Notes

Insertion of Nitrogen Oxide into a Zirconium–Carbon Bond: Reaction of Dialkylbis(cyclopentadienyl)zirconium(IV) Complexes with Nitrogen Oxide†

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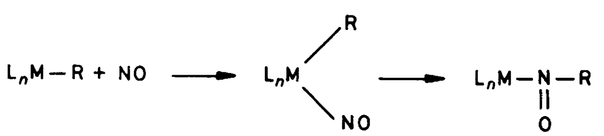
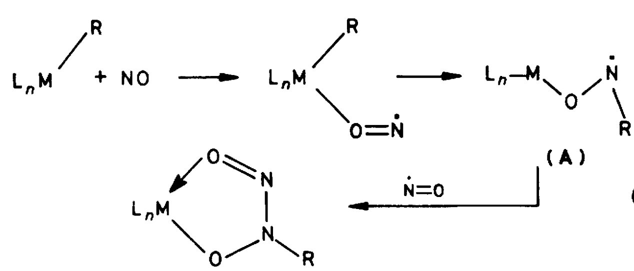
Nitrogen oxide inserts twice into one of the Zr–C σ bonds present in $[Zr(cp)_2R_2]$ (cp = η^5-C_5H_5, R = Me or CH_2Ph), forming an *N*-alkyl-*N*-nitrosohydroxylaminato anion which acts as a bidentate ligand. The structure of $[Zr(cp)_2(CH_2Ph)(O_2N_2CH_2Ph)]$ was elucidated by an *X*-ray diffraction analysis, showing the structural features of the ZrO_2N_2 metallacycle. $[Zr(cp)_2(CH_2Ph)(O_2N_2CH_2Ph)]$ crystallizes in the trigonal space group $R\bar{3}$, with $a = b = c = 18.771(6)$ Å, $\alpha = \beta = \gamma = 116.37(3)$ °, $Z = 6$, and $R = 0.038$.

Nitrosation of organic substrates is a reaction which can be assisted by metals;[1] it has, however, some significantly different features from the so-called 'insertion reaction'.[2] Co-ordination


(1)

of NO [reaction (1)] occurs with a change in the oxidation state of the metal, because of the generation of formally either NO^+ or NO^-, to which the alkyl group can migrate. This seems to suggest that metal alkyls, in which the metal cannot easily undergo redox processes, should follow a different reactivity pattern. Metals having a d^0 electron configuration and a stable high oxidation state hardly undergo reduction, while oxidation is impossible. Moreover, they are oxophilic, preferring oxygen to other donor atoms. Thus, the reactions of NO with metal alkyl derivatives of d^0 configuration may be interpreted as

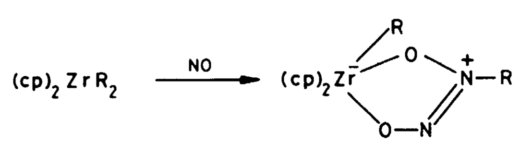

(2)

proceeding through the pathway (2). Alkyl migration to the NO group can occur, but in the absence of a redox process involving the metal the resulting free radical-type product (**A**) can react further with NO giving the known *N*-alkyl-*N*-nitrosohydroxylaminate ligand.[3–9] Reaction (1) occurs with a change in the oxidation state of the metal, while in reaction (2) the metal does not change its oxidation state.

Dialkylbis(cyclopentadienyl)zirconium(IV) complexes have often been used as model compounds in 'insertion reactions'.[10] Their reactivity with NO was briefly described by Wailes *et al.*[11] but the structure of the product was questioned.[8] We have now studied the reaction of NO with two different alkyl derivatives and report an *X*-ray analysis on the final product.

Results and Discussion

Hydrocarbon solutions of dialkylbis(cyclopentadienyl)zirconium(IV), $[Zr(cp)_2R_2]$ [R = Me (**1a**)[12] or CH_2Ph (**1b**)[13]] were saturated with nitrogen oxide (NO) at room temperature, giving crystalline products [reaction (3)]. Both complexes (**1**)


(3)

(**1a**) R = Me (**2a**)
(**1b**) R = CH_2Ph (**2b**)

were found to undergo insertion of two NO molecules *per* zirconium atom, as inferred from elemental analysis. By ^1H n.m.r. spectroscopy each of the products was shown to contain two different types of alkyl groups. A single crystal of complex (**2b**) was obtained and the structure elucidated by *X*-ray diffraction.

