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THE FORMATION AND MOLECULAR STRUCTURE OF DI-η^5-CYCLOPENTADIENYL{2-[(DIMETHYLAMINO)METHYL]PHENYL-*C*,*N*}YTTRIUM

MARVIN D. RAUSCH *[a], DONALD F. FOUST [a], ROBIN D. ROGERS *[b],
and JERRY L. ATWOOD*[c]

Departments of Chemistry, [a] University of Massachusetts, Amherst, Massachusetts 01003, [b] Northern Illinois University, DeKalb, Illinois 60115, and [c] University of Alabama, University, Alabama 35486 (U.S.A.)

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Summary

A reaction between 2-lithio-*N*,*N*-dimethylbenzylamine (**1**) and di-μ-chlorotetra-η^5-cyclopentadienyldiyttrium (**2**) in ethyl ether solution has produced di-η^5-cyclopentadienyl{2-[(dimethylamino)methyl]phenyl-*C*,*N*}yttrium $(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$ (**3**), in 71% yield. The product, which represents the second known aryl derivative of yttrium, has been characterized by elemental analysis and ^{1}H NMR data as well as by a single-crystal X-ray diffraction study.

$(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$ crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters a 8.310(3), b 26.972(8), c 15.548(6) Å, β 95.88(3)°, and D_{calc} 1.35 g cm^{-3} for $Z = 4$. Least-squares refinement gave a final R value of 0.102 using 1739 independent observed reflections. There are two molecules in the asymmetric unit. Each yttrium atom is η^5-coordinated to two cyclopentadienyl ligands and sigma bonded to the *ortho*-carbon and -nitrogen atoms of the dimethylbenzylamine ligand. The Y–C(σ) bond distances are identical at 2.41(2) Å; the two Y–N bond lengths are 2.43(2) and 2.54(2) Å.

Introduction

Recent joint studies in our laboratories have focused in part on the formation and molecular structures of organic derivatives of the Group IIIB metals (Sc, Y, La) [1]. In view of the known dimeric nature of $[(\eta^5\text{-}C_5H_5)_2Y(CH_3)]_2$, as unequivocally established by X-ray crystallographic studies [2], it was of interest to examine aryl derivatives of yttrium. In the present article, we describe the synthesis and molecular structure of di-η^5-cyclopentadienyl{2-[(dimethylamino)methyl]phenyl-*C*,*N*}yttrium (**3**). The only other reported aryl derivative of yttrium is triphenylyttrium, which is described as a brown solid of low solubility in organic solvents, and which is pyrophoric in air [3].

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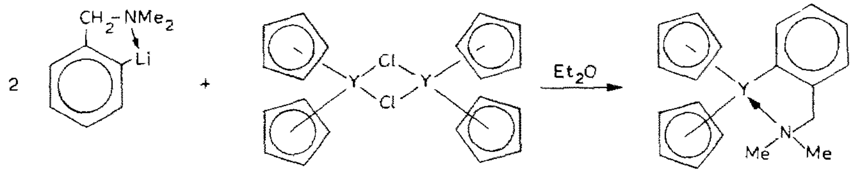
Results and discussion

Recent studies by Manzer and others have demonstrated that reactions of 2-lithio-*N*,*N*-dimethylbenzylamine (**1**) with transition metal halides lead to thermally stable, air-sensitive organometallic compounds whose enhanced stabilities can be attributed to chelation via the *N*,*N*-dimethylamino substituent [4]. Manzer briefly described the organoscandium derivative $(\eta^5\text{-}C_5H_5)_2Sc(C_6H_4\text{-}2\text{-}CH_2NMe_2)$, a result which prompted us to examine the analogous yttrium system. A reaction between two equivalents of **1** and di-μ-chlorotetra-η^5-cyclopentadienyldiyttrium (**2**) in ethyl ether solution produced the yttrium derivative **3** in 71% yield. The product was a white, air-sensitive solid which could be crystallized from toluene/pentane solution at −20°C. Crystals suitable for X-ray diffraction studies were grown by this method. The ^1H NMR spectrum of **3** in $CDCl_3$ solution exhibited a 6-proton singlet at δ 3.30 ppm, assignable to the NMe_2 protons, a 2-proton singlet at δ 3.62 ppm, assignable to the methylene protons, a 10-proton singlet at δ 6.13 ppm, assignable to the cyclopentadienyl ring protons, and a 4-proton multiplet centered at δ 7.00 ppm, assignable to the aromatic ring protons.



