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Synthesis and structure of some palladium(I) cluster compounds containing isocyanide ligands

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Abstract

The reaction of $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4]$ with C_8H_9NC has been shown to occur with substitution of CO by C_8H_9NC to give $[Pd_4(\mu\text{-}CO)_2(\mu\text{-}CNC_8H_9)_2(\mu\text{-}O_2CCH_3)_4]$ (1) with two equivalents of isocyanide and $[Pd_4(\mu\text{-}CNC_8H_9)_4(\mu\text{-}O_2CCH_3)_4]$ (2) with four equivalents of isocyanide. The structure of $[Pd_4(\mu\text{-}CNC_8H_9)_4(\mu\text{-}O_2CCH_3)_4] \cdot CH_2Cl_2$ has been determined by single crystal X-ray diffractometry. The structure is based on a rectangular unit of palladium atoms with the two shorter edges, which have Pd–Pd distances of 2.6572(5) and 2.6668(4) Å, bridged by isocyanide ligands, and the two longer edges, with Pd–Pd distances of 2.8888(4) and 2.9369(4) Å, bridged by two acetate ligands. The bridging isocyanide groups are nearly linear, with C–N–C angles of between 161.2(4) and 169.3(5)°. This leads to relatively high values for the $\nu(NC)$ stretching frequencies in the IR spectrum. Compound 1 has also been synthesised by carbon monoxide reduction of palladium(II) acetate in the presence of isocyanide.

1. Introduction

The synthesis of the palladium(I) cluster compound $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4]$ was first reported in 1978 by carbon monoxide reduction of palladium(II) acetate in acetic acid [1]. It has a structure based on a rectangle of palladium atoms, with the two edges bridged by two carbonyl groups considerably shorter at 2.663(1) Å than the two edges bridged by two acetates (2.909 Å). This compound has since been shown to be a useful precursor for the synthesis of both homo- and heteronuclear cluster compounds. Its reactions can involve retention of the planar Pd_4 core, or its rearrangement to other geometries. Reaction with diphenyldiazomethane results in the substitution of the carbonyl ligands by diphenylcarbenes to give $[Pd_4(\mu\text{-}CPh_2)_4(\mu\text{-}O_2CCH_3)_4]$ [2]; EXAFS data suggest that this compound has a square-planar core, which is consistent with a rearrangement of the acetate ligands so that each Pd–Pd bond is bridged by one acetate and one carbene. This rearrangement is presumably made favourable owing to the steric requirements of the bulky diphenylcarbene ligands. Reaction with 1,10-phenanthroline gives a cluster, $[Pd_4(\mu\text{-}CO)_2(\text{phen})_4](O_2CCH_3)_4$, in which the tetrapalladium core has undergone a rearrangement to a distorted tetrahedron, with the acetates becoming outer-sphere ligands [3].

Reaction of $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4]$ with the molybdenum anion $[CpMo(CO)_3]^-$ gives [4] a mixed palladium-molybdenum cluster $[Pd_4\{CpMo(CO)_3\}_4]^{2-}$ in which the formal oxidation state of the palladium has decreased from +1 to +1/2. The product has a square-planar Pd_4 core with all Pd–Pd bonds bridged by Mo. Reaction with the related manganese anion $[(\eta\text{-}C_5H_4Me)Mn(CN)(CO)_3]^-$ gives [5] a compound containing only two Pd–Pd bonds. The product, $[(OC)Pd(\mu\text{-}NC)Mn(\eta\text{-}C_5H_4Me)(CO)_2]_4$ has a helical structure, with each palladium atom also directly bonded to a manganese atom, a carbonyl ligand, and the nitrogen atom of a nitrile ligand.

Thermolysis of $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4]$ occurs with transfer of oxygen from acetate to CO and elimination of CO_2 [2]. When the reaction was carried out in benzene most of the CO_2 formed from CO reduction was isolated as benzoic acid. $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4]$ has been shown to catalyse the conversion of acetylene in acetic acid into vinyl acetate. Addition

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of 1,10-phenanthroline to solutions of [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] leads to effective and selective catalysts for conversion of propylene and 2-methylpropene in methanol to allylmethyl and methallylmethyl ethers respectively [6]. In view of the useful chemical properties of this tetramer it was decided to investigate the synthesis of the related isocyanide complexes.