The structure consists of monomeric units $[Zr(cp)_2(CH_2Ph)(O_2N_2CH_2Ph)]$ as shown in the Figure; the most important bond distances and angles are listed in Table 1. The bent $(cp)_2Zr$ unit has an equatorial cavity in which the atoms of the bidentate *N*-alkyl-*N*-nitrosohydroxylaminate ligand and the alkyl carbon are located. The dihedral angle between the equatorial mean plane Zr,O(1),O(2),C(17) and the plane Zr,cp(1),cp(2) is 90.0(6)°. The geometry of the $(cp)_2Zr$ moiety unit and the Zr–C(17) bond distance are very close to that observed in other similar compounds.[10] Five-co-ordination of the metal is a common feature for $(cp)_2Zr$ derivatives containing oxygen-donor ligands.[10] The two Zr–O distances differ significantly

† *Supplementary data available* (No. SUP 56363, 3 pp.): thermal parameters, other bond distances. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

[Zr–O(1) 2.200(6), Zr–O(2) 2.264(8) Å]. The atoms Zr, O(1), O(2), N(1), N(2), and C(27) are nearly coplanar, the greatest deviation [0.023(7) Å] being for O(1). The N–N bond length [1.269(15) Å] is the shortest reported for *N*-alkyl-*N*-nitrosohydroxylaminato-complexes to date;[4,7] when compared with data for a hyponitrito-complex (N–N 1.16—1.26 Å),[14] it provides evidence of marked double-bond character. We have adopted such a description [see (**a**) below], though it must be regarded as a limiting formula. Formula (**c**) is probably the least important, because N(1)–O(1) is longer than N(2)–O(2) [1.327(10) *vs.* 1.294(6) Å]. This assumption is likely to be valid also for a rhenium complex whose structure was reported by Wilkinson and co-workers.[7] Anyway, π-electron delocalization over the whole chelating group (ONNO) seems to be a general feature of the published structures,[4,7] which all show the M[ONN(R)O] system to be planar.[6]

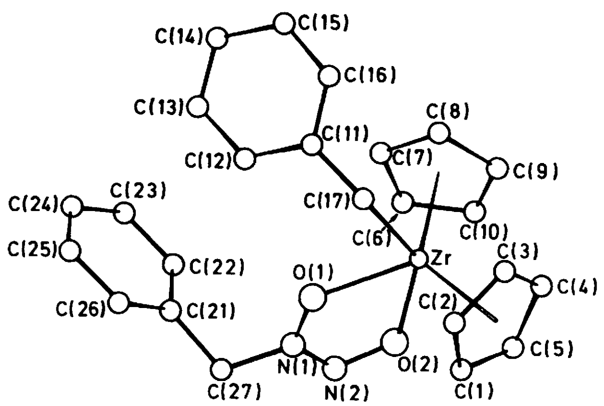


Figure. The molecular structure of [Zr(cp)$_2$(CH$_2$Ph)(O$_2$N$_2$CH$_2$Ph)]

By following reactivity pattern (2), [Zr(cp)$_2$R$_2$] may be added to the series[3–9] of d^0 and d^{10} metal alkyl complexes which yield *N*-alkyl-*N*-nitrosohydroxylaminate ligands on reaction with nitrogen oxide. This class may be differentiated from the paramagnetic analogues which undergo either NO deoxygenation[8,9] or an inappropriately named insertion reaction leading to metal-co-ordinated nitrosoalkanes[2] [reactivity pattern (1)]. It is known, however, that NO deoxygenation occurs, in some cases even with diamagnetic metal alkyls.[9]

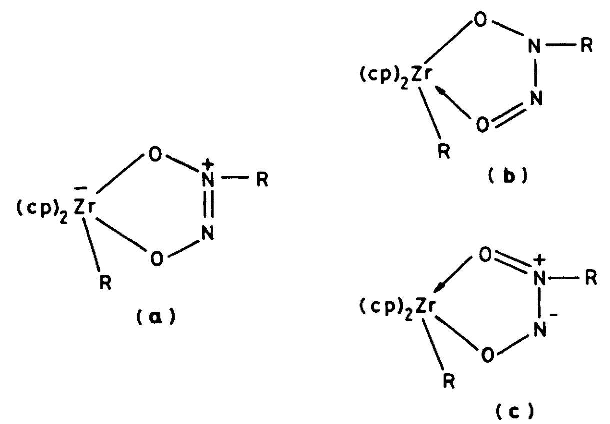


Table 1. Selected bond distances (Å) and angles (°)