(**1**) (**2**) (**3**)

The structure of **3** has been verified by a single-crystal X-ray diffraction study. Figure 1 contains the results for the two crystallographically independent molecules. Both are drawn with the $(\eta^5\text{-}C_5H_5)_2Y$ units in nearly the same perspective, and the difference in overall conformation is apparent (from the environment of the nitrogen atom). This is also revealed in the torsional angles C(1)–C(2)–C(7)–N(1) 32.2° and C(20)–C(21)–C(26)–N(2) −34.1°. Another manifestation of the difference of the amine portion is found in the Y–N bond lengths: Y(1)–N(1) 2.43(3) Å and Y(2)–N(2) 2.54(2) Å. The two Y–C bond distances are equal at 2.41(2) Å (Table 1). A stereoscopic view of the unit cell packing is shown in Fig. 2.

Although the high esd's associated with the Y–N and Y–C lengths make detailed comparisons meaningless, the values do appear quite reasonable. Based on related structures a Y–N of ca. 2.5 Å is expected [5]. Likewise, Y–C(σ) lengths in the range of 2.4 to 2.5 Å are predicted from the metal–carbon distances in $[Li(THF)_4][Lu(C_8H_9)_4]$ [6] and $[Li(THF)_4][Yb\{CH(SiMe_3)_2\}_3Cl]$ [7]. Both Y–C(σ) and Y–N lengths are near the values recently found for the homoleptic $Lu(C_6H_4\text{-}2\text{-}CH_2NMe_2)_3$ [8].

Experimental

All reactions, manipulations and crystallizations were conducted under an atmosphere of dry, deoxygenated argon, using standard Schlenk tube techniques. All glassware was warmed with a heat gun during the evacuation/ filling cycles to insure removal of traces of water. Ethyl ether and THF were predried over sodium and