2. Results and discussion

Addition of 2 equivalents of C$_8$H$_9$NC in toluene to a THF solution of [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] led to a rapid darkening in colour. After stirring for 30 min, reduction of volume of the solvent under reduced pressure gave a yellow powder which was recrystallised from dichloromethane-diethyl ether to give yellow crystals of [Pd$_4$(μ-CO)$_2$(μ-CNC$_8$H$_9$)$_2$(μ-O$_2$CCH$_3$)$_4$] (1). Repetition of the reaction using 4 equivalents of C$_8$H$_9$NC gave yellow crystals of [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] (2) after recrystallisation from dichloromethane-diethyl ether. Compounds 1 and 2 were characterised on the basis of IR and ^{1}H-NMR spectroscopic data, microanalyses and, in the case of 2, a single-crystal X-ray diffraction study. Complex 1 may be converted to 2 by the addition of 2 further equivalents of isocyanide. It has also been shown to be possible to synthesise 1 from the carbon monoxide reduction of palladium(II) acetate in the presence of isocyanide, with toluene as the solvent. This reaction gives other products as well, including small amounts of 2. The routes to 1 and 2 are summarised in Scheme 1.

2.1. X-Ray crystallographic analysis of 2

The structure of compound 2 was confirmed by a single-crystal X-ray crystallographic investigation, details of which are summarised in Table 1. The relevant atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3. The cluster is illustrated in Fig. 1, in which all non-hydrogen atoms are shown for clarity. The four palladium atoms form a distorted rectangle with two short Pd–Pd distances of 2.6668(4) and 2.6572(5) Å and two considerably longer Pd–Pd distances of 2.8888(4) and 2.9369(4) Å . There

TABLE 1. Crystal data for [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] (2)

Formula	C$_{44}$H$_{48}$N$_4$O$_8$Pd$_4$·CH$_2$Cl$_2$
M	1186.49
	(1271.42 including dichloromethane)
Crystal system	Triclinic
Space group	P$\bar{1}$ (no. 2)
a /Å	13.112(2)
b /Å	21.523(3)
c /Å	10.968(2)
α /°	93.11(1)
β /°	124.80(1)
γ /°	99.64(1)
U /Å^3	2423.3
Z	2
D_c /g cm^{-3}	1.715
$F(000)$	1260
linear absorption coefficient /cm^{-1}	15.803
crystal colour	orange
Data collection	
X-radiation	Mo Kα, λ = 0.71069 Å
θ_{min}, θ_{max} /°	0, 27
min., max. h, k, l	−1,16; −27,27; −14,14
ω-scan width /°	1.2 + 0.35 tan θ
horizontal aperture /mm	3.5
total data collected	11631
total unique data	10572
total observed data	
[$I > 3\sigma(I)$]	7994
merging R factor	0.011
Absorption correction	ψ-scan profile min./max. correction 1.34, 1.66
Refinement	
no. of parameters	568
ratio data:parameters	14.07
weighting scheme	Chebyshev (coefficients 11.076, −2.190, 8.117, 0.383)
Final R	0.039
Final R_w	0.045

is some distortion from a regular rectangle, the Pd–Pd–Pd angles ranging from 82.28(1) to 97.72(1)°. The two shorter Pd–Pd bonds are both bridged by two isocyanide ligands and the two longer Pd–Pd bonds by two acetate ligands. The Pd–C bond lengths range from 1.987(4) to 2.006(4) Å, and these are slightly shorter than the Pd–C$_{br}$ distances in [Pd$_3$(μ-CNCy)$_3$(CNCy)$_3$], which average 2.072(13) Å [7]. The

[Pd(O$_2$CCH$_3$)$_2$]

[Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] $\xrightarrow{\text{2 XylNC}}$ [Pd$_4$(μ-CO)$_2$(μ-CNC$_8$H$_9$)$_2$(μ-O$_2$CCH$_3$)$_4$]

CO, C$_8$H$_9$NC

4C$_8$H$_9$NC   2C$_8$H$_9$NC

1

[Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$]

2

Scheme 1.

