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LETTER

Palladium(II) Cyclic Carbene Complexes from 3-Isocyanopropylacrylate. X-ray Structure of cis-{$PdCl_2(PPh_3)[\overline{C{-}N(H){-}(CH_2)_2{-}N}{-}(CH_2)_3{-}O{-}C(O){-}CH{=}CH_2]$}

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We have recently reported [1] on the bonding ability of 3-isocyanopropylacrylate (3-IPA) towards palladium(II) and on the X-ray molecular structure of cis-[$PdCl_2(PPh_3)$(3-IPA)] (1). In this complex 3-IPA behaves as a normal isocyanide ligand, with no participation of the acrylic double bond in any intra- or intermolecular bonding interaction. We have also described the addition reaction of aziridine to 1, which leads to the isolation of the cyclic five-membered carbene derivative (title compound) (2), in good yield. Complex 2 could be an interesting prototype of a novel class of metal–carbene acrylic monomers suitable to be copolymerized to give molecularly dispersed metal–carbene entities [2], potentially useful for diverse catalytic applications [3]. Moreover, the Pd–CNR → Pd–carbene conversion could be a convenient strategy for the protection of the metal-to-matrix bond from undesired nucleophilic attack [4].

We herein report on (i) the X-ray structure of 2; (ii) the synthesis of derivatives of PMe_2Ph analogues of **1** and **2** (*i.e.* **3** and **4**); (iii) some preliminary observations on the stability of complexes **1**–**4** towards reduction to metal under dihydrogen.

Although the formation of cyclic carbene complexes of palladium(II) by reaction of aziridine with isocyanide complexes has been already reported in these laboratories [5], a conclusive structural determination was not available. In fact, **2** is the first cyclic carbene palladium(II) complex which is fully characterized by X-ray analysis.

The molecular structure of **2** is depicted in Fig. 1.

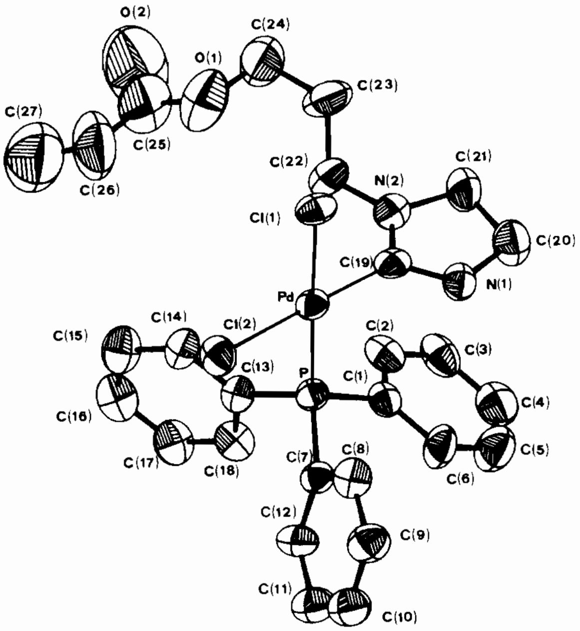

Fig. 1. ORTEP view of **2**.

Crystallographic analysis reveals that the lattice of **2** is built up of monomeric species, with no significant intermolecular interactions. The *cis* configuration of the reacting isocyanide complex is preserved and the geometry around the metal centre is almost perfectly planar. The heterocyclic ring is strongly tilted from the dsp^2 plane (dihedral angle: 98.2(2)°) in agreement with a related case, i.e. cis-$PtBr_2(PPh_3)$-[$\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)$] (dihedral angle: 102.1°) [6].