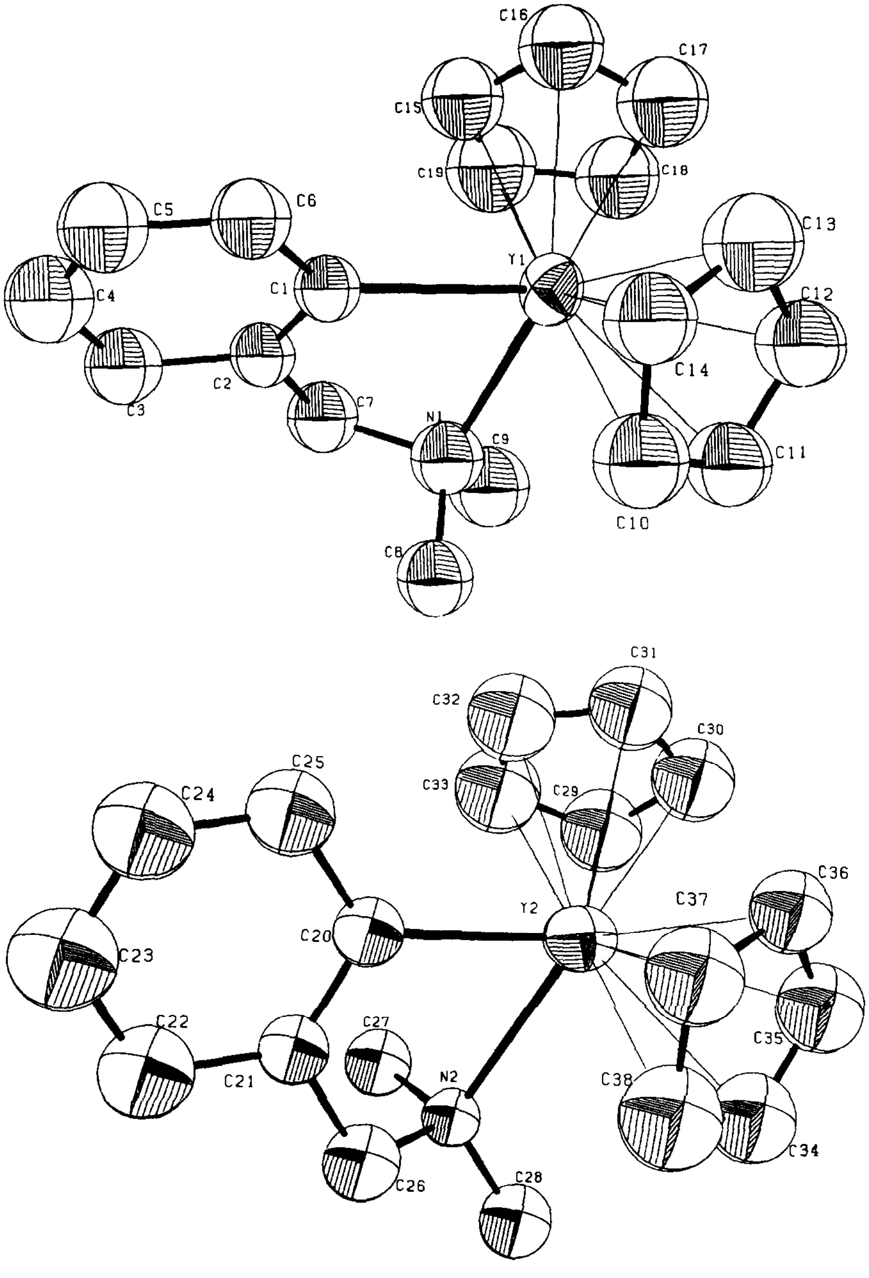


Fig. 1. Molecular structures and atom-labeling schemes of the two independent molecules of $(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

subsequently distilled under argon from sodium benzophenone. Pentane and toluene were dried over CaH_2 and freshly distilled from CaH_2 under argon before use. Thionyl chloride was purified by distillation under argon from quinoline, followed by subsequent fractionation of the distillate from linseed oil [9]. The nearly colorless

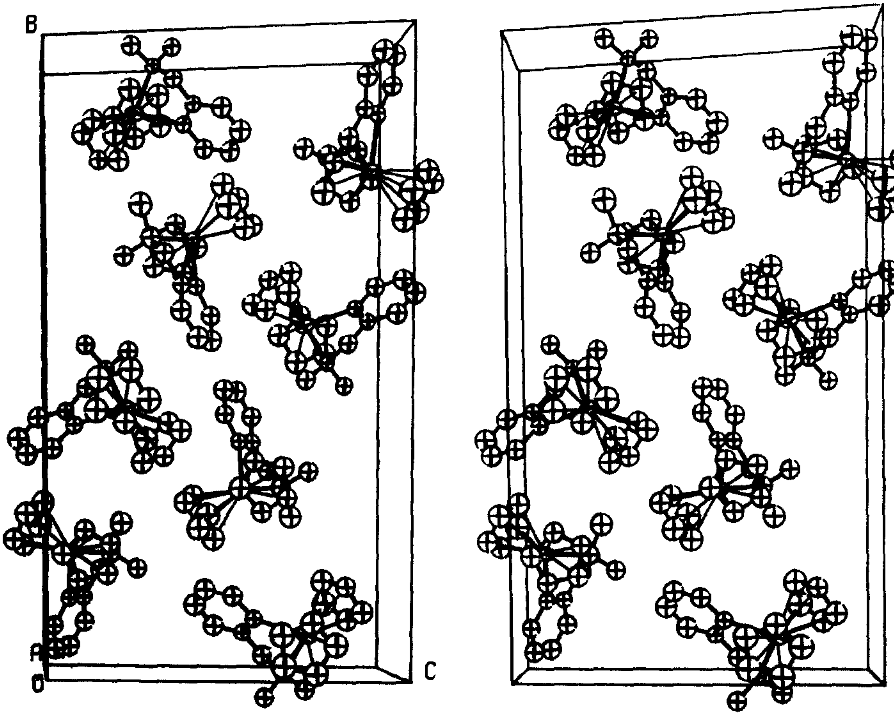


Fig. 2. Stereoscopic view of the unit cell packing in $(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$.

product was stored under argon until use. Anhydrous yttrium trichloride was obtained from Research Organic/Inorganic Chemical Co. It was purified by refluxing ca. 50 g of the material over 300 ml of purified thionyl chloride for 2 days. Following distillation of the thionyl chloride, the slightly grey anhydrous product was vacuum dried and stored under argon until use. ^{1}H NMR spectra were recorded on a Varian A-60 instrument. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Preparation of di-μ-chlorotetra-η^5-cyclopentadienyldiyttrium (2)

