2368 *Inorg. Chem.* **1980**, *19*, 2368-2374

Contribution from the Department of Chemistry,
University of Alabama, University, Alabama 35486

Pyrrolyl Complexes of the Early Transition Metals. 1. Synthesis and Crystal Structure of $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$, $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$, and $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$

R. VANN BYNUM, WILLIAM E. HUNTER, ROBIN D. ROGERS, and JERRY L. ATWOOD*

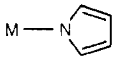
Received December 28, 1979

The crystal structures of $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$, $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$, and $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$ have been determined from three-dimensional X-ray data measured by counter methods. Dicyclopentadienyldipyrrolyltitanium(IV) crystallizes in the monoclinic space group $P2_1$ with unit cell dimensions $a = 7.986$ (4) Å, $b = 10.660$ (5) Å, $c = 9.726$ (5) Å, $\beta = 113.77$ (4)°, and $Z = 2$ for $\rho_{calcd} = 1.36$ g cm^{-3}. Full-matrix least-squares refinement has led to a final R factor of 0.029 based on 1293 observed reflections. The pyrrolyl groups are bonded to the titanium atom through an sp^2-hybridized nitrogen atom; the average Ti–N–centroid(σ-pyrrolyl) angle is 166°. Short Ti–N bond lengths, 2.070 (5) and 2.100 (4) Å, are observed. The zirconium analogue crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.597$ (5) Å, $b = 8.198$ (5) Å, $c = 19.546$ (8) Å, $\beta = 91.20$ (4)°, and $Z = 4$ for $\rho_{calcd} = 1.53$ g cm^{-3}. Refinement based on 2237 observed reflections gave a final R value of 0.018. The average Zr–N–centroid(σ-pyrrolyl) angle is 164°, and the Zr–N bond distances are 2.167 (2) and 2.171 (2) Å. Bis[hexakis(tetrahydrofuran)sodium]hexapyrrolylzirconium(IV) belongs to the rhombohedral space group $R\bar{3}$ with $a = 12.850$ (6) Å, $\alpha = 79.15$ (4)°, and $Z = 1$ for $\rho_{calcd} = 1.15$ g cm^{-3}. The compound in the crystalline state is 62% by weight tetrahydrofuran. The zirconium atom resides on a site with $\bar{3}$ point symmetry, and the sodium atom lies on a threefold axis. About the zirconium atom the geometry is octahedral with N–Zr–N angles of 90°. The Zr–N–centroid(σ-pyrrolyl) angle is 179°, and the Zr–N bond length is 2.198 (6) Å. In each of the three compounds very short metal–nitrogen bonds and the orientation of the pyrrolyl ligands are indicative of a bonding scheme which involves an appreciable d_π–p_π interaction. Reaction of $(\eta^5\text{-}C_5H_5)_2MCl_2$ with $NaNC_4H_4$ in THF at room temperature leads to the formation of the slightly air sensitive $(\eta^5\text{-}C_5H_5)_2M(\eta^1\text{-}NC_4H_4)_2$. For M = Zr, at reflux temperature the cyclopentadienyl ligands are removed, and the hexapyrrolylzirconium anion results.

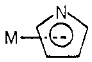
Introduction

While the chemistry of cyclopentadienyl complexes of the transition metals has burgeoned, very few compounds containing the isoelectronic pyrrolyl anion, $NC_4H_4^-$, have been produced. Azaferrocene, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}NC_4H_4)$,[1,2] and $(\eta^5\text{-}NC_4H_4)Mn(CO)_3$[3] were prepared in the early 1960's, and several studies on these compounds subsequently appeared.[4] The reports show that the complexes are similar to those of the cyclopentadienyl group but are less stable. The entire area of heterocyclic π-complexes of the transition metals has been recently reviewed.[5]

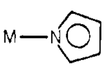
Our interest was focused on pyrrolyl complexes because of the ability of the ligand to bond in either a σ fashion (I) or a π fashion (II). Previous studies on the tetracyclopentadienyls of titanium, zirconium, and uranium have shown that the smallest ion, Ti^{4+}, possesses two π-bonded and two σ-bonded groups,[6] while the largest, U^{4+}, is π bonded to all four.[7] Zr^{4+} is intermediate in size and exhibits three π- and one σ-cyclopentadienyl.[8] Since the $NC_4H_4^-$ ion is relatively a weaker π-bonding but a stronger σ-bonding ligand than $C_5H_5^-$, we decided to investigate pyrrolyl complexes of group 4B metals. These studies, reported herein, show not only that the pyrrolyl ligand presents prospects of a rich and varied chemistry but also that the dominant bonding mode for $NC_4H_4^-$ to titanium and zirconium can best be represented as III, not I or II.



I



II



III

Experimental Section

The synthetic work was carried out by Schlenk techniques under nitrogen or in a Kewaunee drybox. Solvents were distilled from $LiAlH_4$ (tetrahydrofuran, THF) or sodium (toluene) under an atmosphere of nitrogen. $(\eta^5\text{-}C_5H_5)_2MCl_2$ compounds (M = Ti, Zr) were purchased from Alfa Inorganics and used without further purification. Pyrrole was purchased from Aldrich and was distilled prior to use. The mass spectral analyses were performed by the Analytical Services Department at the University of Alabama.

Synthesis of Pyrrolylsodium. Excess sodium sand was prepared in toluene, the toluene removed, and THF added. Freshly distilled pyrrole (67 g, 1 mol) as a 50% solution in THF was added dropwise over several hours. Gas evolution was noted, and heat was given off. After the mixture was stirred overnight, the excess sodium was removed and the solution diluted to 1 L with THF. The pyrrolylsodium thus prepared was used as a 1 M solution in THF.

Synthesis of Dicyclopentadienyldipyrrolyltitanium(IV). $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (1.24 g, 5 mmol) was dissolved in ca. 100 mL of THF. Pyrrolylsodium (0.89 g, 10 mmol) was added via syringe. The color of the solution immediately changed from red to black. After 24 h, the solvent was removed under vacuum and the residue extracted with toluene. The solution thus obtained was filtered and on cooling produced black, air-stable crystals (1.13 g, 73%).

Synthesis of Dicyclopentadienyldipyrrolylzirconium(IV). $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (1.46 g, 5 mmol) was dissolved in ca. 100 mL of THF. Pyrrolylsodium (0.89 g, 10 mmol) was added via syringe. The solution changed from colorless to bright yellow. After being stirred overnight, the reaction mixture was taken to dryness under vacuum and the yellow residue extracted with toluene. This solution was filtered and on cooling produced yellow, mildly air-sensitive crystals (1.40 g, 80%). The mass spectrum gave a parent ion peak (^{90}Zr) at m/e 352. The other major peaks corresponded to successive loss of the pyrrolyl groups ($M^+ - 66$ and $M^+ - 132$). The peak corresponding to the loss of one pyrrolyl group was the most intense.

