Crystal and Molecular Structure of (Tri-*tert*-butyl-η^5-cyclopentadienyl)-(1,2,4-tri-*tert*-butyl-η^3-cyclopentenyl)nickel

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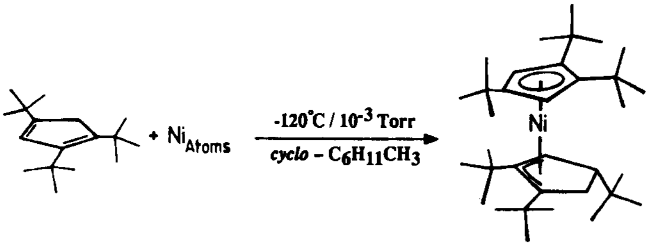
(Tri-*tert*-butyl-η^5-cyclopentadienyl)(1,2,4-tri-*tert*-butyl-η^3-cyclopentenyl)nickel (**1**) is accessible by the metal vapor route. The molecule adopts a slipped sandwich structure in the solid state with the nickel atom η^5-η^3-coordinated to the five-membered rings. Its ^{13}C-NMR data are reported together with data on (*tert*-butyl-η^5-cyclopentadienyl)(*tert*-butyl-η^3-cyclopentenyl)nickel **2** and (di-*tert*-butyl-η^5-cyclopentadienyl)(di-*tert*-butyl-η^3-cyclopentenyl)nickel **3**.

Highly substituted cyclopentadienyl rings have a great potential as ligands in organometallic complexes. The best example is the pentamethylcyclopentadienyl ring ligand (Cp*). Nevertheless, other substituted cyclopentadienyl ring systems which offer a combination of enhanced steric and electronic effects gain increased importance in the synthetis of new organometallic compounds[1]. Therefore, it is desirable to characterize the structures of the complexes in order to obtain information about the coordination of these ligands. To our knowledge no crystal structure on compounds containing the bulky 1,2,4-tri-*tert*-butyl-cyclopentadienyl ligand (tBu$_3$Cp) has been described so far. In our studies of the complexation of substituted cyclopentadienes towards various naked metal atoms we have reported π complexation of tBu$_3$Cp with nickel atoms[2] (Scheme 1). With this highly crowded ligand no cluster formation could be observed as it was found for the lower substituted *mono-* and *di-tert*-butylcyclopentadienes[2]. From the spectroscopic data (^{1}H NMR, MS) a η^5-η^3 coordination mode of the complexed nickel atom with a sandwich-type molecular structure for **1** has been assumed[2]. The results of an X-ray structure determination are reported here which confirm the proposed structure in the solid state.

Scheme 1. Synthesis of **1** by the metal vapor route



1

Compound **1** cyrstallizes from a concentrated toluene/pentane solution as red cubes at −30°C. The molecule adopts a slipped sandwich structure in which one planar tBu$_3$Cp ligand is η^5-coordinated whereas the second ring is ligated in an allylic fashion to the carbon atoms C18, C19, and C20 leaving C21 and C22 uncomplexed which is reflected in longer bond distances to C18 and C20 (Figure 1). This coordination mode has been suggested and is well-known for nickel[3]. To our knowledge we report here for the first time on a solid-state structure characterization of a compound containing this binding mode for the five-membered cyclopentenyl ring[4].

