Work is continuing on cation exchange, addition and removal as well as on the binding of other interstitial atoms.

Extended Hückel MO calculations carried out on isolated octahedral $Zr_6Cl_{18}^{4-}$ and $Zr_6Cl_{18}int^{n-}$ (int = C, B, Be) clusters[7] reveal that four of eight Zr–Zr bonding orbitals in the empty cluster are stabilized by interaction with the interstitial's s and p orbitals and form four lower lying orbitals primarily responsible for Zr–int bonding (although these retain some Zr–Zr bonding character). There remain four unchanged Zr–Zr bonding orbitals, the energy of which are dependent only on the size of the cluster, and four Zr–int antibonding orbitals appear at high energies. For electron counting purposes, the interstitial atom can be considered to "donate" its valence electrons to the cluster MOs since the *number* of bonding orbitals is unchanged, although the interstitial is doubtlessly somewhat negative.[4] The HOMO-LUMO gap for 14-electron clusters is calculated to be ~1.4 eV, consistent with the observed stability.

Acknowledgment. This research has been supported in part by National Science Foundation Grant DMR-8318616. Robin P. Ziebarth has also held Proctor and Gamble and Gilman fellowships.

Registry No. $Zr_6Cl_{12}Be$, 96929-11-2; $Zr_6Br_{12}B$, 96929-14-5; $KZr_6Cl_{13}Be$, 96929-12-3; $Zr_6Cl_{13}B$, 96929-13-4; $Zr_6Br_{13}Br$, 96948-42-4; $Zr_6Cl_{14}C$, 96929-15-6; $Zr_6Cl_{14}B$, 96929-16-7; $Zr_6Cl_{15}N$, 96948-43-5; $Na_2Zr_6Cl_{15}C$, 96929-20-3; $KZr_6Cl_{15}C$, 96929-22-5; $CsKZr_6Cl_{15}B$, 96929-23-6; $K_2Zr_6Cl_{15}B$, 96929-24-7; $Na_4Zr_6Cl_{15}Be$, 96929-25-8; $Zr_6Cl_{18}^{4-}$, 96964-12-4; $Zr_6Cl_{18}C^{8-}$, 96929-26-9; $Zr_6Cl_{18}B^{7-}$, 96929-28-1; $Zr_6Cl_{18}Be^{2-}$, 96929-27-0; Zr, 7440-67-7; $ZrCl_4$, 10026-11-6; NaCl, 7647-14-5; CsCl, 7647-17-8; KCl, 7447-40-7; C, 7440-44-0; B, 7440-42-8; Be, 7440-41-7; ZrNCl, 13932-08-6.

Supplementary Material Available: Structural parameters and refinement data for $KZr_6Cl_{13}Be$ (1 page). Ordering information is given on any current masthead page.

Methylaluminum Bis(2,6-di-*tert*-butyl-4-alkylphenoxide). A New Reagent for Obtaining Unusual Equatorial and Anti-Cram Selectivity in Carbonyl Alkylation

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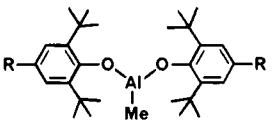
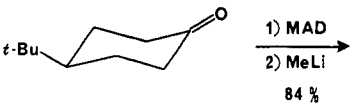
The carbonyl alkylation process has long been studied, and constitutes one of the most fundamental bond constructions in organic synthesis.[1] In contrast to the recent, extensive efforts in this area for the development of a stereoselective alkylating agent for obtaining axial alcohols from cyclohexanones,[2] there exists no reliable methodology available for the selective synthesis of equatorial alcohols.[3] Here we describe *a conceptually new approach* to this problem which involves a bulky organoaluminum compound, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide)[4] or methylaluminum bis(2,4,6-tri-*tert*-butylphenoxide)

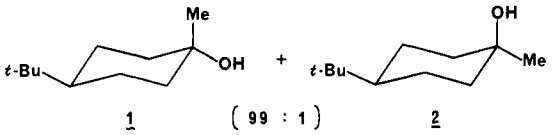


MAD : R = Me
MAT : R = *t*-Bu

(abbreviated to MAD or MAT, respectively), as a key reagent for stereoselective activation of a carbonyl moiety.

