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Crystal structure of (η^5-2,4-dimethylpentadienyl)[η^2-*rel*-(a*R*)-a-[[(1*R*,5*E*)-5-[(1,1-dimethylethyl)imino]-1,3-dimethyl-2-cyclopenten-1-yl]methyl]-*N*-(1-methylethyl)benzenemethanaminato-κN][2-(isocyano-κC)-2-methylpropane]zirconium, $Zr(C_7H_{11})(C_{22}H_{33}N_2)(C_4H_9NC)$

R. D. Ernst*, V. Kulsomphob and A. M. Arif

University of Utah, Department of Chemistry, 315 S. 1400 E., Rm. 2020, Salt Lake City, Utah 84112-0850, U.S.A.

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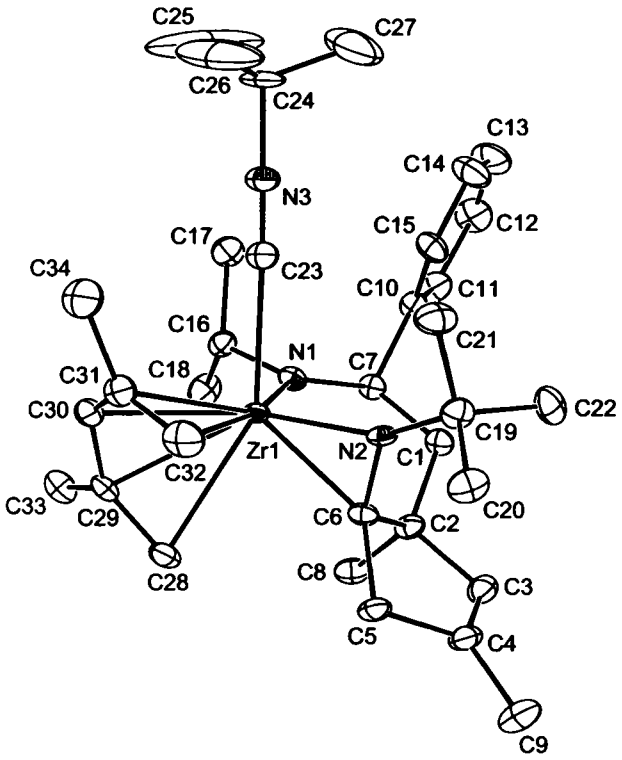

Abstract

$C_{34}H_{53}N_3Zr$, triclinic, $P\bar{1}$ (no. 2), a = 10.752(4) Å, b = 12.245(3) Å, c = 12.720(5) Å, α = 82.60(2)°, β = 82.88(3)°, γ = 86.66(2)°, V = 1646.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.060, $wR_{ref}(F^2)$ = 0.077, T = 173 K.

Source of material

The compound is readily prepared [1] by the low temperature reaction of a slight excess of *t*-butyl isocyanide with the coupling product formed between the $Zr(2,4\text{-}C_7H_{11})_2$ fragment (C_7H_{11} = dimethylpentadienyl) and $C_6H_5C(H)N(i\text{-}C_3H_7)$ [2]. Crystallization may then be achieved by cooling concentrated solutions in ether to –30°. All manipulations were carried out under a nitrogen atmosphere.

Experimental details

The methyl groups of the uncoupled isocyanide ligand were subject to a somewhat severe disorder. Electron density maps revealed this to be a result of rotational rather than positional disorder, so a single location was assigned to each carbon atom. The positional parameters for the hydrogen atoms on the uncoupled pentadienyl ligand's metal-bound carbon atoms were refined in order to provide more detailed information on their locations relative to the dienyl plane. Positional parameters for key hydrogen atoms on the coupled fragment composed of the imine and other pentadienyl units were also refined, in order to confirm that no hydrogen atom transfers had occurred, while the remaining hydrogen atoms were placed in fixed locations.

Discussion

The compound incorporates single 2,4-dimethylpentadienyl and *t*-butyl isocyanide ligands, along with a more complicated ligand derived from a second 2,4-dimethylpentadienyl group, an imine ($C_6H_5CH{=}N(i\text{-}C_3H_7)$), and a second *t*-butyl isocyanide. A similar ligand also was found in a titanium cyclopentadienyl complex [3]. The present structure is composed primarily of single bonds between the nonmetallic atoms, with the exceptions being the delocalized pentadienyl C—C bonds (from C28 to C32), the isocyanide triple bond (between C23 and N3, 1.143(7) Å), the C3=C4 double bond (1.339(8) Å), the C6—N2 bond (1.422(6) Å), and the bonds in the phenyl ring.