While the Pd–Cl(1) distance is comparable to that observed in **1** (2.356(2) versus 2.350(4) Å), the Pd–Cl(2) distance is significantly longer in **2** (2.367)-(3) versus 2.317(4) Å), thus confirming a higher *trans* effect of the carbene with respect to the isocyanide ligand [7]. Pd–P distances in **1** and **2** are also

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TABLE 1. Spectral and analytical data relative to complex 3

IR		^1H NMR		$^{31}P\{^1H\}$ NMR	Elemental analysis^c
$\tilde{\nu}$		δ^a	J	δ^b	
2240^d	(C≡N, s)	7.82–7.44 (m, P*Ph*)		8.64	C 39.88
1724^d	(C=O, s)	6.35–5.80 (m, vinyl)			(39.63)
1633^e	(C=C, s)	4.09 (t, OCH_2)	5.6^f		H 4.25
281, 325^e	(Pd–Cl, m)	3.55 (t, NCH_2)	6.8^f		(4.43)
		2.03 (d, P*Me*)	12.7^g		N 2.98
		1.85 (q, $-CH_2-$)	6.2^f		(3.08)

[a] ppm, internal reference TMS, CD_2Cl_2, multiplicity and relevant protons in parentheses. [b] ppm, external reference H_3PO_4 (aq.) 85% wt./wt., CD_2Cl_2. [c] Weight percent, calculated values in parentheses. [d] cm^{-1}, CH_2Cl_2, absorbing groups in parentheses. [e] cm^{-1}, nujol mull, absorbing groups in parentheses. [f] $^3J_{HH}$, Hz. [g] $^2J_{PH}$, Hz.

quite similar each other (2.256(4) versus 2.244(2) Å), while the Pd–C (carbene) distance in **2** (1.943(9) Å) is somewhat longer than the Pd–C (isocyanide) in **1** (1.9(2) Å), and significantly shorter than in the diaminocarbene complex $\{Cl(PMe_2Ph)(\overline{CH_2CH_2CH_2NH})Pd[C(\overline{NCH_2CH_2CH_2})(NHAr)]\}$ (Ar = *p*-$MeOC_6H_4$) [8].

Bond distances and angles in the heterocyclic carbene ring (substantially planar) compare well with those observed for *cis*-$PtBr_2(PPh_3)[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)]$ [6]. In the polymerizable moiety $CH_2{=}CH{-}C(O)O(CH_2)_3^-$ in **1** and **2**, the structural data compare well, in particular the C=C distances being identical in both cases, i.e. 1.30(2) Å.

The reactivity towards dihydrogen of complexes **1** and **2**, and of their $PMePh_2$ analogs (**3** and **4**) was also tested. In fact, dihydrogen may be a reagent able to cleave the metal–carbon bond. Interestingly, this expectation was recently proven by reacting H_2 with $PdCl_2(3\text{-IPA})_2$ [9] in MeOH.

We find here that a carbene functionality seems to be suitable for preventing both the metal–carbon bond fission and metal reduction in THF, but not in MeOH.

Moreover, 1,2-dichloroethane (DCE) appears to be a solvent in which metal reduction does not occur, even without previous conversion of the metal coordinated isocyanide into a cyclic carbene species.

It is apparent that these preliminary observations will be quite useful for stabilizing the matrix to metal bond in managing metal complexes of macromolecular isocyanides, under nucleophilic conditions.

Experimental

All solvents were of reagent grade and were used as received. 3-IPA, **1** and **2** were synthesized according to ref. 1. ^1H and ^{31}P NMR spectra were recorded on a Varian FT-80A at room temperature. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua.

Preparation of cis-$\{PdCl_2(PMe_2Ph)[CN{-}(CH_2)_3{-}O{-}C(O){-}CH{=}CH_2]\}$ *(3)*

$[PdCl_2(PPhMe_2)]_2$ (0.74 g, 1.18 mmol) was suspended in benzene (100 ml) and a solution of 3-IPA (0.33 g, 2.41 mmol) in benzene (50 ml) was added dropwise at room temperature, under nitrogen, in a period of 30 min. The reaction mixture was stirred for an additional 30 min. Then it was filtered and concentrated under reduced pressure. Upon addition of Et_2O (50 ml) a pale-yellow solid precipitated, which was filtered and recrystallized from CH_2Cl_2/Et_2O. Yield: 0.79 g (73%). Spectral and analytical data are collected in Table 1.