Method 1. To 200 ml of THF at 0°C was added with stirring 24.4 g (125 mmol) of dried yttrium trichloride in small increments [10]. To this slurry was added 265 mmol of cyclopentadienylsodium in 250 ml of THF (prepared from 6.0 g of sodium and 27.0 ml of freshly cracked cyclopentadiene). The reaction mixture was allowed to warm to room temperature and then heated at reflux overnight. The solvent was removed under vacuum and the residue was sublimed at 250°C and 10^{-4} Torr. $[(\eta^5\text{-}C_5H_5)_2YCl]_2$ was collected as a white crystalline solid (22.8 g, 72%). ^{1}H NMR (THF) δ6.16 (s, C_5H_5), ($CDCl_3$) δ6.33 (s, C_5H_5).

Method 2. Dried yttrium trichloride (9.76 g, 50.0 mmol) was slowly added with stirring to 300 ml of THF at 0°C. To this slurry was added 26.90 g (100 mmol) of sublimed cyclopentadienylthallium. The reaction mixture was allowed to warm to room temperature and then heated at reflux overnight. The solvent was removed under vacuum and the residue dried under vacuum at 50°C. The resulting solid was

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) FOR $(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$

Atoms	Distance	Atoms	Distance
Y(1)–N(1)	2.43(2)	Y(1)–C(1)	2.41(2)
Y(1)–C(10)	2.68(3)	Y(1)–C(11)	2.61(3)
Y(1)–C(12)	2.63(3)	Y(1)–C(13)	2.62(3)
Y(1)–C(14)	2.62(3)	Y(1)–C(15)	2.63(3)
Y(1)–C(16)	2.67(3)	Y(1)–C(17)	2.63(3)
Y(1)–C(18)	2.68(3)	Y(1)–C(19)	2.67(3)
Y(2)–N(2)	2.54(2)	Y(2)–C(20)	2.41(2)
Y(2)–C(29)	2.62(3)	Y(2)–C(30)	2.63(3)
Y(2)–C(31)	2.62(3)	Y(2)–C(32)	2.64(3)
Y(2)–C(33)	2.67(3)	Y(2)–C(34)	2.67(3)
Y(2)–C(35)	2.66(3)	Y(2)–C(36)	2.64(3)
Y(2)–C(37)	2.63(3)	Y(2)–C(38)	2.67(3)
Y(1)–Cent 1	2.35	Y(1)–Cent 2	2.39
Y(2)–Cent 3	2.36	Y(2)–Cent 4	2.38

Atoms	Angle	Atoms	Angle
N(1)–Y(1)–C(1)	72.2(8)	N(2)–Y(2)–C(20)	71.9(7)
Y(1)–N(1)–C(7)	107(1)	Y(1)–N(1)–C(8)	116(2)
C(7)–N(1)–C(8)	106(2)	Y(1)–N(1)–C(9)	119(2)
C(7)–N(1)–C(9)	101(2)	C(8)–N(1)–C(9)	106(2)
Y(2)–N(2)–C(26)	103(1)	Y(2)–N(2)–C(27)	108(1)
C(26)–N(2)–C(27)	108(2)	Y(2)–N(2)–C(28)	118(1)
C(26)–N(2)–C(28)	110(2)	C(27)–N(2)–C(28)	109(2)
Cent 1–Y(1)–Cent 2	129	Cent 1–Y(1)–N(1)	110
Cent 1–Y(1)–C(1)	112	Cent 2–Y(1)–N(1)	113
Cent 2–Y(1)–C(1)	103	Cent 3–Y(2)–Cent 4	129
Cent 3–Y(2)–N(2)	118	Cent 3–Y(2)–C(20)	106
Cent 4–Y(2)–N(2)	108	Cent 4–Y(2)–C(20)	105

heated in a sublimer under vacuum at 100°C until no further liquid was observed arising from the residue (ca. 2 h). Unreacted cyclopentadienylthallium was then sublimed at 120°C and 10^{-4} Torr, followed by sublimation of $[(\eta^5\text{-}C_5H_5)_2YCl]_2$ at 200–225°C and 10^{-4} Torr as a yellow-white solid (11.07 g, 87%). $[(\eta^5\text{-}C_5H_5)_2YCl]_2$ is marginally soluble in THF, chloroform or hot toluene.