Of greatest interest is the nature of the C6—N2 bond, and its interaction with the metal center. Given that the C6—N2 bond is only slightly shorter than the C—N single bonds in the structure, which range from 1.457(7) Å – 1.479(6) Å, it seems most appropriate to regard C6—N2 also as a single bond. This would then require a Zr—C6 single bond, and ideally a Zr—N2 single bond. However, the planar environment about N2 indicates significant π donation from N2 to Zr, which would lead to some Zr—N multiple bonding. The environment about N1 also indicates a π donor interaction, and similar Zr—N bond lengths are observed (d(Zr—N1) = 2.069(4) Å, d(Zr—N2) = 2.043(4) Å). These π donations allow the complex to achieve the favored 18 electron configuration for the formal Zr(IV) center; in contrast, were one to regard the interaction of the C6–N2 fragment with the metal as simple π coordination of a C6=N2 bond, one would have a Zr(II) complex with only a 16 electron configuration. The complex therefore becomes a relatively rare example of a higher valent metal pentadienyl compound [4], and this formulation is consistent with the presence of a short Zr—C30 bond (2.525(6) Å), with the bonds to subsequent atoms becoming somewhat longer (d(Zr—C29) = 2.577(5) Å, d(Zr—C31) = 2.691(5) Å, d(Zr—C28) = 2.552(6) Å, d(Zr—C32) = 2.768(6) Å). Also consistent is the short-long-long-short pattern of dienyl C—C bonds (1.390(9) Å, 1.434(8) Å, 1.431(9) Å, and 1.358(9) Å, respectively, from C28 to C32).

* Correspondence author (e-mail: ernst@chem.utah.edu)

Table 1. Data collection and handling.

Crystal:	orange prism, size 0.27 × 0.42 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.511 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, $\theta/2\theta$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6105, 5770
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\,\sigma(I_{obs})$, 5198
$N(param)_{refined}$:	377
Programs:	SIR97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.358(6)	0.063(6)	0.355(5)	0.05
H(1B)	2*i*	0.300(6)	0.006(5)	0.460(5)	0.05
H(3)	2*i*	0.455(6)	0.094(6)	0.564(5)	0.05
H(5A)	2*i*	0.474(6)	0.404(6)	0.399(5)	0.05
H(5B)	2*i*	0.340(6)	0.388(6)	0.506(5)	0.05
H(7)	2*i*	0.107(6)	0.047(6)	0.415(5)	0.05
H(8A)	2*i*	0.1781	0.1289	0.5849	0.05
H(8B)	2*i*	0.2087	0.2523	0.5761	0.05
H(8C)	2*i*	0.1258	0.2133	0.4977	0.05
H(9A)	2*i*	0.5985	0.3634	0.5586	0.05
H(9B)	2*i*	0.5562	0.2742	0.6522	0.05
H(9C)	2*i*	0.6529	0.2433	0.5585	0.05
H(11)	2*i*	0.0816	−0.1375	0.3811	0.05
H(12)	2*i*	0.1210	−0.2806	0.2730	0.05
H(13)	2*i*	0.2436	−0.2535	0.1107	0.05
H(14)	2*i*	0.3368	−0.0849	0.0556	0.05
H(15)	2*i*	0.3059	0.0556	0.1650	0.05
H(16)	2*i*	−0.0077	0.2570	0.2437	0.05
H(17A)	2*i*	−0.1077	0.1271	0.1666	0.05
H(17B)	2*i*	0.0295	0.1436	0.1153	0.05
H(17C)	2*i*	−0.0025	0.0408	0.1969	0.05
H(18A)	2*i*	−0.0816	0.1955	0.4220	0.05
H(18B)	2*i*	−0.1781	0.1765	0.3458	0.05
H(18C)	2*i*	−0.0932	0.0788	0.3900	0.05
H(20A)	2*i*	0.7000	0.3194	0.2221	0.05
H(20B)	2*i*	0.5887	0.4059	0.2237	0.05
H(20C)	2*i*	0.6148	0.3321	0.3279	0.05
H(21A)	2*i*	0.5006	0.3282	0.0809	0.05
H(21B)	2*i*	0.6181	0.2484	0.0755	0.05
H(21C)	2*i*	0.4851	0.2021	0.0885	0.05
H(22A)	2*i*	0.5318	0.0788	0.2510	0.05
H(22B)	2*i*	0.6661	0.1230	0.2295	0.05
H(22C)	2*i*	0.5888	0.1269	0.3405	0.05
H(25A)	2*i*	0.1399	0.1900	−0.2192	0.05
H(25B)	2*i*	0.1054	0.1482	−0.0993	0.05
H(25C)	2*i*	0.0852	0.2721	−0.1403	0.05
H(26A)	2*i*	0.2476	0.3849	−0.1906	0.05
H(26B)	2*i*	0.3858	0.3426	−0.1852	0.05
H(26C)	2*i*	0.3113	0.3087	−0.2719	0.05
H(27A)	2*i*	0.4272	0.1522	−0.1247	0.05
H(27B)	2*i*	0.3165	0.0747	−0.0897	0.05
H(27C)	2*i*	0.3509	0.1168	−0.2096	0.05
H(28A)	2*i*	0.225(6)	0.495(6)	0.368(5)	0.05
H(28B)	2*i*	0.125(6)	0.439(6)	0.442(5)	0.05
H(30)	2*i*	0.024(6)	0.484(6)	0.155(5)	0.05
H(32A)	2*i*	0.388(6)	0.525(6)	0.113(5)	0.05
H(32B)	2*i*	0.342(6)	0.518(6)	0.228(5)	0.05
H(33A)	2*i*	−0.1285	0.4579	0.2860	0.05
H(33B)	2*i*	−0.0865	0.3757	0.3796	0.05
H(33C)	2*i*	−0.1121	0.4994	0.3935	0.05
H(34A)	2*i*	0.1126	0.5283	−0.0049	0.05
H(34B)	2*i*	0.2255	0.6043	−0.0191	0.05
H(34C)	2*i*	0.2484	0.4787	−0.0241	0.05