TABLE 2. Atomic coordinates for [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] (2)

Atom	x	y	z
Pd(1)	0.42658(3)	0.43136(2)	0.07337(3)
Pd(2)	0.64910(3)	0.51576(1)	0.19485(3)
Pd(3)	0.92732(3)	0.04253(2)	0.10341(3)
Pd(4)	0.97881(3)	−0.06996(2)	0.08006(4)
N(1)	0.4949(4)	0.5426(2)	0.3019(4)
N(2)	0.6446(4)	0.3781(2)	0.1451(4)
N(3)	0.7035(3)	−0.0673(2)	−0.1022(4)
N(4)	1.1073(4)	0.0016(2)	0.3907(4)
O(11)	0.2438(3)	0.4409(2)	0.0105(4)
O(12)	0.8108(3)	0.5163(2)	0.1922(4)
O(21)	0.3346(3)	0.3423(2)	−0.0821(3)
O(22)	0.7199(3)	0.6157(2)	0.2861(4)
O(31)	0.7938(3)	0.0937(2)	−0.0492(4)
O(32)	1.1469(4)	−0.1053(2)	0.2028(4)
O(41)	1.0561(3)	0.1319(2)	0.2462(4)
O(42)	0.8831(4)	−0.1530(2)	−0.0967(4)
Cl(1000)	0.9880(2)	0.3019(1)	−0.0025(3)
Cl(1001)	0.9511(3)	0.2845(2)	−0.2889(3)
C(11)	0.5123(4)	0.5127(2)	0.2261(4)
C(12)	0.5052(5)	0.5816(2)	0.4154(6)
C(13)	0.6127(6)	0.5876(3)	0.5625(6)
C(14)	0.6166(9)	0.6246(4)	0.6746(8)
C(15)	0.524(1)	0.6542(4)	0.644(1)
C(16)	0.420(1)	0.6477(4)	0.496(1)
C(17)	0.4056(6)	0.6104(3)	0.3750(8)
C(18)	0.7182(7)	0.5573(4)	0.6000(8)
C(19)	0.2900(7)	0.6008(4)	0.215(1)
C(21)	0.5974(4)	0.4205(2)	0.1384(4)
C(22)	0.7376(4)	0.3432(2)	0.1862(5)
C(23)	0.8524(5)	0.3621(3)	0.3331(6)
C(24)	0.9412(5)	0.3249(4)	0.3710(7)
C(25)	0.9158(7)	0.2728(4)	0.2732(9)
C(26)	0.8022(7)	0.2554(3)	0.1327(8)
C(27)	0.7106(5)	0.2904(3)	0.0848(6)
C(28)	0.8766(6)	0.4166(3)	0.4410(6)
C(29)	0.5845(6)	0.2716(3)	−0.0703(7)
C(31)	0.8127(4)	−0.0435(2)	−0.0217(4)
C(32)	0.5845(4)	−0.1109(2)	−0.1832(5)
C(33)	0.4818(5)	−0.0953(3)	−0.3098(5)
C(34)	0.3628(5)	−0.1393(4)	−0.3871(7)
C(35)	0.3499(6)	−0.1948(4)	−0.3383(9)
C(36)	0.4516(7)	−0.2100(3)	−0.2146(8)
C(37)	0.5733(5)	−0.1679(2)	−0.1320(6)
C(38)	0.5000(7)	−0.0340(4)	−0.3567(8)
C(39)	0.6856(7)	−0.1834(3)	0.0052(8)
C(41)	1.0449(4)	−0.0038(2)	0.2596(5)
C(42)	1.1754(4)	−0.0043(2)	0.5431(5)
C(43)	1.2795(5)	0.0449(3)	0.6492(6)
C(44)	1.3470(6)	0.0370(4)	0.8009(6)
C(45)	1.3111(7)	−0.0164(4)	0.8406(7)
C(46)	1.2060(7)	−0.0648(4)	0.7327(7)
C(47)	1.1343(5)	−0.0592(3)	0.5793(6)
C(48)	1.3172(6)	0.1039(3)	0.6031(8)
C(49)	1.0219(7)	−0.1106(3)	0.4627(8)
C(111)	0.1706(4)	0.4636(2)	−0.1009(5)
C(112)	0.0450(5)	0.4680(4)	−0.1277(7)
C(121)	0.2847(4)	0.3384(2)	−0.2206(5)
C(122)	0.2260(6)	0.2719(3)	−0.3147(6)
C(131)	0.7855(5)	0.1136(2)	−0.1591(5)
C(132)	0.6855(6)	0.1501(3)	−0.2464(6)