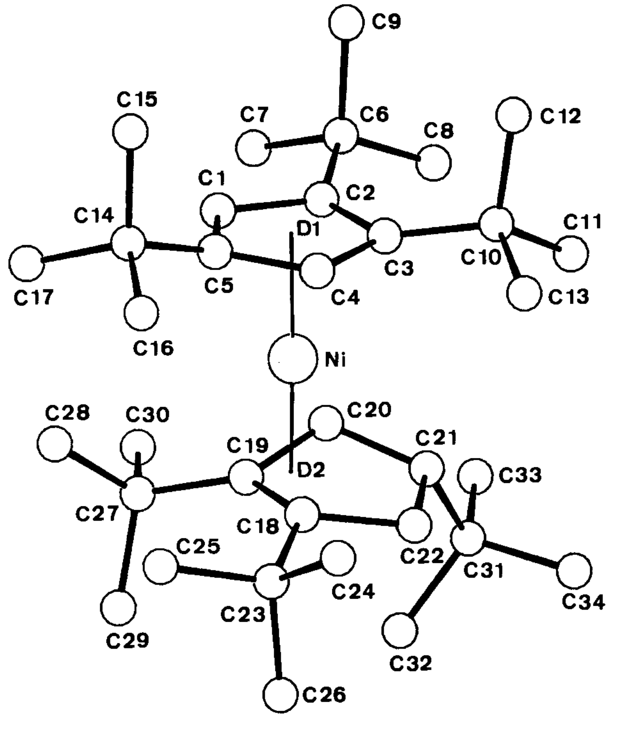


Fig 1. Molecular structure of **1**. Selected distances [Å]: Ni−D1 1.803(3), Ni−D2 1.741(4), Ni−C18 2.036(3), Ni−C19 1.971(3), Ni−C20 2.024(4), C18−C19 1.451(5), C18−C22 1.519(5), C19−C20 1.443(5), C20−C21 1.473(5), C21−C22 1.538(5); angle: D2−Ni−D1 172.9(1)°; deviation from plane C1,C2,C3,C4,C5: C6 = 9.8°, C10 = 13.1°, C14 = 18.1°, deviation from plane C18,C19,C20: C23 = 2.6°, C27 = 6.1°, deviation from plane C18,C20,C21,C22 : C31 = 53.8°

The allylic ring system in **1** shows a bending of 15.7° against the plane of the η^5-coordinated tBu$_3$Cp ring and is folded along the C18−C20 axis against the plane C18,C20,C21,C22 (max. deviation from planarity 0.04Å by 25.3°. The carbon atoms of all six *tert-*

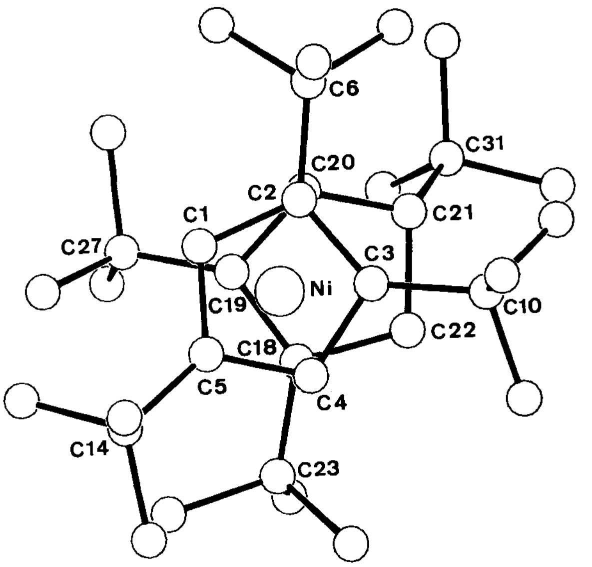
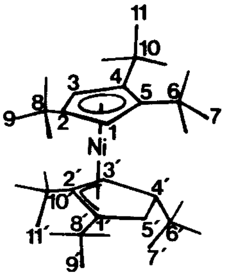


Figure 2. Projection of the molecular structure of **1** onto the plane of the η^5-*t*Bu$_3$Cp ring

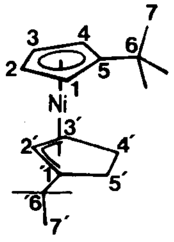
butyl groups are bent away from the nickel center with C14 at the η^5-*t*Bu$_3$Cp ring showing the largest tilt. This is due to a steric interaction with the *tert*-butyl groups at C18 and C19 of the allylic ring system. For the trimethylsilyl ligands in 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)ferrocene an angle of 12.5° has been found[1k]. C31 is bent out of the plane C18,C20,C21,C22 by 53.8°. It is interesting to note that the five-membered rings adopt a staggered conformation (Figure 2). This contradicts our earlier assumption of **1** having an eclipsed conformation[2] as found in the above mentioned ferrocene derivative where virtually eclipsed cyclopentadienyl rings and two eclipsed trimethylsilyl groups are found in the solid state. The observed geometry of **1** may be attributed to the strong deformation of the η^3-bonded ring system and the interaction of the *tert*-butyl groups. This is supported by the significant longer Ni–η^5-*t*Bu$_3$Cp distance [Ni–D1 = 1.803(3) Å] compared to hexakis(trimethylsilyl)ferrocene (1.686Å)[1k]. The bending of the atoms C18, C20, C21, C22, and C31 leaves the nickel atom accessible to attack. This explains the higher sensitivity of **1** e.g. to oxygen as compared to the less bulkier mono- and di-*tert*-butyl-substituted homologs **2** and **3**[2].