MAD can be prepared in situ from trimethylaluminum and 2,6-di-*tert*-butyl-4-methylphenol (molar ratio, 1:2) in toluene at room temperature for 1 h.[4] Treatment of 4-*tert*-butylcyclohexanone with MAD (3 equiv) in toluene and subsequent addition





1 (99 : 1) 2

of methyllithium in ether at −78 °C gave rise to a mixture of isomeric methyl carbinols in 84% yield, 99% of which was found to be equatorial alcohol **1**.[5] Use of MAT gave the similar stereoselectivity (ax/eq = 0.5:99.5).[6] Methyllithium solely is reported to undergo preferential equatorial attack to furnish the axial/equatorial ratio of 79:21.[2a] While MAD and MAT have proved to be most satisfactory, some variation in the reagent was studied in detail under the similar conditions. Accordingly, the reaction of 4-*tert*-butylcyclohexanone with methyllithium in the presence of modified organoaluminum reagents[7] producing the axial and equatorial alcohols **2** and **1** gives the following axial/equatorial ratios: Me_2AlOPh (72:28); dimethylaluminum 2,4,6-trimethylphenoxide (69:31); dimethylaluminum 2,6-di-*tert*-butyl-4-methylphenoxide (5:95). The effect of exact stoichiometry in the reagent has also been examined and each 3 equiv of methyllithium and MAD was found to be satisfactory.[8]

Some other examples are listed in Table I, which also includes the results in the absence of modified organoaluminum reagents for comparison. Clearly, MAD and MAT have played a crucial role for the stereoselective synthesis of hitherto unaccessible equatorial alcohols from cyclohexanone systems.[9] The use of simple Grignard reagents as nucleophile is also highly efficient and in certain cases the stereoselection is virtually complete.[10]

(1) Review: Ashby, E. C. *Chem. Rev.* **1975**, *75*, 521.

(2) Recent stereoselective syntheses of axial alcohols from cyclohexanones: (a) MacDonald, T. L.; Still, W. C. *J. Am. Chem. Soc.* **1975**, *97*, 5280. (b) Ashby, E. C.; Lin, J. J.; Watkins, J. J. *Tetrahedron Lett.* **1977**, 1709. (c) Ashby, E. C.; Willard, G. F. *J. Org. Chem.* **1978**, *43*, 4094. (d) Ashby, E. C.; Noding, S. A. *Ibid*, **1979**, *44*, 4371. (e) Weidmann, B.; Seebach, D. *Helv. Chim. Acta* **1980**, *63*, 2451. (f) Weidmann, B.; Maycock, C. D.; Seebach, D. *Ibid*, **1981**, *64*, 1552. (g) Reetz, M. T. Top. Curr. Chem. **1982**, *106*, 1 and references cited therein.

(3) The previous attempt for equatorial alkylation with alkylaluminums was made by Ashby et al. (a) Laemmle, J. T.; Ashby, E. C.; Roling, P. V. *J. Org. Chem.* **1973**, *38*, 2526. (b) Ashby, E. C.; Laemmle, J. T. *ibid*, **1975**, *40*, 1469. Unfortunately, all organoaluminums except trimethyl- and triphenylaluminum gave large amounts of reduction product.

(4) Starowieyski, K. B.; Pasynkiewicz, S.; Skowrońska-Ptasińska, M. *J. Organomet. Chem.* **1975**, *90*, C43.

(5) The typical experimental procedure is provided by the methylation of 4-*tert*-butylcyclohexanone (entry 3 in Table I). To a solution of 2,6-di-*tert*-butyl-4-methylphenol (1.322 g, 6 mmol) in toluene (10 mL) was added a 2 M hexane solution of trimethylaluminum (3 mmol) and the resulting clear solution was stirred at room temperature for 1 h. The mixture was then cooled to −78 °C and 4-*tert*-butylcyclohexanone (154 mg, 1 mmol) followed by a 1.54 M ethereal solution of methyllithium (3 mmol) was added at −78 °C. The solution was maintained at this temperature for 2 h. The reaction mixture was poured into 1 N HCl and the organic layer was washed with brine. The combined ether extracts were, after concentration, purified by column chromatography on silica gel to give a mixture of **1** and **2** (143 mg, 84% yield), the ratio of which was determined by GC on a 25-m PEG-HT capillary column to be 99:1.