Synthesis of Bis[hexakis(tetrahydrofuran)sodium]hexapyrrolylzirconium(IV). $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (2.92 g, 10 mmol) was dissolved

---

[1] Joshi, K. K.; Pauson, P. L.; Qazi, A. R.; Stubbs, W. H. *J. Organomet. Chem.* **1964**, *1*, 471.

[2] King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 796.

[3] Joshi, K. K.; Pauson, P. L. *Proc. Chem. Soc., London* **1962**, 326.

[4] See, for example: Fayer, M. D.; Harris, C. B. *Inorg. Chem.* **1969**, *8*, 2792. Pyshnograeva, N. I.; Setkina, V. N.; Andrianov, V. G.; Struchkov, Y. T.; Kursanov, D. N. *J. Organomet. Chem.* **1977**, *128*, 381.

[5] Pannell, K. H.; Kalsotra, B. L.; Parkanyi, C. *J. Heterocycl. Chem.* **1978**, *15*, 1057.

[6] Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Takats, J. *J. Am. Chem. Soc.* **1971**, *93*, 3592.

[7] Burns, J. H. *J. Organomet. Chem.* **1974**, *69*, 225.

[8] Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238.

0020-1669/80/1319-2368$01.00/0

Table I. Crystal Data

compound	$(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$	$(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$	$[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$
mol wt	310.3	353.6	1399.0
linear abs coeff, cm^{-1}	5.82	6.98	2.08
calcd density, g cm^{-3}	1.36	1.53	1.15
max cryst dimens, mm	0.32 × 0.40 × 0.56	0.35 × 0.44 × 0.52	0.50 × 0.50 × 0.65
space group	$P2_1$	$P2_1/c$	$R\bar{3}$
molecules/unit cell	2	4	1
cell constants[a]			
a, Å	7.986 (4)	9.597 (5)	12.850 (6)[b]
b, Å	10.660 (5)	8.198 (5)	
c, Å	9.726 (5)	19.546 (8)	
β, deg	113.77 (4)	91.20 (4)	79.15 (4)
cell vol, Å^3	757.7	1537.5	2020.8

[a] Mo Kα radiation, 0.710 69 Å. Ambient temperature of 22 °C. [b] Crystal system is rhombohedral: $a = b = c$; $\alpha = \beta = \gamma$.

Table II. Final Fractional Coordinates and Thermal Parameters[a, b] for $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$

atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	0.4447 (1)	0.7500	0.71711 (9)	0.0101 (1)	0.00777 (8)	0.0088 (1)	0.0006 (1)	0.00273 (9)	−0.0003 (1)
N(1)	0.3238 (6)	0.8012 (4)	0.4894 (5)	0.0181 (9)	0.0114 (5)	0.0099 (5)	0.0009 (5)	0.0055 (6)	−0.0001 (4)
N(2)	0.3351 (6)	0.9073 (4)	0.7740 (5)	0.0153 (9)	0.0085 (5)	0.0103 (6)	0.0004 (5)	0.0045 (6)	−0.0006 (4)
C(1)	0.3992 (9)	0.5284 (7)	0.7002 (8)	0.018 (1)	0.0100 (7)	0.017 (1)	0.0012 (8)	0.004 (1)	−0.0021 (8)
C(2)	0.4329 (8)	0.5619 (6)	0.8483 (7)	0.020 (1)	0.0092 (7)	0.0144 (9)	0.0000 (8)	0.0021 (9)	0.0016 (7)
C(3)	0.2951 (9)	0.6397 (6)	0.8483 (7)	0.027 (2)	0.0089 (6)	0.0138 (9)	−0.0028 (9)	0.009 (1)	0.0007 (7)
C(4)	0.1681 (7)	0.6516 (6)	0.6970 (7)	0.013 (1)	0.0092 (6)	0.0166 (9)	−0.0014 (7)	0.0056 (8)	−0.0003 (6)
C(5)	0.2313 (7)	0.5822 (6)	0.6074 (7)	0.017 (1)	0.0088 (6)	0.0145 (9)	−0.0016 (7)	0.0036 (8)	−0.0025 (6)
C(6)	0.7169 (8)	0.8722 (7)	0.8411 (8)	0.009 (1)	0.0117 (8)	0.018 (1)	−0.0024 (7)	0.0013 (9)	−0.0000 (8)
C(7)	0.7448 (6)	0.757 (1)	0.9113 (6)	0.0115 (9)	0.0135 (7)	0.0149 (8)	−0.002 (1)	−0.0018 (7)	0.001 (1)
C(8)	0.7504 (9)	0.6658 (8)	0.811 (1)	0.009 (1)	0.014 (1)	0.033 (2)	0.0024 (9)	0.002 (1)	−0.005 (1)
C(9)	0.716 (1)	0.725 (1)	0.674 (1)	0.011 (1)	0.030 (2)	0.023 (1)	0.002 (1)	0.008 (1)	−0.007 (1)
C(10)	0.6991 (9)	0.854 (1)	0.6941 (9)	0.011 (1)	0.024 (2)	0.017 (1)	−0.003 (1)	0.005 (1)	0.005 (1)
C(11)	0.3569 (8)	0.7640 (8)	0.3690 (6)	0.027 (1)	0.0100 (7)	0.0127 (7)	−0.002 (1)	0.0106 (8)	−0.0021 (8)
C(12)	0.219 (1)	0.8006 (7)	0.2395 (6)	0.037 (2)	0.0128 (8)	0.0086 (7)	−0.007 (1)	0.007 (1)	−0.0020 (6)
C(13)	0.0926 (9)	0.8632 (6)	0.2774 (6)	0.026 (1)	0.0109 (8)	0.0099 (7)	−0.0028 (9)	−0.0000 (9)	0.0004 (6)
C(14)	0.1582 (7)	0.8624 (6)	0.4304 (6)	0.017 (1)	0.0127 (8)	0.0104 (7)	0.0026 (8)	0.0021 (7)	0.0007 (6)
C(15)	0.3669 (8)	1.0256 (6)	0.7324 (7)	0.019 (1)	0.0086 (6)	0.0136 (9)	0.0007 (8)	0.0062 (9)	0.0010 (6)
C(16)	0.2431 (9)	1.1108 (6)	0.7380 (7)	0.024 (1)	0.0079 (6)	0.0143 (9)	0.0020 (8)	0.0040 (9)	−0.0003 (6)
C(17)	0.1261 (7)	1.0438 (6)	1.7873 (6)	0.016 (1)	0.0112 (7)	0.0130 (8)	0.0020 (8)	0.0037 (8)	−0.0040 (6)
C(18)	0.1837 (7)	0.9231 (6)	0.8078 (6)	0.014 (1)	0.0104 (6)	0.0103 (7)	−0.0012 (7)	0.0042 (7)	−0.0029 (6)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
H(1)[C(1)]	0.4825	0.4726	0.6626	H(10)[C(10)]	0.6752	0.9199	0.6143
H(2)[C(2)]	0.5409	0.5329	0.9429	H(11)[C(11)]	0.1224	0.8529	0.8443
H(3)[C(3)]	0.2792	0.6752	0.9377	H(12)[C(12)]	0.0163	1.0806	0.8046
H(4)[C(4)]	0.0545	0.7032	0.6625	H(13)[C(13)]	0.2372	1.2029	0.7115
H(5)[C(5)]	0.1647	0.5700	0.4945	H(14)[C(14)]	0.4710	1.0444	0.7006
H(6)[C(6)]	0.7133	0.9564	0.8905	H(15)[C(15)]	0.4676	0.7123	0.3758
H(7)[C(7)]	0.7596	0.7408	1.0202	H(16)[C(16)]	0.2171	0.7839	0.1350
H(8)[C(8)]	0.7712	0.5677	0.8361	H(17)[C(17)]	−0.0278	0.9007	0.2048
H(9)[C(9)]	0.7099	0.6792	0.5782	H(18)[C(18)]	0.0957	0.9017	0.4925