Preparation of di-η^5-cyclopentadienyl{2-[(dimethylamino)methyl]phenyl-C,N}yttrium (3)

To a slurry of 3.28 g (6.44 mmol) of $[(\eta^5\text{-}C_5H_5)_2YCl]_2$ in 150 ml of ethyl ether was added 2.05 g (14.5 mmol) of 2-lithio-*N*,*N*-dimethylbenzylamine [4]. The reaction mixture was stirred for 1 h and filtered. The residue was washed with ethyl ether and the combined ether filtrate was reduced in volume to ca. 50 ml under reduced pressure. Pentane (150 ml) was added and the mixture was cooled to −20°C. The resulting crystalline solid was collected by filtration, washed with pentane and vacuum dried, leaving 3.23 g (71%) of white air-sensitive $(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$. An analytically pure sample was obtained by recrystallization from 1/1 toluene-pentane at 0°C; m.p. (dec.) 270°C. Anal. Found: C, 64.67; H, 6.07; N, 3.87. $C_{19}H_{22}NY$ calcd.: C, 64.59; H, 6.07; N, 3.91%.

X-ray data collection, structure determination, and refinement for $(\eta^5\text{-}C_5H_5)_2\text{-}Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$

Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($2\theta > 20°$) accurately centered on the diffractometer are given in Table 2. The space group was uniquely determined as $P2_1/c$ from the systematic absences.

Data were collected on an Enraf–Nonius CAD-4 diffractometer by the ω-2θ scan technique. The method has been previously described [11]. A summary of data collection parameters is given in Table 2. The intensities were corrected for Lorentz, polarization effects, and for absorption.

Calculations were carried out with the SHELX system of computer programs [12]. Neutral atom scattering factors for Y, N and C were taken from Cromer and Waber [14], and the scattering for yttrium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman [14]. Scattering factors for H were from ref. 15.

Density considerations necessitated the presence of two molecules in the asymmetric unit. Inspection of a Patterson map revealed the presence of the two

TABLE 2

CRYSTAL DATA AND SUMMARY OF INTENSITY DATA COLLECTION AND STRUCTURE REFINEMENT

Compound	$(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$
Mol.wt.	353.3
Space group	$P2_1/c$
Cell constants	
a, Å	8.310(3)
b, Å	26.972(8)
c, Å	15.548(6)
β, deg	95.88(3)
Cell vol, Å^3	3466.6
Molecules/unit cell	8
ρ(calc), g cm^{-3}	1.35
μ(calc), cm^{-1}	34.60
Radiation	Mo-K_α
Max crystal dimensions, mm	0.55 × 0.58 × 1.00
Scan width	0.80 × 0.20 tanθ
Standard reflections	006, 080
Decay of standards	±2%
Reflections measured	2829
2θ range	2–36°
Reflections observed, $I > 2\sigma(I)$	1739
No. of parameters varied	179
GOF	6.78
R	0.102
R_w	0.108

TABLE 3

FINAL FRACTIONAL COORDINATES FOR $(\eta^5\text{-}C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$