(6) Since MAT easily solidifies in toluene, we used CH_2Cl_2 for the preparation of MAT.

(7) The modified organoaluminum reagents were prepared in situ from trimethylaluminum and the corresponding phenols in toluene at room temperature for 1 h.

(8) When 2 equiv each of methyllithium and MAD was employed, a 1:99 mixture of axial and equatorial alcohols was obtained in 59% yield. With 1 equiv of the reagents the yield was further lowered to 31% in an ax/eq ratio of 2:98.

(9) Other strong Lewis acids such as $TiCl_4$ and $BF_3{\cdot}OEt_2$ were not effective.

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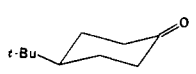
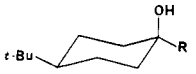
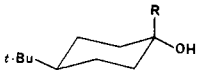
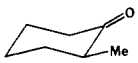
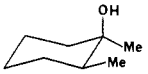
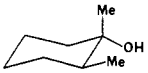
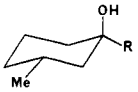
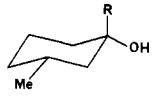
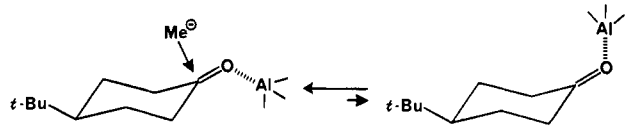
Table I. Stereoselective Alkylation of Cyclohexanones[a]

entry	ketone	nucleophile[b]	Lewis acid[c]	yield, %[d]	ratio (ax/eq)[e]
					
1		MeLi	none		79:21[g]
2			DAD	81	5:95
3			MAD	84	1:99
4			MAT	92	0.5:99.5
5		MeLi + MAD[f]		78	84:16
6		EtMgBr	none	95	48:52
7			MAD	91	0:100
8		BuMgBr	none	58	56:44
9			MAD	67	0:100
10		AllylMgBr	none	86	48:52
11			MAD	90	9:91
					
12		MeLi	none		92:8[g]
13			DAD	80	58:42
14			MAD	84	14:86
15			MAD	90	7:93[h]
16			MAT	80	10:90[h]
17		MeLi + MAD[f]		81	91:9
					
18		MeLi	none	80	83:17
19			DAD	77	48:52
20			MAD	69	9:91[h]
21			MAT	95	3:97[h]
22		BuMgBr	none	86	79:21
23			MAD	75	1:99
24		AllylMgBr	none	95	56:44
25			MAD	72	24:76

[a] Unless otherwise noted, alkylation was carried out using an ketone, nucleophile, and Lewis acid (1:3:3 molar ratio) at −78 °C for 2–3 h. [b] Used as an ethereal solution. [c] Dimethylaluminum 2,6-di-*tert*-butyl-4-methylphenoxide, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide), and methylaluminum bis(2,4,6-tri-*tert*-butylphenoxide) are abbreviated to DAD, MAD, and MAT, respectively. [d] Isolated yield. [e] Determined by GC analysis. [f] The ketone was added to an equimolar mixture of MeLi and MAD in ether–toluene at −78 °C. [g] See ref 2a. [h] The reaction was conducted at −95 °C for 3 h.

Introduction of large alkyl groups into the more hindered position of a ketone seems to be sluggish. Alkylation of 2-methylcyclohexanone with ethyl- or butylmagnesium bromide in the presence of MAD resulted in recovery of the starting ketone. Unfortunately, this method is not applicable to some cyclopentanone systems. Attempted reaction of 3-methylcyclopentanone with propylmagnesium bromide gave the corresponding cyclopentanols without any stereoselectivities. It should be noted that the present alkylation possesses high chemoselectivity. Aldehydes and cyclic ketones are readily susceptible toward the nucleophilic attack of organometallic compounds in the presence of MAD, while acyclic ketones and esters are reluctant to the MAD-mediated alkylations under the standard conditions.[11]

The exceedingly high equatorial selectivity observed herein may be ascribed to the eminent affinity of the oxygenophilic MAD and MAT for carbonyl oxygen.[12,13] Thus treatment of 4-*tert*-butylcyclohexanone with MAD or MAT would produce the stable 1:1 complex **3** or **4**. Here the bulky aluminum reagent upon



3 **4**

coordination has resulted in the preferential formation of the sterically favored isomer **3** rather than the alternative **4**. Then methyllithium as nucleophile appears to attack the carbonyl carbon of complex **3** from the sterically less hindered side leading to the equatorial alcohol **1** in accord with the experimental findings. The initial ate complex formation by the attack of methyllithium to the aluminum reagent followed by reaction with the ketone seems to be unlikely, since treatment of the ketone with a mixture of methyllithium and MAD at low temperature gave results similar to those in the sole addition of methyllithium (entries 5 and 17).