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For all hydrogen atoms B = 5.00 Å^2.

in ca. 250 mL of THF. Pyrrolylsodium (1.78 g, 20 mmol) was added via syringe. The solution color immediately changed to yellow. It was then refluxed for 12 h, after which time it was filtered and cooled. Large yellow plates appeared in quantity. The rapid loss of THF by the crystals prohibited analysis by a method other than X-ray diffraction.

X-ray Data Collection and Solution and Refinement of the Structure of $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$. Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 36°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Systematic absences in $0k0$, $k \neq 2n$, allow the space group to be $P2_1$ or $P2_1/m$. Subsequent solution and refinement showed that the acentric $P2_1$ is the correct choice.

Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were measured by the ω–2θ scan technique in the usual manner.[9] As a check on the stability of the instrument and crystal, three reflections were measured after every 50 reflections; no significant variation was noted. One independent quadrant of data was measured out to $2\theta = 50°$, and a slow scan was performed on 1293 unique reflections. This set consisted of those for which $I \geq 3\sigma(I)$ and was used in the subsequent structure determination and refinement. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The function $w(|F_o| - |F_c|)^2$ was minimized.[10] No corrections were made for extinction. Neutral-atom scattering factors were taken from the compilations of Cromer and Waber[11] for Ti, N, and C, and that of Ti was corrected for the real and imaginary components of anomalous dispersion.[12] Scattering factors for H were from ref 13.

---

(9) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 46.

(10) Crystallographic programs used on a UNIVAC 1110 include ORFLS (structure factor calculation and least-squares refinement, by W. R. Busing, K. O. Martin, and H. A. Levy), ORFFE (distances and angles with esd's, by W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program), and BPL (least-squares planes, by W. E. Hunter).

(11) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(12) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

Table III. Final Fractional Coordinates and Thermal Parameters[a,b] for $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$

atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zr	0.21624 (2)	0.05329 (3)	0.38649 (1)	0.00620 (2)	0.00845 (3)	0.001647 (6)	−0.00018 (2)	0.000138 (8)	0.00017 (1)
N(1)	0.4333 (2)	0.0877 (3)	0.3610 (1)	0.0078 (2)	0.0132 (4)	0.00278 (6)	−0.0008 (2)	0.0006 (1)	−0.0003 (1)
N(2)	0.2239 (2)	0.2032 (2)	0.4778 (1)	0.0105 (2)	0.0113 (3)	0.00189 (5)	0.0004 (2)	0.00025 (9)	0.0000 (1)
C(1)	0.1483 (3)	0.3127 (3)	0.3240 (1)	0.0139 (4)	0.0117 (4)	0.00209 (7)	0.0015 (3)	−0.0006 (1)	0.0014 (2)
C(2)	0.0257 (3)	0.2464 (4)	0.3490 (2)	0.0107 (4)	0.0202 (6)	0.00257 (9)	0.0062 (4)	0.0001 (1)	0.0021 (2)
C(3)	0.0006 (3)	0.0999 (5)	0.3148 (2)	0.0097 (4)	0.0232 (7)	0.0039 (1)	−0.0020 (4)	−0.0027 (2)	0.0028 (2)
C(4)	0.1082 (4)	0.0763 (4)	0.2688 (1)	0.0178 (5)	0.0196 (6)	0.00222 (8)	0.0014 (5)	−0.0025 (2)	−0.0006 (2)
C(5)	0.1976 (3)	0.2095 (4)	0.2744 (1)	0.0142 (4)	0.0183 (6)	0.00173 (7)	0.0015 (4)	0.0002 (1)	0.0017 (2)
C(6)	0.2987 (3)	−0.1961 (3)	0.4517 (2)	0.0123 (4)	0.0103 (4)	0.0033 (1)	0.0001 (3)	−0.0006 (1)	0.0018 (2)
C(7)	0.1645 (3)	−0.1633 (3)	0.4735 (2)	0.0164 (4)	0.0105 (4)	0.00278 (9)	−0.0010 (4)	0.0022 (2)	0.0015 (2)
C(8)	0.0721 (3)	−0.1872 (4)	0.4190 (2)	0.0089 (3)	0.0115 (5)	0.0050 (1)	−0.0023 (3)	0.0014 (2)	0.0011 (2)
C(9)	0.1489 (3)	−0.2384 (3)	0.3627 (2)	0.0143 (4)	0.0096 (4)	0.0036 (1)	−0.0028 (3)	−0.0007 (2)	−0.0009 (2)
C(10)	0.2887 (3)	−0.2428 (3)	0.3831 (2)	0.0117 (4)	0.0090 (4)	0.0037 (1)	0.0011 (3)	0.0014 (2)	−0.0001 (2)
C(11)	0.5074 (3)	0.0168 (4)	0.3096 (1)	0.0085 (3)	0.0145 (5)	0.00296 (9)	0.0005 (3)	0.0007 (1)	−0.0004 (2)
C(12)	0.6190 (3)	0.1094 (4)	0.2938 (1)	0.0090 (3)	0.0216 (6)	0.00245 (8)	−0.0003 (4)	0.0012 (1)	0.0009 (2)
C(13)	0.6159 (3)	0.2454 (4)	0.3363 (2)	0.0103 (3)	0.0200 (6)	0.00287 (9)	−0.0063 (4)	0.0001 (1)	0.0006 (2)
C(14)	0.5017 (3)	0.2308 (3)	0.3762 (1)	0.0092 (3)	0.0142 (5)	0.00223 (7)	−0.0024 (3)	−0.0003 (1)	−0.0002 (2)
C(15)	0.1929 (3)	0.3667 (3)	0.4858 (1)	0.0168 (4)	0.0105 (4)	0.00210 (8)	0.0008 (4)	0.0003 (1)	0.0001 (1)
C(16)	0.2468 (4)	0.4242 (4)	0.5453 (2)	0.0192 (5)	0.0128 (5)	0.00256 (8)	−0.0016 (4)	0.0006 (2)	−0.0013 (2)
C(17)	0.3137 (3)	0.2946 (4)	0.5779 (1)	0.0115 (4)	0.0214 (6)	0.00231 (8)	−0.0004 (4)	−0.0008 (1)	−0.0016 (2)
C(18)	0.2992 (3)	0.1632 (4)	0.5370 (1)	0.0096 (3)	0.0154 (5)	0.00219 (7)	0.0019 (3)	−0.0002 (1)	−0.0003 (2)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
H(1)[C(1)]	0.190 (3)	0.407 (4)	0.337 (2)	H(10)[C(10)]	0.361 (3)	−0.277 (4)	0.357 (2)
H(2)[C(2)]	−0.028 (3)	0.291 (4)	0.379 (2)	H(11)[C(11)]	0.477 (3)	−0.081 (4)	0.288 (1)
H(3)[C(3)]	−0.074 (3)	0.042 (4)	0.322 (2)	H(12)[C(12)]	0.687 (3)	0.083 (4)	0.260 (1)
H(4)[C(4)]	0.119 (3)	−0.024 (4)	0.239 (1)	H(13)[C(13)]	0.673 (3)	0.334 (4)	0.338 (1)
H(5)[C(5)]	0.275 (3)	0.224 (4)	0.251 (2)	H(14)[C(14)]	0.465 (3)	0.305 (4)	0.408 (1)
H(6)[C(6)]	0.383 (3)	−0.185 (4)	0.477 (1)	H(15)[C(15)]	0.138 (3)	0.420 (4)	0.456 (2)
H(7)[C(7)]	0.137 (3)	−0.128 (4)	0.514 (2)	H(16)[C(16)]	0.241 (3)	0.534 (4)	0.559 (1)
H(8)[C(8)]	−0.015 (3)	−0.180 (4)	0.422 (2)	H(17)[C(17)]	0.363 (3)	0.294 (4)	0.618 (2)
H(9)[C(9)]	0.115 (3)	−0.268 (4)	0.320 (2)	H(18)[C(18)]	0.332 (3)	0.061 (4)	0.544 (1)