Preparation of cis-$\{PdCl_2(PMe_2Ph)[\overline{C{-}N(H){-}(CH_2)_2{-}N}{-}(CH_2)_3{-}O{-}C(O){-}CH{=}CH_2]\}$ *(4)*

Complex **3** (0.70 g, 1.54 mmol) dissolved in THF (30 ml) was treated at 0°C with aziridine (92 μl, 1.84 mmol). After 10 min, the ice bath was removed and the reaction mixture was allowed to warm to room temperature, with stirring. Complex **4** began to precipitate within 15 h. After an overnight stirring at room temperature, **4** was filtered and washed with Et_2O (3 × 20 ml). The complex was then recrystallized from CH_2Cl_2/Et_2O and dried under vacuum. Yield: 0.46 g (61%). Spectral and analytical data are collected in Table 2.

Reactivity Tests of Complexes 1–4 with Dihydrogen

The investigated complexes, dissolved in 10 cm^3 of MeOH, THF or DCE, were allowed to interact with H_2 (1 atm.), under vigorous stirring for the required time, at room temperature. The individual tests and the relevant results are collected under separate headings.

TABLE 2. Spectral and analytical data relative to complex **4**

IR		^{1}H NMR		^{31}P{^{1}H} NMR	Elemental analysis^d
$\tilde{\nu}^a$		δ^b	J	δ^c	
3265	(N–H, s)	8.87 (s, NH)		8.96	C 41.29
1720	(C=O, s)	7.85–7.30 (m, PPh)			(41.03)
1628, 1615	(C=C, m)	6.53–5.84 (m, vinyl)			H 4.98
1522	(C=N, s)	4.10 (t, OCH_2)	6.6^e		(5.06)
282, 314	(Pd–Cl, s)	3.94–3.03 (m, NCH_2)			N 5.38
		2.03 (m, –CH_2–)			(5.63)
		1.80 (d, PMe)	11.9^f		
		1.78 (d, PMe')	11.9^f		

^{a}cm^{-1}, nujol mull, absorbing groups in parentheses. ^{b}ppm, internal reference TMS, DMSO-d$_6$, multiplicity and relevant protons in parentheses. ^{c}ppm, external reference H_3PO_4 (aq.) 85% wt./wt., DMSO-d$_6$. ^{d}Weight percent, calculated values in parentheses. ^{e}$^3J_{HH}$, Hz. ^{f}$^2J_{PH}$, Hz.

1 and 2 in MeOH

30 mg of **1** and 6 mg of **2** underwent complex decomposition with quantitative formation of Pd metal after 24 h.

1 and *2 in THF*

Whereas 19 mg of **1** decomposed quantitatively to Pd metal after seven days, 9 mg of **2** did not show any evidence of decomposition during the same time as **1**.

1 and 2 in DCE

23 mg and 15 mg, respectively, of the two complexes did not decompose after three days.

3 and 4 in THF

90 mg of **3** and 110 mg of **4** gave quantitative reduction to Pd metal after two days.

Crystal Structure Determination of Complex 2 (Title Compound)

Suitable crystals of **2** were grown from a dichloromethane solution to which diethyl ether (1:1) was added and allowed to slowly diffuse (15 days). Characteristics of the data collection (2° $<\theta<$ 27°) processing and refinement are given in Table 3.

The data were collected at room temperature on a Philips PW 1100 four circle diffractometer, operating in the $\theta/2\theta$ scan mode (scan width = 1.0°, scan speed = 0.02° s^{-1}). During the data collection three standard reflections were measured every 180 min to check for the stability of the crystal. Mo Kα radiation was selected by a graphite monochromator crystal. No absorption correction was applied.

The Pd atom was located from the Patterson map. The subsequent Fourier synthesis revealed the position of all non-hydrogen atoms. The structure was refined by full-matrix least-square methods, allowing all the atoms to vibrate anisotropically. Hydrogen atoms were not introduced in the calculation. The scattering factors were taken from the International Tables for X-ray Crystallography [10]. All calculations were performed on a MicroVAX 2000, using Shelx 76 [11], PARST [12] and ORTEP [13] packages. Fractional coordinates are given in Table 4. Bond distances and angles are collected in Tables 5 and 6.