Even more significant is the stereoselective alkylation of α-chiral aldehydes in the presence of MAD or MAT. Despite the numerous studies for achieving the Cram selectivity with ordinary α-chiral aldehydes, the corresponding anti-Cram selectivity has not been realized so far for lack of appropriate methodologies.[14,15]

(10) Both alkylation and reduction occurred concurrently by the use of *sec*-alkyl and *tert*-alkylmagnesium halides as nucleophile. Alkylation with other functionalized nucleophiles such as vinyl and phenyl anions proceeded slowly under the standard conditions and upon warming to −20 °C resulted in no equatorial selectivity.

(11) Attempted reaction of 6-undecanone with EtMgBr and MAD at −78 °C for 2 h produced the desired alkylation product in only 15% yield with 80% recovery of the starting ketone. Moreover, the similar treatment of ethyl phenylacetate with the EtMgBr–MAD system resulted in 95% recovery of the ester.

(12) The association of organoaluminum reagents through electron deficient bonds is an common phenomenon. However, in view of the bulky phenoxy group, MAD and MAT exist as monomeric aluminum species in nature, which could exhibit their high oxygenophilicity.[4]

(13) For synthetic applications of the high oxygenophilicity of organoaluminum reagents, see: Maruoka, K.; Yamamoto, H. *Angew. Chem., Int. Ed. Engl.*, in press.

(14) General review: (a) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: New York, 1971. (b) Eliel, E. L. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2A, p 125.

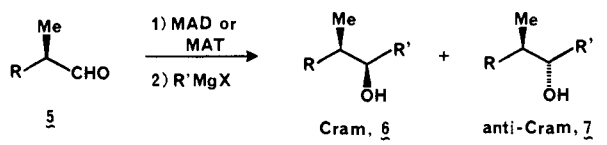
(15) For an excellent Cram selectivity in the Lewis acid mediated reaction of silyl ketone acetals with ordinary aldehydes, see: Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667.

Table II. Cram/Anti-Cram Selectivity in the Alkylation of α-Substituted Aldehydes[a]

entry	aldehyde, **5**	nucleophile	Lewis acid	yield, %[b]	Cram (**6**): *anti*-Cram (**7**)[c]
1	R = Ph	MeMgI	none	64	72:28
2			MAT	96	7:93
3		EtMgBr	none	78	84:16
4			MAD	90	25:75
5			MAT	98	20:80
6			MAT	90	13:87[d]
7		BuMgBr	none	89	87:13
8			MAT	98	33:67
9		BuC≡CMgBr	none	79	78:22
10			MAT	96	41:59
11	R = 1-cyclohexenyl	MeMgI	none	64	79:21
12			MAT	84	2:98
13		EtMgBr	none	87	94:6
14			MAD	76	34:66
15			MAT	98	17:83
16		BuMgBr	none	88	96:4
17			MAT	97	26:74
18	R = cyclohexyl	MeMgI	none	81	82:18
19			MAD	88	22:78
20			MAT	75	23:77
21		BuMgBr	none	81	89:11
22			MAT	89	77:23

[a] Alkylation was generally performed using an aldehyde, Grignard reagent, and Lewis acid (1:3:3 molar ratio) at −78 °C for 1–2 h. [b] Isolated yield. [c] Determined by GC analysis. [d] The reaction was carried out at −95 °C for 1–2 h.