The ^{13}C-NMR data of the three new nickel complexes **1**, **2**, and **3** are reported in Table 1 for completion. The data are consistent with the earlier derived structures[2] and will not be discussed in detail here. Nevertheless, it appears noteworthy that the close resemblance of the chemical shift and the coupling constant for C-3′

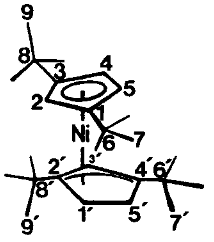
Table 1. ^{13}C{^{1}H}-NMR spectroscopic data of **1**, **2**, and **3** (δ, [D$_8$]toluene, 30°C)



1



2



3

Comp.			Ring C		
	C-1[a]	C-2	C-3	C-4	C-5
1	86.7 d (d)[b] [93.0 (s)]	119.8 (s)[b] [112.1 (s)]	86.1 d (d)[b] **[63.8, d, 157]**	115.8 (s)[b] [52.1 (d)]	114.0 (s)[b] [39.5 (t)]
2	85.0 d (q)[b] [97.5 (s)]	87.2 d (q)[b] [82.0 (d)]	89.0 d (q) **[59.7, d, 163]**	85.7 d (q)[b] [31.7 (t)]	120.5 (s) s. C-4′
3[c]	121.8 (s)[b] [32.7 (t)]	81.4 (d)[f] **[93.87** (s)][f]	118.7 (s)[b] [79.0 (d)][f]	85.3 (d) **[93.85** (s)][b]	82.8 (d) [32.2 (t)][b]
Comp.			*tert*-Butyl		
	C-6[a]	C-7	C-8	C-9	C-10
1	34.8 (s)[d] [33.7 (s)]	34.4 (quint)[e] [27.6 q (hex)]	33.5 (s)[d] [32.9 (s)]	34.2 q (quint)[e] [32.0 q (quint)]	33.6 (s)[d] [32.4 (s)]
1	C-11 32.9 q (quint) [32.0 q (quint)]				
2	31.2 8s) [33.8 (s)]	32.3 (q) [30.0 (q)]			
3	31.0 (s)	32.8 (q)	31.7 (s)	32.2 (q)	

[a] Shifts and ^1J(CH) (±2 Hz) in brackets denote equally numbered ring positions (e.g. 2,2′) at the η^3- and η^5-bonded rings. — [b] Arbitrary assignment with chemically equivalent ring positions is possible. — [c] Measured at –30°C. — [d]–[f] Arbitrary assignment.

Table 2. Data concerning the crystal structure determination of **1**

Molecular formula $C_{34}H_{60}Ni$, molecular weight 527.6 g·mol^{-1}, crystal color dark red, crystal size 0.32x0.39x0.39 mm, a = 17.287(1), b = 11.555(1), c = 17.681(1) Å, β = 115.37(1)°, V = 3191.1 Å^3, d_{cal}= 1.10 g·cm^{-3}, μ = 9.60 cm^{-1}, Cu–K_α radiation, λ = 1.54178 Å, F(000) = 1168 *e*, Z = 4, crystal system monoclinic, space group $P2_1/a$ [No.14], Enraf–Nonius CAD4 diffractometer, scan mode ω–2θ, $[(\sin\theta)/\lambda]_{max}$ = 0.63 Å^{-1}, 7091 measured reflections [±*h*,+*k*,+*l*], 6548 independent reflections, 5532 observed reflections [I >2σ(I)] for 316 refined parameters, structure solved by heavy atom method, H atom positions calculated and kept fixed in the final refinement stages with thermal parameters = 0.08 Å^2, *R* = 0.067, R_w = 0.087 [w=1/σ^2(Fo)], residual electron density 1.06 *e*Å^{-3}. Final atomic coordinates are given in Table 2

Table 3. Atomic coordinates and thermal parameters [Å^2] for **1**. $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$