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For all hydrogen atoms $B = 5.50$ Å^2.

The position of the titanium atom was deduced by the inspection of a Patterson map, and the subsequent calculation of a difference Fourier map allowed the location of the remaining 20 nonhydrogen atoms. Refinement with isotropic temperature factors led to a reliability factor of $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.097$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.045$. The hydrogen atoms were placed at calculated positions 1.00 Å from the bonded carbon atoms, and their parameters were not refined. Additional cycles of refinement led to final values of $R_1 = 0.029$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.039$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their esd's. A final difference Fourier map showed no feature greater than 0.3 e/Å^3. The standard deviation of an observation of unit weight was 0.60. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table II. (Tables of structure factor amplitudes and best planes results for all three structures in this paper are available.[14])

X-ray Data Collection and Solution and Refinement of the Structure of $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$. Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 40°$) accurately centered on the diffractometer are given in Table I. Systematic absences uniquely define the space group to be $P2_1/c$.

Data were collected as described for the titanium analogue. One independent quadrant of data was measured out to $2\theta = 50°$; a slow scan was performed on 2237 unique observed reflections. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Neutral-atom scattering factors were obtained as noted above, and that of Zr was corrected for the real and imaginary components of anomalous dispersion.

The position of the zirconium atom was deduced by the inspection of a Patterson map, and the subsequent calculation of a difference Fourier map allowed the location of the remaining 20 nonhydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R_1 = 0.085$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.041$. The hydrogen atoms were placed at calculated positions 1.00 Å from the bonded carbon atoms, and their positional parameters were refined. Additional cycles of refinement led to final values of $R_1 = 0.018$ and $R_2 = 0.021$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their esd's. A final difference Fourier map showed no feature greater than 0.3 e/Å^3. The standard deviation of an observation of unit weight was 0.75. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table III.

X-ray Data Collection and Solution and Refinement of the Structure of $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$. Crystals of this compound proved to be the most difficult to handle of any substance encountered in our laboratory. Decomposition via THF loss occurs readily upon removal from the solvent. (This is perhaps expected since the crystals are 62% by weight THF!) Crystals suitable for the X-ray study were eventually mounted in thin-walled glass capillaries in a drybox which had been flooded with THF. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 40°$) accurately centered on the diffractometer are given in Table I.

Data were collected as described above for the dicyclopentadienyldipyrrolyl complexes. One independent hemisphere of data was measured out to $2\theta = 50°$; a slow scan was performed on 1657 unique observed reflections. No crystal decomposition was noted during the course of data collection. The intensities were corrected for Lorentz and polarization effects but not for absorption. Neutral atom scattering factors were obtained and used as noted for $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$.

The positions of the zirconium, sodium, and nitrogen atoms were revealed by application of the direct methods program MULTAN.[15] Scrutiny of a difference Fourier map afforded the coordinates of the remaining nonhydrogen atoms. Refinement with isotropic temperature

---

(14) Supplemental material.

(15) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

Table IV. Final Fractional Coordinates and Thermal Parameters[a,b] for $[Na(OC_4H_6)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$