Zr–O(1)	2.200(6)	Zr–C(17)	2.397(13)
Zr–O(2)	2.264(8)	O(1)–N(1)	1.327(10)
Zr–cp(1)	2.257(11)	O(2)–N(2)	1.294(6)
Zr–cp(2)	2.242(16)	N(1)–N(2)	1.269(15)
		N(1)–C(27)	1.471(7)
cp(1)–Zr–cp(2)	128.4(4)	O(1)–Zr–cp(1)	113.9(4)
C(17)–Zr–cp(2)	100.7(5)	O(1)–Zr–C(17)	72.0(3)
C(17)–Zr–cp(1)	98.8(3)	O(1)–Zr–O(2)	66.9(2)
O(2)–Zr–cp(2)	98.3(4)	Zr–O(1)–N(1)	117.6(6)
O(2)–Zr–cp(1)	97.3(4)	Zr–O(2)–N(2)	121.3(7)
O(2)–Zr–C(17)	138.9(3)	O(1)–N(1)–N(2)	121.7(6)
O(1)–Zr–cp(2)	117.5(3)	O(2)–N(2)–N(1)	112.4(7)
O(1)–N(1)–C(27)	116.7(9)	N(2)–N(1)–C(27)	121.6(8)

Table 2. Fractional atomic co-ordinates × 10^4

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Zr	6 778(1)	2 150(1)	3 520(1)	C(26)	1 018(7)	−2 981(6)	−1 151(6)
O(1)	4 746(3)	88(3)	1 849(3)	C(27)	3 005(6)	−2 206(5)	−223(6)
O(2)	6 336(4)	689(4)	2 032(4)	H(1)	7 081(52)	801(52)	3 845(52)
N(1)	4 377(5)	−838(4)	899(4)	H(2)	6 808(53)	1 766(53)	5 062(52)
N(2)	5 173(5)	−562(5)	964(5)	H(3)	8 543(54)	4 137(54)	6 436(53)
C(1)	7 637(5)	1 696(5)	4 465(5)	H(4)	9 747(53)	4 484(52)	6 060(53)
C(2)	7 499(6)	2 223(6)	5 108(5)	H(5)	8 838(52)	2 499(52)	4 493(52)
C(3)	8 426(7)	3 533(6)	5 897(6)	H(6)	6 033(53)	1 671(52)	1 375(53)
C(4)	9 128(5)	3 819(6)	5 761(6)	H(7)	5 182(53)	2 139(53)	2 024(53)
C(5)	8 614(6)	2 655(6)	4 827(6)	H(8)	6 936(53)	4 138(53)	4 302(53)
C(6)	6 476(7)	2 340(7)	2 191(7)	H(9)	9 127(53)	5 093(53)	5 320(52)
C(7)	6 040(7)	2 637(8)	2 543(8)	H(10)	8 381(53)	3 334(53)	3 422(53)
C(8)	7 144(7)	3 831(7)	3 918(8)	H(12)	3 187(53)	−14(53)	1 393(52)
C(9)	8 240(6)	4 262(6)	4 397(6)	H(13)	1 610(52)	−387(53)	97(52)
C(10)	7 839(7)	3 340(7)	3 346(7)	H(14)	2 241(53)	1 505(53)	1 243(53)
C(11)	4 690(5)	1 942(5)	3 109(5)	H(15)	4 320(52)	3 535(52)	3 381(52)
C(12)	3 410(6)	707(5)	1 788(6)	H(16)	5 783(52)	3 747(52)	4 541(52)
C(13)	2 490(6)	538(6)	1 084(6)	H(171)	5 301(53)	1 480(54)	3 708(53)
C(14)	2 838(7)	1 606(8)	1 691(8)	H(172)	6 325(53)	2 863(54)	4 701(53)
C(15)	4 088(8)	2 827(7)	2 991(8)	H(22)	2 744(54)	−1 493(53)	−1 183(53)
C(16)	4 974(6)	2 982(6)	3 674(6)	H(23)	1 102(53)	−1 874(54)	−2 371(53)
C(17)	5 683(6)	2 142(6)	3 854(5)	H(24)	−584(52)	−2 939(52)	−2 726(52)
C(21)	2 002(5)	−2 371(5)	−919(5)	H(25)	−632(53)	−3 556(52)	−1 924(53)
C(22)	2 036(6)	−1 942(6)	−1 358(6)	H(26)	1 060(53)	−3 194(52)	−714(53)
C(23)	1 084(8)	−2 137(7)	−2 019(7)	H(271)	2 878(52)	−2 518(52)	89(53)
C(24)	99(7)	−2 771(7)	−2 258(6)	H(272)	3 014(54)	−2 611(54)	−699(54)
C(25)	66(7)	−3 184(7)	−1 823(7)				