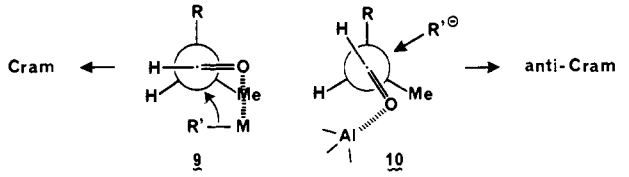
Indeed, the Cram/anti-Cram problem has been one of the long-standing concern relating to the 1,2- and 1,3-asymmetric induction in acyclic systems.[16] We have discovered that unprecedented anti-Cram selectivity is achieved in the MAD- or MAT-mediated alkylation of ordinary α-chiral aldehydes having no ability to be chelated.[17] Thus, addition of α-phenylpropionaldehyde to MAD in toluene at −78 °C gave a yellow aldehyde–MAD complex which on subsequent treatment with ethylmagnesium bromide in ether afforded a mixture of Cram and anti-Cram products **6** and **7** (R



5 Cram, **6** anti-Cram, **7**

= Ph, R′ = Et) in a ratio of 25:75 (90% yield). This is in sharp contrast to the preferential Cram selectivity observed in ordinary alkylations (Cram/anti-Cram = 84:16 with ethylmagnesium bromide solely). In addition, switching the modified aluminum reagent from MAD to MAT further enhanced the anti-Cram selectivity to 20:80–13:87. Selected data presented in Table II clearly demonstrate the high synthetic potential of our new methodology in acyclic stereochemical control. In general, MAT is superior to MAD. Among nucleophiles, methylmagnesium iodide afforded the highest anti-Cram selectivity.[18]

The stereochemistry of ordinary nucleophilic addition to the aldehyde **5** has been postulated to occur from a conformation that places the nucleophile (R′–M) in an antiperiplanar arrangement with the largest group (R) at the adjacent chiral center, leading to the Cram product **6** as depicted in model **9**.[19] In contrast, the



9 **10**

present anti-Cram selectivity may be rationalized by the initial formation of the sterically least hindered complex **10** preferentially on treatment of **5** with MAD or MAT, and subsequent attack of the nucleophile (R′⁻) from the side opposite to the bulky aluminum reagent, producing the anti-Cram product **7** with moderate to high selectivity.

Comparison of our approach with the existing methodologies in carbonyl alkylation points out an important comment. The known alkylations can be divided into two classes depending on the mode of activation of either alkyl group or carbonyl substrate. The nucleophilic addition of highly reactive organometallic compound (alkyllithium, Grignard reagent, etc.) to carbonyl group is most widely utilized.[1,2] The other, less general type of alkylation is effected by the combination of electrophilically activated carbonyl substrate and unactivated alkylation agent.[20] In contrast, the present new alkylation can be interpreted as *the nucleophilic addition of organometallic compound to electrophilically activated carbonyl substrate.* Such an ambiphilically activated alkylation should be categorized into the third, yet unexplored class of alkylation that has proved to exhibit unique selectivity not observable in ordinary alkylations.[21]

Registry No. 1, 16980-56-6; **2**, 16980-55-5; **5** (R = Ph), 93-53-8; **5** (R = 1-cyclohexenyl), 96929-98-5; **5** (R = c-C_6H_{11}), 2109-22-0; **6** (R = Ph; R′ = C≡CBu), 96930-00-6; **6** (R = 1-cyclohexenyl; R′ = Me), 96930-01-7; **6** (R = 1-cyclohexenyl; R′ = Et), 96930-02-8; **6** (R = 1-cyclohexenyl; R′ = Bu), 96930-03-9; **6** (R = c-C_6H_{11}; R′ = Me), 1660-30-6; **6** (R = c-C_6H_{11}; R′ = Bu), 96930-04-0; **6** (R = Ph; R′ = Me), 1502-79-0; **6** (R = Ph; R′ = Et), 1502-77-8; **6** (R = Ph; R′ = Bu), 96929-99-6; **7** (R = Ph; R′ = Me), 1502-80-3; **7** (R = Ph; R′ = Et), 1502-78-9; **7** (R = Ph; R′ = Bu), 96930-05-1; **7** (R = Ph; R′ = C≡CBu), 96930-06-2; **7** (R = 1-cyclohexenyl; R′ = Me), 96930-07-3; **7** (R = 1-cyclohexenyl; R′ = Et), 96930-08-4; **7** (R = 1-cyclohexenyl; R′ = Bu), 96930-09-5; **7** (R = c-C_6H_{11}; R′ = Me), 1499-67-8; **7** (R = c-C_6H_{11}; R′ = Bu), 96930-10-8; MAD, 56252-55-2; MAT, 65260-46-0; Me_2AlOPh, 6062-

(16) (a) Reetz, M. T.; Kesseler, K.; Schmidtberger, S.; Wenderoth, B.; Steinbach, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *22*, 989. (b) Reetz, M. T. *Ibid*, **1984**, *23*, 556.