atom	*x/a*	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zr	0.0000	0.0000	0.0000	0.00684 (6)	0.00684 (6)	0.00684 (6)	−0.00098 (4)	−0.00098 (4)	−0.00098 (4)
Na	0.3235 (2)	0.3235 (2)	0.3235 (2)	0.0136 (3)	0.0136 (3)	0.0136 (3)	−0.0027 (2)	−0.0027 (2)	−0.0027 (2)
O(1)	0.3564 (7)	0.1328 (6)	0.3229 (7)	0.0235 (9)	0.0129 (7)	0.0189 (8)	−0.0017 (6)	−0.0044 (7)	−0.0035 (6)
O(2)	0.3116 (8)	0.3034 (8)	0.5181 (6)	0.025 (1)	0.029 (1)	0.0112 (7)	−0.0087 (9)	−0.0027 (7)	−0.0023 (7)
N(1)	0.0188 (5)	0.0104 (5)	0.8249 (5)	0.0118 (6)	0.0109 (6)	0.0104 (5)	−0.0028 (5)	−0.0007 (5)	−0.0013 (4)
C(1)	0.1136 (8)	0.0052 (8)	0.7530 (8)	0.0140 (9)	0.017 (1)	0.0112 (8)	−0.0047 (8)	0.0007 (7)	−0.0019 (7)
C(2)	0.093 (1)	0.016 (1)	0.6502 (8)	0.021 (1)	0.021 (1)	0.0086 (8)	−0.008 (1)	0.0013 (9)	−0.0020 (8)
C(3)	−0.021 (1)	0.0285 (9)	0.6590 (8)	0.023 (2)	0.019 (1)	0.0097 (9)	−0.007 (1)	−0.0047 (9)	−0.0009 (8)
C(4)	−0.0608 (8)	0.0268 (8)	0.7627 (7)	0.0149 (9)	0.0153 (9)	0.0102 (8)	−0.0030 (7)	−0.0035 (7)	−0.0012 (7)
C(5)	0.360 (2)	0.084 (1)	0.232 (1)	0.060 (4)	0.016 (1)	0.024 (2)	−0.006 (2)	−0.012 (2)	−0.007 (1)
C(6)	0.396 (2)	−0.030 (1)	0.261 (1)	0.051 (4)	0.013 (1)	0.024 (2)	−0.001 (2)	0.001 (2)	−0.005 (1)
C(7)	0.345 (2)	−0.045 (1)	0.371 (2)	0.056 (4)	0.019 (2)	0.027 (2)	−0.013 (2)	0.004 (3)	−0.005 (2)
C(8)	0.376 (2)	0.047 (1)	0.405 (2)	0.066 (5)	0.018 (2)	0.028 (2)	−0.005 (2)	−0.024 (3)	0.000 (2)
C(9)	0.242 (3)	0.266 (3)	0.598 (2)	0.071 (6)	0.092 (7)	0.014 (2)	−0.064 (6)	0.003 (3)	−0.005 (3)
C(10)	0.247 (2)	0.317 (3)	0.694 (2)	0.026 (3)	0.080 (7)	0.021 (2)	0.006 (3)	−0.001 (2)	−0.018 (3)
C(11)	0.339 (2)	0.267 (3)	0.689 (2)	0.039 (4)	0.066 (6)	0.012 (2)	0.010 (4)	−0.007 (2)	−0.005 (2)
C(12)	0.378 (2)	0.316 (3)	0.578 (2)	0.049 (5)	0.112 (9)	0.016 (2)	−0.041 (5)	−0.008 (3)	−0.006 (3)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
H(1)[C(1)]	0.1927	−0.0057	0.7745	H(3)[C(3)]	−0.0663	0.0381	0.5942
H(2)[C(2)]	0.1502	0.0146	0.5773	H(4)[C(4)]	−0.1454	0.0364	0.7944

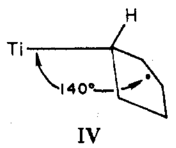
[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For all hydrogen atoms $B = 6.31$ Å^2.

factors gave $R_1 = 0.13$. Conversion to anisotropic thermal parameters, placement of the pyrrolyl hydrogen atoms at calculated positions 1.00 Å from the bonded carbon atoms, and further refinement of the nonhydrogen atoms led to final values of $R_1 = 0.081$ and $R_2 = 0.092$. High thermal motion of the carbon atoms of the THF groups indicated probable disorder, but this problem could not be resolved. The largest parameter shifts in the final cycle of refinement were less than 0.02 of their esd's for all except those related to the THF carbon atoms. For the latter the values ranged as high as 0.80. A final difference Fourier map showed no feature greater than 0.4 e/Å^3, apart from those associated with the THF ligands (∼1 e/Å^3). The standard deviation of an observation of unit weight was 1.52. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table IV.

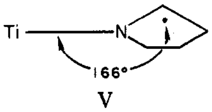
Description of the Structure

$(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$. The molecular structure and atom numbering scheme are shown in Figure 1. The compound is formally isoelectronic with $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$[6] and is similar to it in that each exhibits two π-bonded and two σ-bonded ligands. However, the bonding of the pyrrolyl groups is quite different from that of the σ-cyclopentadienyl groups. This difference is manifest in two structural parameters: the orientation of the pyrrolyl ligands and the apparent strength of the Ti–N bond.

The σ-cyclopentadienyl group is bonded to the titanium atom in a manner normal for an sp^3-hybridized carbon atom (IV). The Ti–C–centroid(σ-cyclopentadienyl) angle is 140°.



IV



V

In $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$ the average Ti–N–centroid(σ-pyrrolyl) angle (V) is 166°, lending credence to a pyrrolyl bonding mode as depicted in III.

The Ti–N bond length, 2.085 (21) Å (Table V), is another noteworthy feature.[35] The Ti–C(σ) bond distance in tetracyclopentadienyltitanium is 2.332 (2) Å.[6] After the appropriate correction for hybridization and covalent radius,[16] the Ti–N bond length is ca. 0.2 Å shorter than its Ti–C counterpart. The normal range for Ti(IV) compounds extends from 2.172 Å in $K_2[Ti_2O_2(C_7H_3O_4N)_2]\cdot 5H_2O$[17] to 2.25 Å in $Ti[OC_6H_4CH{=}N(C_2H_5)]_4$.[18] For compounds in which an appreciable d_π–p_π interaction has been postulated, much shorter Ti–N lengths have been observed: 1.852 (4) Å in $Ti[N(C_2H_5)_2]Cl_3$,[19] 1.905 (8) Å in $Ti[-N(CH_3)Si(CH_3)_2Si(CH_3)_2(CH_3)N-]_2$,[20] and 1.99 (3) Å in $[Ti[N(CH_3)_2]F_2]_4$.[21] However, the latter three compounds provide the titanium atom with an electron count of 12 or less, while $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$ is a 16-electron case. A substantial contraction of bond length for "electron-deficient" situations has been observed with respect to molybdenum compounds[22] and should be operative here as well. A third comparison relates to the Ti–C(carbonyl) distance of 2.031 (11) Å in $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$,[23] for which a significant degree of d-orbital participation from the titanium atom is expected. All

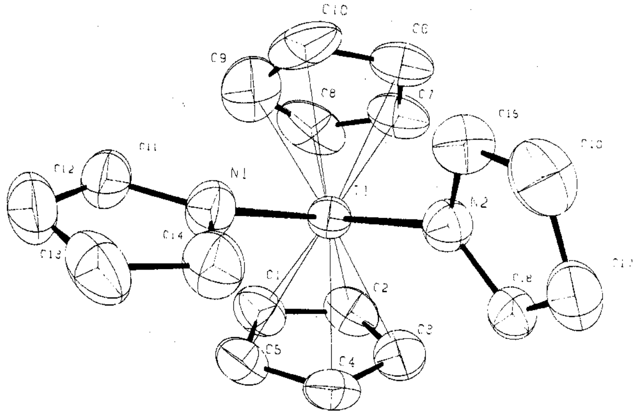


Figure 1. Molecular structure and atom numbering scheme for $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

---

(16) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960.