TABLE 2 (continued)

C(141)	1.1222(5)	0.1649(2)	0.2139(5)
C(142)	1.2184(7)	0.2243(3)	0.3244(7)
C(1000)	1.0466(7)	0.2781(4)	−0.0990(9)

C–N–C angles in the isocyanide ligands lie between 161.2(4) and 169.3(5)°; these are unusually large angles for bridging isocyanides, the majority of compounds characterised showing C–N–C angles between 128(2) and 133(2)°. There are two exceptions to this, namely [Pd$_2$Cl$_2$(μ-CNC$_8$H$_9$)$_2$(py)$_2$], which has C–N–C angles of 157.6(9) and 175.2(13)° [8], and [Pd$_5$(μ-SO$_2$)$_3$(μ-CNC$_8$H$_9$)$_2$(CNC$_8$H$_9$)$_5$], which has C–N–C angles of 168.4(7) and 171.4(8)° [9]. The much smaller degree of bending of the bridging isocyanide ligands in these two clusters and in 2 has a considerable effect on the frequency of the ν(NC) vibration as observed in the IR spectra, as discussed below.

The Pd–Pd bond lengths and angles are very similar to those for [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$], which has short Pd–Pd distances of 2.663(1) Å and long Pd–Pd distances of 2.909 Å and Pd–Pd–Pd angles of 83.4 and 95.6° [1]. The longer Pd–Pd contacts in both 2 and [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] are significantly longer than those in palladium metal [10] but are considerably shorter than those in [Pd$_3$(μ-O$_2$CCH$_3$)$_6$], which are also bridged by two acetate ligands and lie between 3.105(1) and 3.203(1) Å [11]. This suggests that there is a weak bonding interaction between the metal atoms in both 2 and [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$].

2.2. Spectroscopic characterisation of the products

The ^{1}H-NMR spectrum of 1 shows a multiplet in the aryl region, between 7.2 and 7.1 ppm, and singlets at 2.46 ppm and 1.86 ppm, in the intensity ratio 1:2:2, consistent with an acetate:isocyanide ratio of 2:1. The spectrum for 2 shows a multiplet at 7.2–7.0 ppm and singlets at 2.42 and 1.67 ppm in the intensity ratio 1:2:1. This is consistent with an acetate:isocyanide ratio of 1:1.

The IR spectrum of 2 shows ν(NC) at 2010m and 1974s cm^{-1} and ν(CO$_2$) at 1574vs cm^{-1}. These frequencies are high for bridging isocyanides, though it has been noted previously [9] that when bridging isocyanide ligands are linear, ν(NC) stretching frequencies are higher than for bent isocyanides, thus ν(NC) bands for the bridging isocyanides in [Pd$_5$(μ-SO$_2$)$_3$(μ-CNC$_8$H$_9$)$_2$(CNC$_8$H$_9$)$_5$] were observed at 2047s and 1990w cm^{-1}. The IR spectrum of 1 shows peaks at 2064s and 1897s cm^{-1}. Since CO is a better π-acceptor than C$_8$H$_9$NC, the presence of the latter would be expected to reduce the values of ν(CO) from those observed for [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] (1940 and
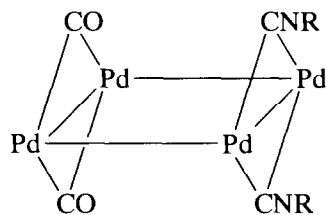
1975 cm^{-1}), and similarly the presence of CO would be expected to increase the value of ν(NC) above those observed for [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$]. Hence

the band at 2064 cm^{-1} can be assigned to ν(NC) and that at 1897 cm^{-1} to ν(CO). A ν(CO)$_2$ band is also observed, at 1567vs cm^{-1}.

