives with the formulas $M[Al(O\text{-}i\text{Pr})_4]$, $M[Zr_2(O\text{-}i\text{Pr})_9]$, $M[Hf_2(O\text{-}i\text{Pr})_9]$, $M[Nb(O\text{-}i\text{Pr})_6]$, and $M[Ta(O\text{-}i\text{Pr})_6]$ (M = Rb or Cs) have been described (*171*).

Following a more detailed study (*172*) of volatile bimetallic isopropoxides of aluminum with alkaline-earth metals, bimetallic isopropoxides of chromium(III) and iron(III), $M[Al(O\text{-}i\text{Pr})_4]_3$ (M = Fe or Cr), and manganese(II), cobalt(II), nickel(II), and copper(II), $M[Al(O\text{-}i\text{Pr})_4]_2$ (M = Mn, Co, Ni, or Cu), have been synthesized (*173*) by the reactions

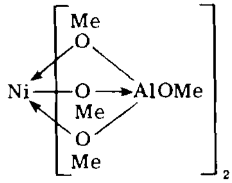
$$CrCl_3 \cdot 3THF + 3K[Al(O\text{-}i\text{Pr})_4] \rightarrow Cr[Al(O\text{-}i\text{Pr})_4]_3 + 3KCl\downarrow + 3THF$$

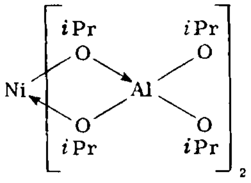
$$FeCl_3 + 3K[Al(O\text{-}i\text{Pr})_4] \rightarrow Fe[Al(O\text{-}i\text{Pr})_4]_3 + 3KCl\downarrow$$

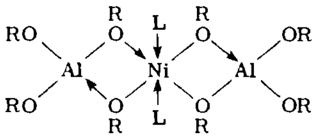
$$MCl_2 + 2K[Al(O\text{-}i\text{Pr})_4] \rightarrow M[Al(O\text{-}i\text{Pr})_4]_2 + 2KCl\downarrow$$

$$M = \text{Mn, Co, Ni, or Cu}$$

All of these bimetallic isopropoxides are colored liquids that are miscible with common organic solvents. They can all be purified by distillation under reduced pressure. Ebullioscopic determination of their molecular weights in benzene showed that they are monomeric. A study of chemical reactions of these products with hydroxy reagents like alcohols and β-diketones has not only yielded new products but has also thrown light on their structural features, which have been corroborated by study of their magnetic and spectroscopic properties (*17, 67*). In some cases the geometry of the molecule appears to be affected by the ramification of the alkyl group. For example, $Ni[Al(OMe)_4]_2$ shows an electronic spectrum characteristic of an octahedral geometry, whereas $Ni[Al(OEt)_4]_2$ and $Ni[Al(O\text{-}i\text{Pr})_4]_2$ show increasing proportions of tetrahedral nickel species in equilibrium with the octahedral form. Furthermore, the effect of steric factors on this equilibrium can be discerned in a finer difference, that is, the spectrum of $Ni[Al(OEt)_4]_2$ in ethanol shows a complete shift to the octahedral species, whereas, in the case of $Ni[Al(O\text{-}i\text{Pr})_4]_2$ in isopropanol, this shift appears to be only partial. For this latter derivative a stronger donor molecule like pyridine is required to change the equilibrium fully to the octahedral species. These structural features can be illustrated as follows.







The octahedral nature of $Ni[Al(OEt)_4]_2$ has been corroborated by a study of the spectral properties of the compounds $M[Al(OR)_4]_2$ (M = Co, Ni, Cu; and R = Me, Et, *n*Pr and *n*Bu) by Stumpp and Hillebrand (*174*).

In view of the interesting properties of these bimetallic alkoxides, it is expected that there would be a rapid development of research into these compounds, particularly later 4d and 5d elements, the alkoxide chemistry of which has just begun to be explored during the last few years.

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