(17) Schwarzenbach, D. *Inorg. Chem.* **1970**, *9*, 2391.

(18) Bradley, D. C.; Hursthouse, M. B.; Rendall, I. F. *Chem. Commun.* **1969**, 672.

(19) Fayos, J.; Mootz, D. *Z. Anorg. Allg. Chem.* **1971**, *380*, 196.

(20) Burger, H.; Wiegel, K.; Thewalt, J.; Schomburg, D. *J. Organomet. Chem.* **1975**, *87*, 301.

(21) Sheldrick, W. S. *J. Fluorine Chem.* **1974**, *4*, 415.

(22) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1519.

(23) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367.

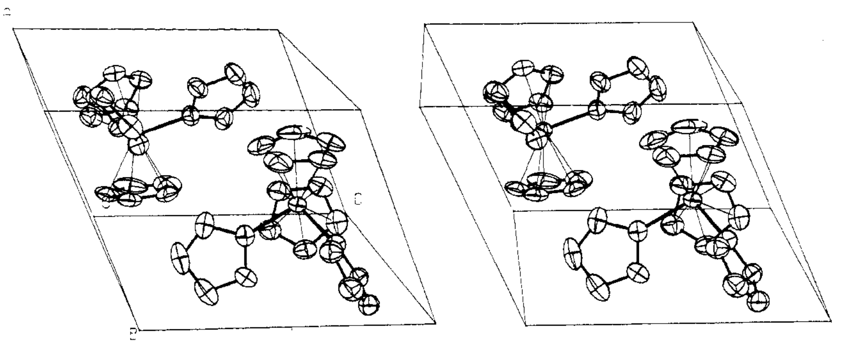


Figure 2. Stereoscopic view of the unit cell contents of $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$.

Table V. Comparison of Bond Lengths (Å) and Angles (Deg) in $(\eta^5\text{-}C_5H_5)_2M(\eta^1\text{-}NC_4H_4)_2$

	M	
bond	Ti	Zr
M-N(1)	2.100 (4)	2.171 (2)
M-N(2)	2.070 (5)	2.167 (2)
M-C(1)	2.386 (7)	2.532 (3)
M-C(2)	2.401 (6)	2.516 (3)
M-C(3)	2.383 (6)	2.506 (3)
M-C(4)	2.380 (5)	2.512 (3)
M-C(5)	2.406 (6)	2.541 (3)
M-C(6)	2.404 (6)	2.528 (3)
M-C(7)	2.382 (4)	2.516 (3)
M-C(8)	2.411 (7)	2.500 (3)
M-C(9)	2.385 (7)	2.519 (3)
M-C(10)	2.404 (7)	2.527 (3)
N(1)-C(11)	1.361 (6)	1.371 (3)
N(1)-C(14)	1.377 (7)	1.373 (3)
C(11)-C(12)	1.356 (8)	1.352 (4)
C(12)-C(13)	1.384 (10)	1.390 (4)
C(13)-C(14)	1.368 (8)	1.361 (4)
N(2)-C(15)	1.377 (8)	1.382 (3)
N(2)-C(18)	1.388 (7)	1.389 (3)
C(15)-C(16)	1.362 (8)	1.343 (4)
C(16)-C(17)	1.410 (9)	1.389 (4)
C(17)-C(18)	1.355 (9)	1.346 (4)

	M	
angle	Ti	Zr
N(1)-M-N(2)	90.4 (2)	95.68 (8)
Cent1-M-Cent2[a]	128.5	128.5
Cent1-M-N(1)	106.5	105.0
Cent1-M-N(2)	108.9	107.8
Cent2-M-N(1)	106.7	106.5
Cent2-M-N(2)	109.1	108.4
C(11)-N(1)-C(14)	105.7 (5)	105.4 (2)
N(1)-C(11)-C(12)	110.4 (6)	110.8 (3)
C(11)-C(12)-C(13)	107.4 (5)	106.6 (2)
C(12)-C(13)-C(14)	106.6 (6)	107.4 (2)
C(13)-C(14)-N(1)	109.8 (6)	109.8 (2)
C(15)-N(2)-C(18)	104.1 (5)	103.9 (2)
N(2)-C(15)-C(16)	112.1 (5)	111.1 (3)
C(15)-C(16)-C(17)	105.5 (6)	107.1 (3)
C(16)-C(17)-C(18)	107.4 (5)	107.3 (2)
C(17)-C(18)-N(2)	110.9 (5)	110.6 (2)
M-N(1)-Cent(η^1-NC_4H_4)[b]	168.5	161.7
M-N(2)-Cent(η^1-NC_4H_4)	163.2	166.9

[a] Cent1 and Cent2 pertain to the centroids of the cyclopentadienyl rings. [b] Cent(η^1-NC_4H_4) is the centroid of the pyrrolyl group.

of the above considerations lead to the conclusion that the Ti–N bond in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$ has a considerable d_π–p_π interaction.

The Ti–C(η^5) bond lengths in the title compound range from 2.380 (7) to 2.411 (7) Å and are slightly larger than those normally found for Ti(IV) compounds[24-26] but agree well with those in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$.[6]

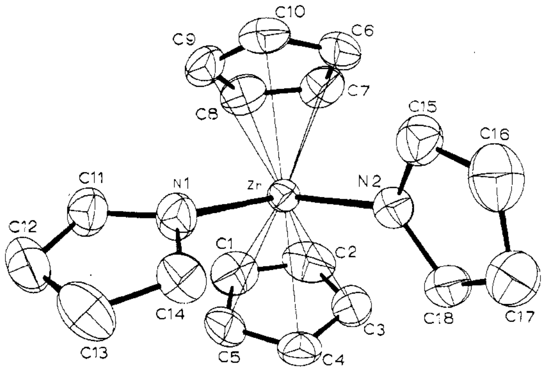


Figure 3. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$.

The centroid(1)–Ti–centroid(2) angle of 128.5° and the N(1)–Ti–N(2) angle of 90.4 (2)° compare rather well with the related values of 129.9 and 86.3° in tetracyclopentadienyltitanium.[6] The remaining angles in the distorted tetrahedral arrangement around the titanium atom in dicyclopentadienyldipyrrolyltitanium (centroid–Ti–N) range from 106.5 to 109.1° and average 107.8°.

The pyrrolyl ligands are each planar to within 0.003 Å.[14] The bond distances within the rings show a tendency for localization of the π-electron density (see VI in the $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$ section), but it is at the border line of significance. The cyclopentadienyl groups are planar to 0.02 Å, and the bond lengths and angles are within the expected range. The unit cell packing diagram (Figure 2) does not reveal any unusual intermolecular contacts.