TABLE 3. Selected bond lengths (Å) and angles (°) for [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] (2)

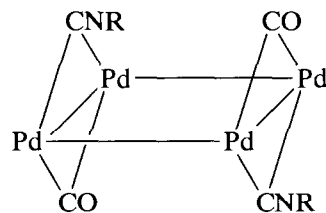|			
Pd(1)–Pd(2)	2.6668(4)	Pd(3)–C(31)	2.001(4)
Pd(1)–Pd(2)'	2.8888(4)	Pd(3)–C(41)	1.998(5)
Pd(1)–O(11)	2.134(3)	Pd(4)–O(32)	2.129(3)
Pd(1)–O(21)	2.135(3)	Pd(4)–O(42)	2.151(3)
Pd(1)–C(11)	2.002(4)	Pd(4)–C(31)	2.006(4)
Pd(1)–C(21)	1.987(4)	Pd(4)–C(41)	1.997(4)
Pd(2)–O(12)	2.135(3)	N(1)–C(11)	1.168(5)
Pd(2)–O(22)	2.129(3)	N(1)–C(12)	1.389(6)
Pd(2)–C(11)	2.000(4)	N(2)–C(21)	1.169(5)
Pd(2)–C(21)	1.990(4)	N(2)–C(22)	1.405(6)
Pd(3)–Pd(4)	2.6572(5)	N(3)–C(31)	1.164(5)
Pd(3)–Pd(4)'	2.9369(4)	N(3)–C(32)	1.394(5)
Pd(3)–O(31)	2.140(3)	N(4)–C(41)	1.165(6)
Pd(3)–O(41)	2.137(3)	N(4)–C(42)	1.402(6)
Pd(2)–Pd(1)–Pd(2)'	83.59(1)	C(41)–Pd(3)–O(31)	173.7(2)
O(11)–Pd(1)–Pd(2)	133.1(1)	C(41)–Pd(3)–O(41)	89.6(2)
O(11)–Pd(1)–Pd(2)'	82.61(9)	C(41)–Pd(3)–C(31)	87.4(2)
O(21)–Pd(1)–Pd(2)	133.3(1)	Pd(3)–Pd(4)–Pd(3)'	97.72(1)
O(21)–Pd(1)–Pd(2)'	83.01(9)	O(32)–Pd(4)–Pd(3)	134.0(1)
O(21)–Pd(1)–O(11)	88.9(2)	O(32)–Pd(4)–Pd(3)'	81.2(1)
C(11)–Pd(1)–Pd(2)	48.2(1)	O(42)–Pd(4)–Pd(3)	133.8(1)
C(11)–Pd(1)–Pd(2)'	99.6(1)	O(42)–Pd(4)–Pd(3)'	75.52(9)
C(11)–Pd(1)–O(11)	90.6(2)	O(42)–Pd(4)–O(32)	90.8(2)
C(11)–Pd(1)–O(21)	177.3(1)	C(31)–Pd(4)–Pd(3)	48.4(1)
C(21)–Pd(1)–Pd(2)	47.9(1)	C(31)–Pd(4)–Pd(3)'	106.0(1)
C(21)–Pd(1)–Pd(2)'	99.7(1)	C(31)–Pd(4)–O(32)	172.4(2)
C(21)–Pd(1)–O(11)	177.6(1)	C(31)–Pd(4)–O(42)	88.8(2)
C(21)–Pd(1)–O(21)	91.0(2)	C(41)–Pd(4)–Pd(3)	48.3(1)
C(21)–Pd(1)–C(11)	89.3(2)	C(41)–Pd(4)–Pd(3)'	117.8(1)
Pd(1)–Pd(2)–Pd(1)'	96.41(1)	C(41)–Pd(4)–O(32)	91.4(2)
O(12)–Pd(2)–Pd(1)	134.0(1)	C(41)–Pd(4)–O(42)	166.7(2)
O(12)–Pd(2)–Pd(1)'	79.36(9)	C(41)–Pd(4)–C(31)	87.3(2)
O(22)–Pd(2)–Pd(1)	134.7(1)	C(12)–N(1)–C(11)	166.6(5)
O(22)–Pd(2)–Pd(1)'	79.03(9)	C(22)–N(2)–C(21)	161.2(4)
O(22)–Pd(2)–O(12)	90.0(1)	C(32)–N(3)–C(31)	164.0(5)
C(11)–Pd(2)–Pd(1)	48.3(1)	C(42)–N(4)–C(41)	169.3(5)
C(11)–Pd(2)–Pd(1)'	108.4(1)	C(111)–O(11)–Pd(1)	123.4(3)
C(11)–Pd(2)–O(12)	172.1(1)	C(111)–O(12)–Pd(2)	127.5(3)
C(11)–Pd(2)–O(22)	90.0(2)	C(121)–O(21)–Pd(1)	123.1(3)
C(21)–Pd(2)–Pd(1)	47.8(1)	C(121)–O(22)–Pd(2)	129.0(3)
C(21)–Pd(2)–Pd(1)'	108.5(1)	C(131)–O(31)–Pd(3)	127.3(3)
C(21)–Pd(2)–O(12)	89.7(2)	C(131)–O(32)–Pd(4)	125.1(3)
C(21)–Pd(2)–O(22)	172.2(1)	C(141)–O(41)–Pd(3)	120.1(3)
C(21)–Pd(2)–C(11)	89.3(2)	C(141)–O(42)–Pd(4)	132.1(3)
Pd(4)–Pd(3)–Pd(4)'	82.28(1)	Pd(2)–C(11)–Pd(1)	83.6(2)
O(31)–Pd(3)–Pd(4)	135.7(1)	N(1)–C(11)–Pd(1)	138.6(4)
O(31)–Pd(3)–Pd(4')	79.47(9)	N(1)–C(11)–Pd(2)	137.8(4)
O(41)–Pd(3)–Pd(4)	129.0(1)	Pd(2)–C(21)–Pd(1)	84.2(2)
O(41)–Pd(3)–Pd(4)'	85.47(9)	N(2)–C(21)–Pd(1)	137.4(4)
O(41)–Pd(3)–O(31)	89.3(1)	N(2)–C(21)–Pd(2)	138.4(4)
C(31)–Pd(3)–Pd(4)	48.6(1)	Pd(4)–C(31)–Pd(3)	83.1(2)
C(31)–Pd(3)–Pd(4)'	95.6(1)	N(3)–C(31)–Pd(3)	138.1(4)
C(31)–Pd(3)–O(31)	93.6(2)	N(3)–C(31)–Pd(4)	138.5(4)
C(31)–Pd(3)–O(41)'	177.0(2)	Pd(4)–C(41)–Pd(3)	83.4(2)
C(41)–Pd(3)–Pd(4)	48.3(1)	N(4)–C(41)–Pd(3)	137.5(4)
C(41)–Pd(3)–Pd(4)'	106.7(1)	N(4)–C(41)–Pd(4)	138.5(4)