Atom	x	y	z	U_{eq}
Ni	0.4884(1)	0.0178(1)	0.2358(1)	0.037(1)
C1	0.4346(2)	0.1096(2)	0.1168(2)	0.043(2)
C2	0.4790(2)	0.1880(2)	0.1857(2)	0.040(2)
C3	0.4338(2)	0.1843(2)	0.2379(2)	0.039(2)
C4	0.3671(2)	0.1012(2)	0.2002(2)	0.042(2)
C5	0.3643(2)	0.0585(2)	0.1241(2)	0.041(2)
C6	0.5456(2)	0.2707(3)	0.1793(2)	0.052(2)
C7	0.5912(3)	0.2152(4)	0.1312(3)	0.092(4)
C8	0.6173(3)	0.3079(5)	0.2590(3)	0.107(5)
C9	0.4995(3)	0.3764(4)	0.1319(4)	0.137(6)
C10	0.4317(2)	0.2627(3)	0.3077(2)	0.054(2)
C11	0.5168(3)	0.2935(6)	0.3785(3)	0.125(5)
C12	0.3851(5)	0.3721(4)	0.2679(3)	0.136(7)
C13	0.3814(3)	0.2060(4)	0.3498(3)	0.094(5)
C14	0.2864(2)	0.0041(3)	0.0539(2)	0.053(2)
C15	0.2323(2)	0.1042(3)	0.0013(2)	0.077(3)
C16	0.2315(3)	−0.0629(4)	0.0864(3)	0.089(3)
C17	0.3119(3)	−0.0733(4)	−0.0015(3)	0.086(3)
C18	0.5182(2)	−0.1232(2)	0.3121(2)	0.045(2)
C19	0.5684(2)	−0.1140(3)	0.2644(2)	0.048(2)
C20	0.6158(2)	−0.0096(3)	0.2998(2)	0.064(3)
C21	0.6340(2)	0.0110(3)	0.3880(2)	0.053(2)
C22	0.5613(2)	−0.0587(4)	0.3945(3)	0.069(3)
C23	0.4551(2)	−0.2153(3)	0.3139(2)	0.063(3)
C24	0.3906(3)	−0.1631(4)	0.3410(3)	0.100(5)
C25	0.4015(3)	−0.2736(4)	0.2273(3)	0.102(4)
C26	0.5037(3)	−0.3134(4)	0.3739(3)	0.091(4)
C27	0.5844(3)	−0.1925(3)	0.2024(2)	0.072(3)
C28	0.5132(4)	−0.2042(6)	0.1186(3)	0.150(6)
C29	0.6202(3)	−0.3093(4)	0.2425(3)	0.086(4)
C30	0.6598(4)	−0.1394(5)	0.1883(4)	0.128(7)
C31	0.7239(2)	−0.0193(3)	0.4559(2)	0.054(2)
C32	0.7435(3)	−0.1464(4)	0.4534(3)	0.104(4)
C33	0.7897(3)	0.0534(5)	0.4418(3)	0.097(4)
C34	0.7295(3)	0.0133(4)	0.5409(3)	0.092(4)

in **1** and **2** compared to that of *C-2′* or *C-4′* in **3** (bold-face numbers) show a structure for **1** with both *tert*-butyl groups in collateral position to be most likely even in solution and rules out an η^3 coordination with a 1,3-location of the *tert*-butyl groups in the η^3 ligand system of **1** as found in **3**.

Experimental

Compounds **1**, **2**, and **3** were synthesized by vaporization of nickel atoms into a cooled solution of the substituted cyclopentadiene in methylcyclohexane by using a rotating metal vapor apparatus as already reported[2]. Deep red-colored single crystals of **1** suitable for X-ray diffraction were obtained from a solution of toluene/pentane (3:1) by cooling to −30 °C over a period of several months. For further spectroscopic data of **1**, **2**, and **3** see ref.[1j]. — ^{13}C-NMR: in [D_8]toluene, Bruker AM 300 (75 MHz) instrument, δ scale relative to TMS with the ^{13}C signals of the solvent as internal standard. — Elemental analysis: Mikroanalytisches Laboratorium Dornis & Kolbe, D-4330 Mülheim/Ruhr, FRG.

1: $C_{34}H_{60}Ni$ (527.6)
Calcd. C 77.31 H 11.56 Ni 11.12
Found C 77.38 H 11.02 Ni 11.54

Crystal Structure Determination of **1**[5]: See Tables 2 and 3.

CAS Registry Numbers

1: 138925-66-3 / **2**: 129337-17-3 / **3**: 129337-19-5 / 1,2,4-(tBu)$_3$C$_5$H$_3$: 129337-16-2 / Ni: 7440-02-0

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[5] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG, on quoting the depository number CSD-55922, the names of the authors, and the journal citation.

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