(17) Cram/anti-Cram selectivity in the reduction of α-chiral ketones: Midland, M. M.; Kwon, Y. C. *J. Am. Chem. Soc.* **1983**, *105*, 3725.

(18) Use of other nucleophiles such as organolithium and organozinc reagents gave less satisfactory results.

(19) (a) Chêrest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. (b) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61. (c) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162.

(20) This type of alkylation is exemplified by the Lewis acid catalyzed addition of allylic silanes and stannanes to carbonyl compounds. See: (a) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981, p 97. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (c) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: New York, 1983; p 173.

(21) An ambiphilically activated reduction of imines with Me_3Al–$LiAlH_4$ system was previously reported. See: Matsumura, Y.; Maruoka, K.; Yamamoto, H. *Tetrahedron Lett.* **1982**, *23*, 1929.

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Cyano Complexes of Trivalent Nickel in Aqueous Solution

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Oxidation of $Ni^{II}(CN)_4^{2-}$ in aqueous solution gives *trans*-diaquatetracyanonickelate(III), which is an excellent precursor for the formation of a new series of nickel(III) complexes. This $Ni^{III}(CN)_4(H_2O)_2^-$ complex is moderately stable at low concentrations ($<2 \times 10^{-4}$ M) in acidic solution (11-min $t_{1/2}$ at 25 °C, pH 1-3) but decays rapidly in base (0.5-s $t_{1/2}$ at pH 10). EPR spectra indicate that it is tetragonally elongated with water molecules in the axial positions. Studies with $^{13}CN^-$ confirm that the unpaired electron is in the nickel d_{z^2} orbital, where it is not affected by the ^{13}C nuclear spin of the equatorially coordinated cyanides. The $Ni^{III}(CN)_4(H_2O)_2^-$ complex undergoes rapid axial substitution with ammonia, imidazole, pyridine, acetonitrile, azide, cyanate, and chloride ions to form bis trans complexes as observed by frozen aqueous EPR. Bipyridyl chelates with nickel(III) to form a mixed cyano complex. Addition of cyanide to the diaqua complex forms $Ni^{III}(CN)_6^{3-}$, which gives temperature-dependent EPR spectra in frozen aqueous solution.

The formation of tetracyanonickelate(III) has been reported in the X-ray irradiation of $Ni(CN)_4^{2-}$ doped in NaCl crystals[1] and by X-ray irradiation in frozen aqueous solution.[2,3] It also has been observed as a transitory species by pulse radiolysis[4] of $Ni(CN)_4^{2-}$. We find that the nickel(III) complex is easily prepared in aqueous solution with a bulk electrolysis column[5,6] or by chemical oxidation.

The cyclic voltammetry gives a formal reduction potential of 1.19 V (vs. NHE) for the $Ni^{III,II}(CN)_4^{-,2-}$ couple between pH 2.0 and 7.2. This potential is 0.37 V higher than the value for the $Ni^{III,II}(H_{-2}Aib_3)^{0,-}$ couple[7,8] and 0.16 V higher than for the $Ni^{III,II}(cyclam)^{3+,2+}$ couple.[9,10]

The UV spectrum of $Ni^{III}(CN)_4(H_2O)_2^-$ has a peak at 255 nm (ϵ 1.16×10^4 M^{-1} cm^{-1}). Mulazzani et al.[4] reported a peak at 250 nm in pulse radiolysis studies, but they also found a second, more intense peak at 270 nm that we do not observe.