Atom	*x/a*	*y/b*	*z/c*
Y(1)	0.5648(3)	0.19985(9)	0.0761(2)
Y(2)	0.0615(3)	0.42713(9)	0.2202(2)
N(1)	0.773(3)	0.1958(8)	0.198(1)
N(2)	0.251(2)	0.4933(6)	0.172(1)
C(1)	0.697(3)	0.1204(9)	0.072(1)
C(2)	0.839(3)	0.1203(9)	0.118(1)
C(3)	0.950(3)	0.077(1)	0.123(2)
C(4)	0.894(4)	0.036(1)	0.075(2)
C(5)	0.750(3)	0.034(1)	0.031(2)
C(6)	0.647(3)	0.076(1)	0.027(2)
C(7)	0.914(3)	0.167(1)	0.169(2)
C(8)	0.729(3)	0.170(1)	0.275(2)
C(9)	0.861(4)	0.245(1)	0.231(2)
C(10)	0.349(3)	0.165(1)	0.177(2)
C(11)	0.353(3)	0.214(1)	0.187(2)
C(12)	0.285(3)	0.235(1)	0.112(2)
C(13)	0.248(3)	0.198(1)	0.048(2)
C(14)	0.289(3)	0.155(1)	0.091(2)
C(15)	0.721(4)	0.209(1)	−0.062(2)
C(16)	0.567(4)	0.220(1)	−0.092(2)
C(17)	0.522(4)	0.262(1)	−0.055(2)
C(18)	0.661(4)	0.281(1)	−0.005(2)
C(19)	0.784(4)	0.242(1)	−0.015(2)
C(20)	0.143(3)	0.4030(9)	0.082(1)
C(21)	0.273(3)	0.4273(9)	0.058(1)
C(22)	0.340(3)	0.417(1)	−0.020(2)
C(23)	0.269(4)	0.383(1)	−0.077(2)
C(24)	0.144(3)	0.358(1)	−0.054(2)
C(25)	0.071(3)	0.366(1)	0.018(2)
C(26)	0.357(3)	0.4649(9)	0.119(2)
C(27)	0.153(3)	0.5287(9)	0.113(2)
C(28)	0.350(3)	0.521(1)	0.239(2)
C(29)	−0.196(4)	0.482(1)	0.229(2)
C(30)	−0.224(4)	0.437(1)	0.278(2)
C(31)	−0.246(4)	0.403(1)	0.213(2)
C(32)	−0.229(4)	0.421(1)	0.135(2)
C(33)	−0.204(4)	0.470(1)	0.142(2)
C(34)	0.285(4)	0.407(1)	0.351(2)
C(35)	0.146(4)	0.393(1)	0.379(2)
C(36)	0.092(3)	0.352(1)	0.330(2)
C(37)	0.206(4)	0.344(1)	0.274(2)
C(38)	0.330(4)	0.382(1)	0.289(2)

independent yttrium atoms. A difference Fourier map phased on the yttrium atoms readily revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.121$. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atom and were not refined. The methyl hydrogen atoms were located with the aid of a difference Fourier map. The nitrogen and carbon atoms were not refined with anisotropic temperature factors because of the paucity of observed reflection data. Virtually no scatter could be found above the two-theta cut-off of 36°, and even in this sphere only 61% were deemed observed, $I > 2\sigma(I)$. Refinement of the yttrium atoms with anisotropic temperature factors led to final values of $R = 0.102$ and $R_w = 0.108$. A final difference Fourier showed no feature greater than 0.4 $e^-/Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 3 *.

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References

1 R.D. Rogers, J.L. Atwood, A. Emad, D.J. Sikora, and M.D. Rausch, J. Organomet. Chem., 216 (1981) 383.

2 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood, and W.E. Hunter, J. Chem. Soc., Dalton Trans., (1979) 54.

3 F.A. Hart, A.G. Massey, and M.S. Saran, J. Organomet. Chem., 21 (1970) 147.

4 L.E. Manzer, J. Amer. Chem. Soc., 100 (1978) 8068. See also references cited therein.

5 W.J. Evans, J.H. Meadows, W.E. Hunter, and J.L. Atwood, J. Am. Chem. Soc., submitted, and references therein.

6 S.A. Cotton, F.A. Hart, M.B. Hursthouse, and A.J. Welch, J. Chem. Soc., Chem. Comm., (1972) 1225.

7 J.L. Atwood, W.E. Hunter, R.D. Rogers, J. Holton, J. McMeeking, R. Pearce, and M.F. Lappert, J. Chem. Soc. Chem. Commun., (1978) 140.

8 A. Wayda, J.L. Atwood, and W.E. Hunter, Organometallics, in press.

9 A.I. Vogel, A Textbook of Practical Organic Chemistry, 3rd edit., Longmans, Green and Co., Ltd: London, 1956, p. 189.

10 Dry YCl_3 will "hiss" when added to THF. The yield of $[(\eta^5\text{-}C_5H_5)_2YCl]_2$ prepared from C_5H_5Na and YCl_3 was tripled when purified YCl_3 was used instead of commercially available YCl_3.

11 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood, and W.E. Hunter, J. Chem. Soc. Dalton Trans., (1979) 45.

12 SHELX, A system of computer programs for X-ray structure determination by G.M. Sheldrick, 1976.

13 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.

14 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.

15 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974, p 72.

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* Tables of thermal parameters, least-squares planes results, and observed and calculated structure factors are available upon request from R.D.R.