On the assumption that the rectangular tetrapalladium core of [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] and [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] is maintained in the intermediate compound [Pd$_4$(μ-CO)$_2$(μ-CNC$_8$H$_9$)$_2$(μ-O$_2$CCH$_3$)$_4$], there are three possible isomers for **1** which vary in the arrangement of the bridging ligands. These are shown schematically below:

CO   CNR

Pd————Pd

Pd————Pd

CO   CNR

A

CNR   CNR

Pd————Pd

Pd————Pd

CO   CO

B

CNR   CO

Pd————Pd

Pd————Pd

CO   CNR
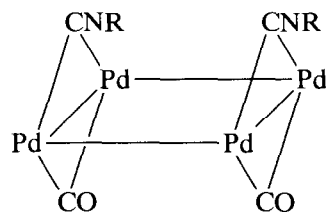
C

Both **A** and **B** have C_{2v} symmetry, so two carbonyl and two isocyanide bands (a$_1$ and b$_1$, and a$_1$ and b$_2$) are expected in the IR spectrum. **C** has C_{2h} symmetry, so only one carbonyl and one isocyanide band (a$_u$) would be expected. The presence of only one carbonyl and one isocyanide band provides good evidence for structure **C**, and solution IR spectral data support this, showing ν(NC) at 2070w and ν(CO) at 1906m cm^{-1}, though it is not possible to dismiss **A** and **B** entirely since the additional bands may be too weak to be observed.