The aqueous room-temperature EPR spectrum of $Ni^{III}(CN)_4(H_2O)_2^-$ is a simple derivative. The g_{iso} value is 2.142, which is smaller than g_{av} values of 2.17-2.20 for nickel(III) peptide complexes[11,12] or 2.157 for the $Ni^{III}(cyclam)(H_2O)_2^{3+}$ complex.[13]

Table I. Frozen Aqueous Glass EPR Parameters for Nickel(III) Cyano Complexes

	$g_\perp$[a]	$g_\parallel$	$A_\perp$	$A_\parallel$
$Ni^{III}(CN)_4(H_2O)_2^-$	2.198	2.007		
$Ni^{III}(CN)_4(Cl)_2^{3-}$	2.161	2.008	9[b]	33.6[b]
$Ni^{III}(CN)_4(NH_3)_2^-$	2.116	2.009	18.3[c]	24.5[c]
$Ni^{III}(CN)_6^{3-}$ (-190 °C)	2.081	2.010	92[d]	100[d]
$Ni^{III}(CN)_6^{3-}$ (-35 °C)	2.056[e]		37.3[d]	

[a] Spectra were simulated with $g_{xx} = g_{yy}$. [b] Cl hyperfine splitting. [c] N hyperfine splitting. [d] ^{13}C hyperfine splitting. [e] g_{iso}.

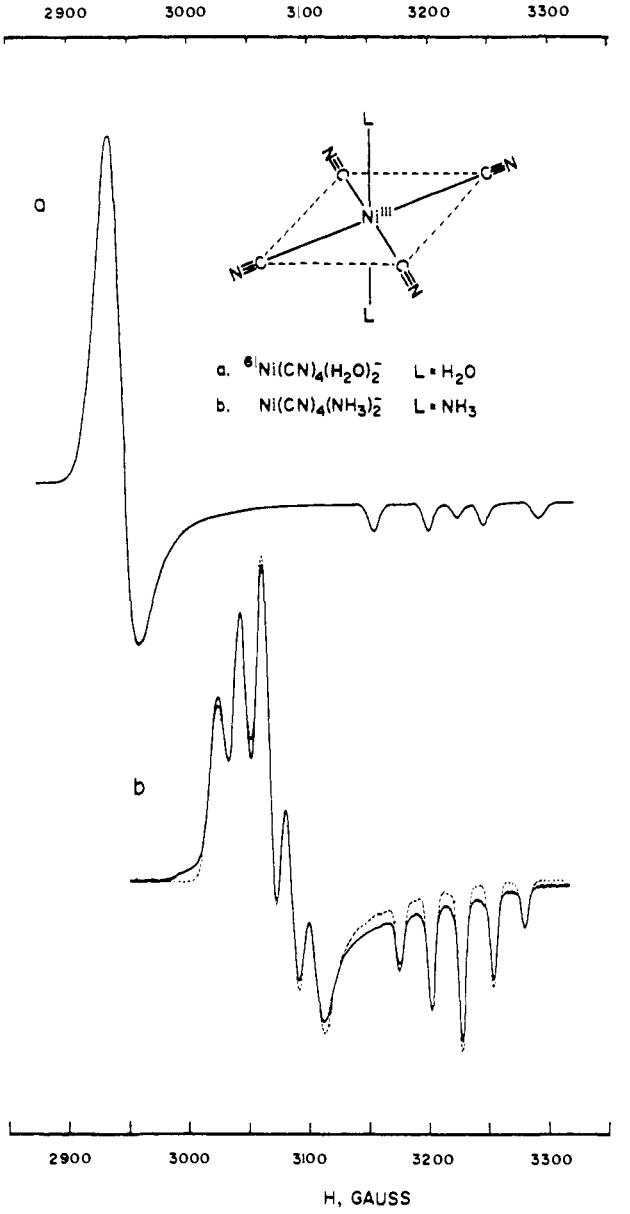

Figure 1. Magnetically dilute frozen aqueous solution X-band EPR spectra of tetracyanonickelate(III) complexes at -150 °C: (a) $^{61}Ni^{III}(CN)_4(H_2O)_2^-$, 88.8% enriched ^{61}Ni; the small peak in the center of the $g_\parallel$ region is the ^{58}Ni $g_\parallel$ peak. (b) $Ni^{III}(CN)_4(NH_3)_2^-$ (from 2.5×10^{-2} M NH_3 and 1.0×10^{-3} M $Ni^{III}(CN)_4(H_2O)_2^-$); the dashed line is the computer simulation used to calculate the g values in Table I.

The UV spectrum of $Ni^{III}(CN)_4(H_2O)_2^-$ has a peak at 255 nm (ϵ 1.16×10^4 M^{-1} cm^{-1}). Mulazzani et al.[4] reported a peak at

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