Zirconium(IV) systems are very oxophilic; therefore it is not surprising that $[Zr(cp)_2R_2]$ deoxygenate NO (though in low yield) concurrently with reaction (2). Traces of $[\{Zr(cp)_2O\}_3]$[15] have been isolated.

Experimental

Reaction between $[Zr(cp)_2Me_2]$ *and* NO.—A procedure similar to that of ref. 11 was adopted. A solution of $[Zr(cp)_2Me_2]$[12] (1.277 g, 4.88 mmol) in n-heptane (50 cm^3) was saturated with NO. Precipitation of a white solid began immediately. Gas was absorbed during 15 min and stirring was continued for a further 30 min. The liquid was then decanted off and the solid washed with n-heptane (50 cm^3). The liquid was again decanted off; the residue was dried *in vacuo* and redissolved in toluene (20 cm^3). On adding n-heptane (50 cm^3) and cooling to −78 °C, white crystals were isolated, washed with n-heptane (10 cm^3), and dried *in vacuo*, yield 0.79 g. This solid contains a small amount of $[\{Zr(cp)_2O\}_3]$[15] which can be recovered by recrystallation from CCl_4–n-heptane in which the oxo-compound is insoluble {Found: C, 45.9; H, 5.15; N, 9.10. Calc. for $[Zr(cp)_2Me(O_2N_2Me)]$: C, 46.3; H, 5.15; N, 9.0 %}. ^1H N.m.r. (CCl_4): δ 5.7 (s, 10 H), 3.7 (s, 3 H), and 0.0 (s, 3 H).

Reaction between $[Zr(cp)_2(CH_2Ph)_2]$ *and* NO.—A solution of $[Zr(cp)_2(CH_2Ph)_2]$[13] (1.054 g, 2.61 mmol) in toluene (50 cm^3) was saturated with NO: gas was quickly absorbed and the colour changed from intense yellow to light yellow. The solution was concentrated *in vacuo* (to 20 cm^3) and n-heptane (30 cm^3) was added. A yellow product (0.8 g) was obtained on cooling {Found: C, 62.4; H, 4.60; N, 5.90. Calc. for $[Zr(cp)_2(CH_2Ph)(O_2N_2CH_2Ph)]$: C, 62.2; H, 5.20; N, 6.05%}. ^1H N.m.r. (in CCl_4): δ 2.1 (s, 2 H), 5.1 (s, 2 H), 5.5 (s, 10 H), and 7 (m, 10 H). Crystals suitable for *X*-ray analysis were obtained from CCl_4–n-heptane.

Crystal Structure Determination of $[Zr(cp)_2(CH_2Ph)(O_2N_2CH_2Ph)]$.—*Crystal data*. $C_{24}H_{24}N_2O_2Zr$, $M = 463.7$, trigonal, space group $R\bar{3}$, $a = b = c = 18.771(6)$ Å, $\alpha = \beta = \gamma = 116.37(3)°$, $U = 3\,191.0$ Å^3, $Z = 6$, $D_c = 1.447$ g cm^{-3}, $F(000) = 1\,428$, μ(Mo-K_α) = 5.3 cm^{-1}, $\lambda = 0.7107$ Å.

Intensity data [5 123 reflections, 2 563 with $I > 3.0\sigma(I)$; $2.5 < \theta < 28.0°$, at 295 K] were measured on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (ω–2θ scan technique). Lorentz polarization corrections were applied, but no corrections were made for absorption in view of the shape of the crystal used (a parallelepiped, 0.32 × 0.32 × 0.48 mm) and of the low linear absorption coefficient. The Zr atom was located in a three-dimensional Patterson map. The structure was determined by conventional Fourier techniques and refined successively in space group $R\bar{3}$ by blocked full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were located from a difference map and isotropically refined in the last cycles. The refinement finally converged at $R = 0.038$. Unit weights were used since these gave acceptable agreement analysis. The final atomic co-ordinates are given in Table 2. Calculations were carried out using the SHELX system of programs.[16]

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