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr(1)	2*i*	0.21882(5)	0.32028(4)	0.25158(4)	0.0241(2)	0.0128(2)	0.0139(2)	−0.0017(2)	−0.0039(2)	−0.0033(2)
N(1)	2*i*	0.1296(4)	0.1736(3)	0.2977(3)	0.019(2)	0.020(2)	0.017(2)	−0.004(2)	0.004(2)	−0.003(2)
N(2)	2*i*	0.3983(4)	0.2660(3)	0.2729(3)	0.028(2)	0.016(2)	0.010(2)	−0.006(2)	−0.003(2)	−0.001(2)
N(3)	2*i*	0.2539(5)	0.2550(4)	−0.0175(3)	0.039(2)	0.024(2)	0.018(2)	−0.003(2)	−0.004(2)	−0.005(2)
C(1)	2*i*	0.2948(5)	0.0720(4)	0.4037(4)	0.027(3)	0.016(2)	0.024(2)	−0.004(2)	−0.002(2)	−0.001(2)
C(2)	2*i*	0.3118(5)	0.1731(4)	0.4603(4)	0.031(3)	0.019(2)	0.017(2)	−0.005(2)	−0.006(2)	0.001(2)
C(3)	2*i*	0.4233(5)	0.1641(5)	0.5241(4)	0.032(3)	0.028(3)	0.024(2)	0.000(2)	−0.009(2)	−0.001(2)
C(4)	2*i*	0.4763(5)	0.2611(5)	0.5196(4)	0.031(3)	0.035(3)	0.022(2)	−0.003(2)	−0.009(2)	−0.008(2)
C(5)	2*i*	0.4093(5)	0.3484(4)	0.4482(4)	0.031(3)	0.025(2)	0.023(2)	−0.006(2)	−0.010(2)	−0.007(2)
C(6)	2*i*	0.3443(5)	0.2786(4)	0.3788(4)	0.025(2)	0.016(2)	0.019(2)	−0.006(2)	−0.002(2)	−0.005(2)
C(7)	2*i*	0.1721(5)	0.0674(4)	0.3544(4)	0.025(2)	0.015(2)	0.019(2)	−0.005(2)	−0.000(2)	0.001(2)
C(8)	2*i*	0.1952(6)	0.1939(5)	0.5370(4)	0.035(3)	0.033(3)	0.020(2)	−0.009(2)	−0.001(2)	−0.004(2)
C(9)	2*i*	0.5804(6)	0.2880(6)	0.5775(5)	0.045(3)	0.049(4)	0.037(3)	−0.011(3)	−0.020(2)	−0.005(3)
C(10)	2*i*	0.1907(5)	−0.0256(4)	0.2832(4)	0.026(2)	0.015(2)	0.029(3)	−0.005(2)	−0.008(2)	−0.002(2)
C(11)	2*i*	0.1347(6)	−0.1264(5)	0.3155(5)	0.043(3)	0.021(3)	0.033(3)	−0.012(2)	−0.010(2)	0.003(2)
C(12)	2*i*	0.1574(7)	−0.2114(5)	0.2502(5)	0.061(4)	0.015(2)	0.050(3)	−0.010(3)	−0.014(3)	−0.003(2)
C(13)	2*i*	0.2305(7)	−0.1959(5)	0.1549(5)	0.071(4)	0.023(3)	0.046(3)	−0.001(3)	−0.009(3)	−0.015(2)
C(14)	2*i*	0.2857(7)	−0.0962(5)	0.1223(5)	0.063(4)	0.027(3)	0.034(3)	0.004(3)	0.004(3)	−0.010(2)
C(15)	2*i*	0.2663(6)	−0.0122(4)	0.1873(5)	0.035(3)	0.018(2)	0.033(3)	−0.001(2)	0.002(2)	−0.006(2)