3. Experimental section

Reactions were routinely carried out by use of Schlenk-line techniques under pure dry dinitrogen, with dry dioxygen-free solvents. Microanalyses (C, H and N) were carried out by Mr. M. Gascoyne and his staff at Oxford. Infrared spectra were recorded on a Perkin-Elmer FT1710 spectrometer as Nujol mulls between KBr discs and ^{1}H-NMR spectra using a Bruker AM-300
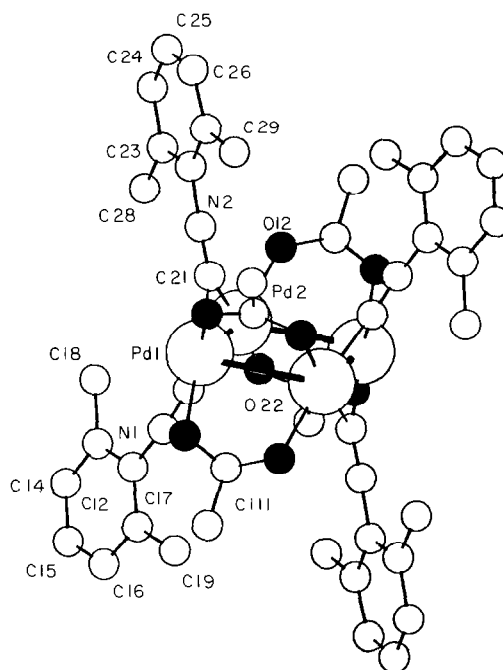
Fig. 1. Molecular structure of [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$]. For reasons of clarity the hdyrogen atoms have been omitted and the oxygen atoms of the acetate ligands have been shown in black.

spectrometer operating at 299.96 MHz and referenced to TMS. [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] was prepared by the procedure described in reference 1.

3.1. Syntheses

[Pd$_4$(μ-CO)$_2$(μ-CNC$_8$H$_9$)$_2$(μ-O$_2$CCH$_3$)$_4$] (**1**) from [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$]. [Pd$_4$(μ-CO)$_4$(μ-O$_2$C-CH$_3$)$_4$] · (AcOH)$_2$ (0.10 g, 0.11 mmol) was dissolved in THF (20 cm^3) and a solution of C$_8$H$_9$NC (0.029 g, 0.22 mmol) in toluene (5 cm^3) was added. The mixture was stirred for 30 min and the volume of solvent then reduced to give a yellow solid. This was recrystallised from dichloromethane–diethyl ether to give yellow crystals of the product. Yield 0.070 g (71%).

[Pd$_4$(μ-CO)$_2$(μ-CNC$_8$H$_9$)$_2$(μ-O$_2$CCH$_3$)$_4$] (**1**) from [Pd(O$_2$CCH$_3$)$_2$]. [Pd(O$_2$CCH$_3$)$_2$] (0.30 g, 1.33 mmol) and C$_8$H$_9$NC (0.088 g, 0.67 mmol) were dissolved in toluene (20 cm^3) and CO bubbled through the solution. The mixture was stirred under CO for 1 h and the volume of solvent was then reduced under reduced pressure to give a yellow powder. This was washed with acetone and recrystallised from dichloromethane–diethyl ether to give yellow crystals of the product. Yield 0.170 g (52%). (Found: C, 34.5; H, 2.9; N, 2.8; C$_{28}$H$_{30}$N$_2$O$_{10}$Pd$_4$ requires C, 34.3; H, 3.1; N, 2.9%). ν(NC) at 2064s; ν(CO) at 1897s cm^{-1}; ν(CO$_2$) at 1567vs cm^{-1}; δ(^{1}H) (CDCl$_3$) at 7.2–7.1 ppm (Ar, 6H), 2.46 ppm (CH_3–Ar, 12H), 1.86 ppm (CH_3–CO$_2$–, 12H).

[Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] (2) from [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$]. [Pd$_4$(μ-CO)$_4$(μ-O$_2$CCH$_3$)$_4$] · (AcOH)$_2$ (0.10 g, 0.11 mmol) was dissolved in THF (20 cm^3) and a solution of C$_8$H$_9$NC (0.059 g, 0.45 mmol) in toluene (5 cm^3) was added. The mixture was stirred for 30 min and the volume of solvent then reduced to give a yellow solid. This was recrystallised from dichloromethane–diethyl ether to give yellow crystals of the product. Yield 0.107 g (80%).

[Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] (2) from [Pd$_4$(μ-CO)$_2$(μ-CNC$_8$H$_9$)$_2$(μ-O$_2$CCH$_3$)$_4$]. [Pd$_4$(μ-CO)$_2$(μ-CNC$_8$H$_9$)$_2$(μ-O$_2$CCH$_3$)$_4$] (0.10 g, 0.094 mmol) was dissolved in dichloromethane (20 cm^3) and a solution of C$_8$H$_9$NC (0.025 g, 0.19 mmol) in toluene (5 cm^3) was added. The mixture was stirred for 30 min and the solvent then removed under reduced pressure, and the residue was recrystallised from dichloromethane-diethyl ether to give yellow crystals of the product. Yield 0.09 g (74%). (Found: C, 42.3; H, 4.0; N, 4.3; C$_{44}$H$_{48}$N$_4$O$_8$Pd$_4$ · CH$_2$Cl$_2$ requires C, 42.5; H, 4.0; N, 4.4%). ν(NC) at 2010m, 1974s; ν(CO$_2$) at 1574 cm^{-1}. δ(^{1}H) (CDCl$_3$) at 7.2–7.0 ppm (Ar, 12H), 2.42 ppm (CH_3–Ar, 24H), 1.67 ppm (CH_3–CO$_2$–, 12 H).

3.2. Crystal structure determination of [Pd$_4$(μ-CNC$_8$H$_9$)$_4$(μ-O$_2$CCH$_3$)$_4$] · CH$_2$Cl$_2$(2)

Crystals of compound 2 used in the analysis were grown by the slow diffusion of diethyl ether into a dichloromethane solution. A single crystal of dimensions 0.3 × 0.3 × 1.0 mm was mounted in a Lindemann tube and transferred to the goniometer head of an Enraf-Nonius CAD-4 diffractometer. Experimental details of the crystallographic determination are summarised in Table 1. An absorption correction based on azimuthal scans of the crystal was applied to the data (minimum/maximum corrections 1.34, 1.66).

The positions of the palladium atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located in subsequent Fourier difference electron density syntheses [12,13]. The hydrogen atoms were included in calculated positions. The

asymmetric unit comprised two halves of two crystallographically distinct molecules which were essentially identical. The other halves of the molecules lie in adjacent unit cells. All non-hydrogen atoms were assigned anisotropic thermal parameters in the final cycles of least-squares refinement which converged at R 0.039 and R_w 0.045.

Supplementary data have been deposited with the Cambridge Crystallographic Data Centre.

References

1 I. I. Moiseev, T.A. Stromnova, M.N. Vargaftig, G. Ja. Mazo, Lj. G. Kuz'mina and Yu. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, (1978) 27.
2 T.A. Stromnova, I.N. Busygina, D.I. Kochubey and I.I. Moiseev, *J. Organomet. Chem.*, 417 (1991) 193.
3 M.N. Vargaftik, T.A. Stromnova, T.S. Khodashova, M.A. Porai-Koshits and I.I. Moiseev, *Koord. Khim.*, 7 (1981) 132.
4 T.A. Stromnova, I.N. Busygina, S.B. Katser, A.S. Antsyshkina, M.A. Porai-Koshits and I.I. Moiseev, *J. Chem. Soc., Chem. Commun.*, (1988) 114.
5 P. Braunstein, B. Oswald, A. Tiripicchio and M. Tiripicchio Camellini, *Angew. Chem., Int. Ed. Engl.*, 29 (1990) 1140.
6 I.I. Moiseev, *Pure Appl. Chem.*, 61 (1989) 1755.
7 C.G. Francis, S.I. Khan and P.R. Morton, *Inorg. Chem.*, 23 (1984) 3680.
8 Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 25 (1986) 3327.
9 A.D. Burrows, H. Fleischer and D.M.P. Mingos, *J. Organomet. Chem.*, in press.
10 F.R. Hartley, *The Chemistry of Palladium and Platinum*, J. Wiley and Sons, New York, 1973.
11 A.C. Skapski and M.L. Smart, *J. Chem. Soc., Chem. Commun.*, (1970) 658.
12 G.M. Sheldrick, *SHELXS-86*, program for crystal structure determination, University of Göttingen, 1986.
13 D.J. Watkin, J.R. Carruthers and P.W. Betteridge, *CRYSTALS, User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1985.