$(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$. The molecular structure and atom numbering scheme are shown in Figure 3. While tetracyclopentadienyltitanium and dicyclopentadienyldipyrrolyltitanium are similar in overall structure, the zirconium analogues differ obviously from each other. On the other hand, the two $(\eta^5\text{-}C_5H_5)_2M(\eta^1\text{-}NC_4H_4)_2$ (M = Ti, Zr) compounds are closely related, and the arguments for a substantial d_π–p_π contribution to the Ti–N bond also hold for the Zr–N bond. The Zr–N–centroid(σ-pyrrolyl) angles average 164° compared to 131° for Zr–C–centroid(σ-cyclopentadienyl) in $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$, and the Zr–N length, 2.169 (3) Å, is very short as measured against the Zr–C(σ-cyclopentadienyl) length, 2.447 (6) Å.[8] The range of Zr–N lengths extends from 2.081 (4) Å in the Zr(II) compound $[[\eta^5\text{-}C_5(CH_3)_5]_2ZrN_2]_2N_2$[27] to 2.539 (8) Å in $Zr[OC_6H_6CH{=}N(C_2H_5)]_4$.[28] The length in $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$ cor-

---

(24) Epstein, E. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 211.

(25) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

(26) Mattia, J.; Humphrey, M. B.; Rogers, R. D.; Atwood, J. L.; Rausch, M. D. *Inorg. Chem.* **1978**, *17*, 3257.

(27) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351.

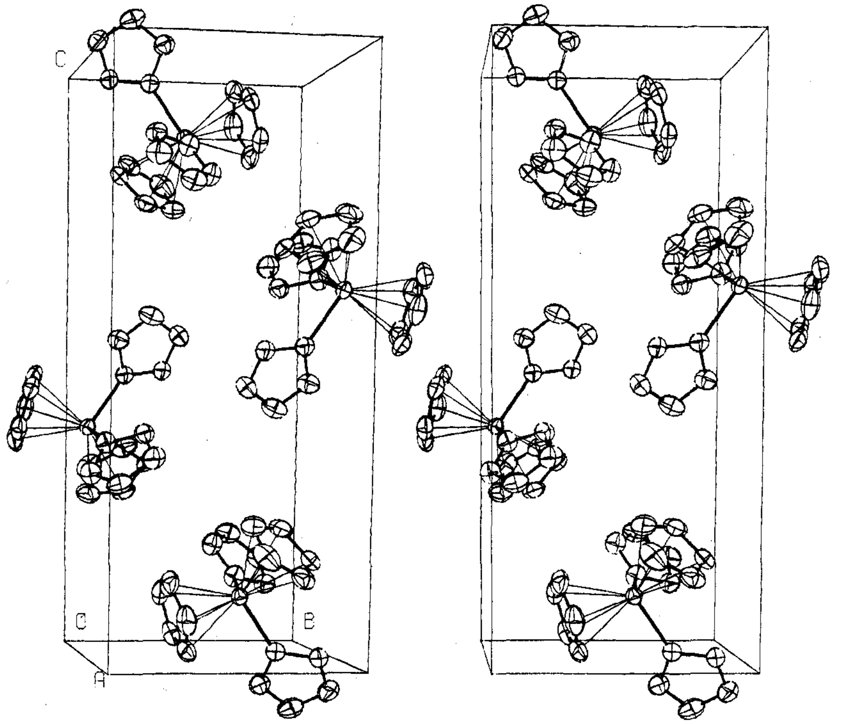


Figure 4. Unit cell packing for $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$.

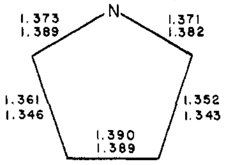
responds most closely to 2.117 (7) Å in $(\eta^5\text{-}C_5H_5)_2Zr(NCO)_2$[29] and 2.182 (2) Å in $Zr(NCS)_4(C_{10}H_8N_2)_2$.[30]

An important difference is that the Zr–N distance is actually *shorter* than the Zr–C(carbonyl) length of 2.187 (4) Å found in $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$.[31] (For the titanium analogues, the Ti–N length is 0.054 Å *longer* than that of Ti–C(carbonyl).)

The Zr–C(η^5) bond lengths range from 2.500 (3) to 2.541 (3) Å and average 2.520 (16) Å. These values are well within the range bounded by $(\eta^5\text{-}C_5H_5)_2Zr[CH(C_6H_5)_2]_2$, 2.513 (15) Å,[32] and $(\eta^5\text{-}C_5H_5)_2Zr[CH(Si(CH_3)_3)_2](C_6H_5)$, 2.543 (14) Å.[33]

The centroid(1)–Zr–centroid(2) angle, 128.5°, is identical with that found in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$, but the N(1)–Zr–N(2) angle, 95.68(8)°, is 5° greater than that for the titanium analogue. The angle is presumably contracted in the latter due to nonbonded repulsions involving the cyclopentadienyl groups.

The pyrrolyl groups are each planar to 0.006 Å. The bond distances show a significant degree of localization of π-electron density (VI, distances are in angstroms), but when all aspects



VI

of the bonding are considered, the major contribution comes from III. The cyclopentadienyl groups are planar to within

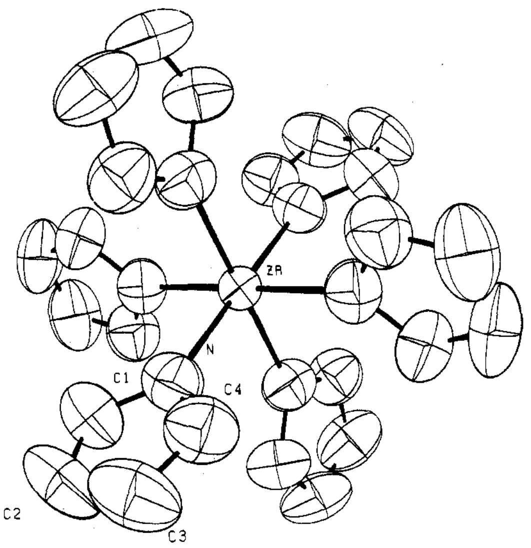


Figure 5. Structure of the $[Zr(\eta^1\text{-}NC_4H_4)_6]^{2-}$ anion.

0.007 Å, and the bond distances and angles are within the expected range. The stereoscopic view of the unit cell contents (Figure 4) does not reveal any unusual intermolecular contacts.

$[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$. The anion, together with the atom numbering scheme, is shown in Figure 5, and the unit cell contents are revealed in Figure 6. The zirconium atom resides on a site with $\bar{3}$ point symmetry, and the sodium atom lies on a threefold axis. Thus, there are two independent THF molecules and one pyrrolyl group in the asymmetric unit.