C(16)	2*i*	0.0016(5)	0.1812(4)	0.2702(4)	0.027(3)	0.021(2)	0.024(2)	−0.004(2)	−0.007(2)	−0.001(2)
C(17)	2*i*	−0.0221(5)	0.1171(5)	0.1785(5)	0.025(3)	0.036(3)	0.040(3)	−0.006(2)	−0.009(2)	−0.011(2)
C(18)	2*i*	−0.0972(6)	0.1556(6)	0.3661(5)	0.028(3)	0.047(3)	0.033(3)	−0.004(2)	−0.003(3)	0.001(3)
C(19)	2*i*	0.5301(5)	0.2481(4)	0.2279(4)	0.023(2)	0.027(3)	0.030(3)	−0.007(2)	−0.004(2)	−0.005(2)
C(20)	2*i*	0.6167(5)	0.3347(5)	0.2528(5)	0.030(3)	0.037(3)	0.030(3)	−0.013(2)	−0.003(2)	−0.002(2)
C(21)	2*i*	0.5339(6)	0.2576(6)	0.1068(5)	0.028(3)	0.054(3)	0.027(3)	−0.008(3)	0.004(2)	−0.012(3)
C(22)	2*i*	0.5844(5)	0.1333(5)	0.2659(5)	0.020(3)	0.032(3)	0.048(3)	−0.001(2)	0.002(2)	−0.010(3)
C(23)	2*i*	0.2482(5)	0.2773(4)	0.0675(4)	0.036(3)	0.018(2)	0.020(2)	−0.004(2)	−0.004(2)	−0.000(2)
C(24)	2*i*	0.2632(7)	0.2279(5)	−0.1279(4)	0.060(4)	0.042(3)	0.012(2)	−0.008(2)	−0.002(3)	−0.014(2)
C(25)	2*i*	0.138(1)	0.208(1)	−0.1484(8)	0.126(7)	0.41(1)	0.059(4)	−0.149(7)	0.032(5)	−0.120(5)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(26)	2*i*	0.306(2)	0.3245(9)	−0.2003(6)	0.25(1)	0.076(6)	0.021(4)	−0.040(8)	0.011(6)	−0.014(4)
C(27)	2*i*	0.346(2)	0.135(1)	−0.1389(8)	0.43(2)	0.180(7)	0.042(5)	0.225(7)	−0.069(7)	−0.054(5)
C(28)	2*i*	0.1422(6)	0.4627(5)	0.3776(4)	0.053(3)	0.023(3)	0.025(3)	0.008(3)	−0.009(2)	−0.011(2)
C(29)	2*i*	0.0543(6)	0.4710(4)	0.3052(4)	0.039(3)	0.019(2)	0.029(3)	0.008(2)	−0.007(2)	−0.012(2)
C(30)	2*i*	0.0866(6)	0.4887(4)	0.1917(4)	0.044(3)	0.017(2)	0.029(3)	0.004(2)	−0.012(2)	−0.006(2)
C(31)	2*i*	0.2028(6)	0.5152(4)	0.1283(5)	0.053(3)	0.011(2)	0.030(3)	−0.001(2)	−0.014(2)	0.001(2)
C(32)	2*i*	0.3173(6)	0.5196(5)	0.1620(5)	0.055(4)	0.021(3)	0.035(3)	−0.010(3)	−0.004(3)	0.000(2)
C(33)	2*i*	−0.0807(6)	0.4490(6)	0.3447(5)	0.044(3)	0.043(3)	0.042(3)	0.014(3)	−0.004(3)	−0.018(3)
C(34)	2*i*	0.1968(7)	0.5334(5)	0.0089(5)	0.070(4)	0.026(3)	0.033(3)	−0.002(3)	−0.009(3)	0.006(3)

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