The geometry about the zirconium atom is octahedral with all N–Zr–N′ angles near 90°. The pyrrolyl ligands are bonded to the zirconium atom precisely as depicted in III: the Zr–N–centroid(σ-pyrrolyl) angle is 179°. The Zr–N bond length, 2.198 (6) Å (Table VI), is significantly larger (Δ = 0.029 (7) Å = 4.1σ) than the 2.169 (3) Å length found in $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$. On the basis of the electron count, one would expect the Zr–N bond distance to be shorter in $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$. Since the opposite is found,

---

(28) Bradley, D. C.; Hursthouse, M. B.; Rendall, I. F. *Chem. Commun.* **1970**, 358.

(29) Work by: Kossiakoff, A. A.; Wood, R. H.; Burmeister, J. L., referenced in ref 27.

(30) Peterson, E. J.; VonDreele, R. B.; Brown, T. M. *Inorg. Chem.* **1976**, *15*, 309.

(31) Atwood, J. L.; Rogers, R. D.; Floriani, C., unpublished results.

(32) Atwood, J. L.; Barker, G. K.; Holton, J.; Hunter, W. E.; Lappert, M. F.; Pearce, R. *J. Am. Chem. Soc.* **1977**, *99*, 6645.

(33) Jeffery, J.; Lappert, M. F.; Luong-Thi, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081.

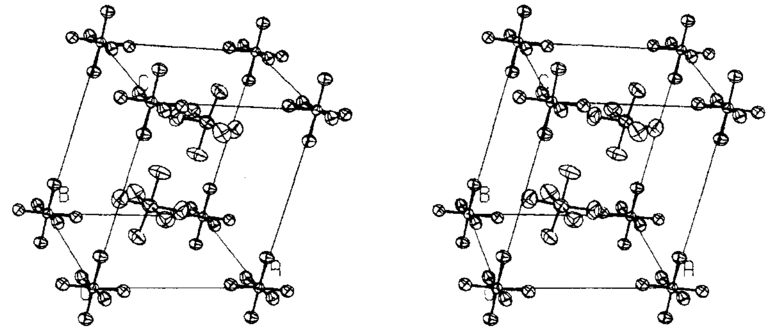


Figure 6. Stereographic view of the unit cell packing for $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$. For clarity only the inner coordination spheres of the zirconium and sodium atoms are shown. Those containing the zirconium atoms are at the corners of the cell.

Table VI. Bond Distances (Å) and Angles (Deg) for $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$

	Distances		
Zr–N	2.198 (6)	O(1)–C(5)	1.42 (1)
N–C(1)	1.383 (10)	C(5)–C(6)	1.45 (2)
C(1)–C(2)	1.375 (12)	C(6)–C(7)	1.43 (2)
C(2)–C(3)	1.420 (14)	C(7)–C(8)	1.49 (2)
C(3)–C(4)	1.333 (12)	C(8)–O(1)	1.40 (2)
C(4)–N	1.375 (10)	O(2)–C(9)	1.31 (2)
Na–O(1)	2.409 (8)	C(9)–C(10)	1.52 (3)
Na–O(2)	2.444 (8)	C(10)–C(11)	1.23 (2)
		C(11)–C(12)	1.49 (3)
		C(12)–O(2)	1.30 (2)
	Angles		
Zr–N–Cent[a]	179.2	C(8)–O(1)–C(5)	105 (1)
N–Zr–N′[b]	90.0 (2)	O(1)–C(5)–C(6)	107 (1)
N–Zr–N″	180.0	C(5)–C(6)–C(7)	100 (2)
Zr–N–C(1)	127.3 (6)	C(6)–C(7)–C(8)	98 (2)
Zr–N–C(4)	127.7 (6)	C(7)–C(8)–O(1)	105 (2)
C(4)–N(1)–C(1)	105.0 (7)	C(9)–O(2)–C(12)	96 (1)
N(1)–C(1)–C(2)	110.2 (9)	O(2)–C(9)–C(10)	107 (2)
C(1)–C(2)–C(3)	106.0 (9)	C(9)–C(10)–C(11)	85 (3)
C(2)–C(3)–C(4)	107.0 (9)	C(10)–C(11)–C(12)	95 (2)
C(3)–C(4)–N(1)	111.8 (9)	C(11)–C(12)–O(2)	107 (2)
O(1)–Na–O(2)	93.5 (3)	O(2)–Na–O(2)′	89.8 (3)
O(1)–Na–O(1)′	90.5 (3)	O(1)–Na–O(2)″	175.0 (3)
O(1)–Na–O(2)′	86.5 (3)		

[a] Cent refers to the centroid of the pyrrolyl ring. [b] Primed atoms are related to those in Table IV by either a $\bar{3}$ (N) or threefold (O) operation.

steric effects associated with the placement of six rather bulky σ-bonded ligands about the zirconium atom must be important.

The sodium atom also exists in a regular octahedral environment with O–Na–O angles ranging from 86 to 93°. The two independent Na···O approaches are 2.409 (8) and 2.444 (8) Å. The complex contains 62% THF by weight; this is the highest THF content of any solid coordination compound to our knowledge.[34]

The pyrrolyl ligand is planar to within 0.009 Å. Although the bond lengths are not of high accuracy, they do show the localization discussed previously. Because of the large thermal parameters and probable disorder of the THF molecules, no meaningful parameters can be derived for them.

Conclusions

The interaction of pyrrolylsodium with dichlorodicyclopentadienylzirconium(IV) in THF produces the expected result at room temperature: dicyclopentadienyldipyrrolylzirconium(IV). However, at reflux temperature the cyclopentadienyl ligands are removed, and the hexapyrrolylzirconium(IV) anion results. This unusual behavior has important synthetic ramifications which are currently under investigation.

In each of the three compounds under discussion, very short metal–nitrogen bonds have been observed. This observation together with the overall geometry of the pyrrolyl linkage lends credence to a bonding scheme which involves an appreciable d_π–p_π interaction.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$, 11077-90-0; $(\eta^5\text{-}C_5H_5)_2Zr(\eta^1\text{-}NC_4H_4)_2$, 73587-39-0; $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$ complex, 73587-42-5; $(\eta^5\text{-}C_5H_5)_2TiCl_2$, 1271-19-8; $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, 1291-32-3; $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$ salt, 73587-46-9.

Supplementary Material Available: Listings of structure factor amplitudes and complete best planes results for all three structures (34 pages). Ordering information is given on any current masthead page.

---

(34) The compound $[Li(THF)_4]_2[U(C_2B_9H_{11})_2Cl_2]$ contains 50% by weight THF: Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769.

(35) Professor T. A. Albright has pointed out that the Ti–N bond lengths (which differ by 0.030 (6) Å, 5σ) are in accord with the predictions of Lauher and Hoffmann: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.