TABLE 3. Crystal data for $[PdCl_2(PPh_3)(\overline{C-NH-(CH_2)_3-N}-(CH_2)_3-O-C(O)-CH=CH_2)]$

Empirical formula	$C_{27}H_{29}N_2Cl_2O_2PPd$
Color	white
Crystal dimensions (mm)	0.28 × 0.18 × 0.11
Crystal system	triclinic
Space group	$P1$
Cell dimensions	
a (Å)	14.671(5)
b (Å)	10.984(4)
c (Å)	10.078(3)
α (°)	116.91(2)
β (°)	73.14(3)
γ (°)	102.59(4)
Molecules/cell	2
V (Å^3)	1378.76
D_{calc} (g/cm^3)	1.50
Wavelength (Å)	0.7107
Molecular weight	621.821
No. unique reflections	5966
No. with $F > 3\sigma(F)$	4028
Final residual R	0.050
Final residual R_w ($w = 1/\sigma^2(F)$)	0.045

TABLE 4. Fractional coordinates and thermal parameters for $[PdCl_2(PPh_3)(\overline{C-NH-(CH_2)_2-N}-(CH_2)_3-O-C(O)-CH=CH_2)]$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq} (Å^2)
Pd	0.17280(4)	0.00916(5)	0.45558(6)	0.0452(3)
Cl(1)	0.10268(12)	−0.21420(15)	0.32730(19)	0.063(1)
Cl(2)	0.21498(13)	−0.05154(16)	0.625767(20)	0.066(1)
P	0.23732(12)	0.22441(5)	0.57412(19)	0.044(1)
C(1)	0.36616(42)	0.23665(60)	0.54874(67)	0.043(3)
C(2)	0.42047(47)	0.36852(65)	0.58416(73)	0.050(4)
C(3)	0.52078(49)	0.37663(75)	0.56266(81)	0.049(4)
C(4)	0.56827(51)	0.25920(83)	0.49355(84)	0.057(4)
C(5)	0.51591(50)	0.13008(78)	0.44316(83)	0.054(4)
C(6)	0.41358(47)	0.11869(65)	0.46778(72)	0.052(4)
C(7)	0.18747(43)	0.29453(57)	0.77763(65)	0.049(4)
C(8)	0.23501(48)	0.40874(63)	0.88099(73)	0.071(4)
C(9)	0.18637(55)	0.47318(66)	1.03339(80)	0.081(5)
C(10)	0.09093(56)	0.42766(71)	1.08535(79)	0.080(5)
C(11)	0.04417(49)	0.31322(73)	0.98188(79)	0.064(4)
C(12)	0.09240(47)	0.24499(65)	0.82728(76)	0.054(4)
C(13)	0.21795(43)	0.35283(56)	0.51983(72)	0.049(4)
C(14)	0.14955(49)	0.44601(67)	0.61458(80)	0.072(4)
C(15)	0.13689(56)	0.54245(74)	0.57001(90)	0.093(5)
C(16)	0.18928(57)	0.54658(72)	0.43104(95)	0.083(5)
C(17)	0.25834(50)	0.45028(70)	0.33474(82)	0.067(4)
C(18)	0.27197(45)	0.35486(61)	0.38096(73)	0.061(4)
C(19)	0.13398(44)	0.054969(54)	0.32004(71)	0.047(4)
N(1)	0.05360(35)	0.11817(48)	0.35599(58)	0.048(3)
C(20)	0.04305(50)	0.15003(73)	0.23051(83)	0.064(4)
C(21)	0.12954(53)	0.08673(74)	0.09926(81)	0.078(5)
N(2)	0.17986(38)	0.03996(50)	0.17654(61)	0.060(3)
C(22)	0.27146(49)	−0.02029(71)	0.09528(78)	0.063(4)
C(23)	0.25048(57)	−0.16600(80)	−0.03847(86)	0.085(5)
C(24)	0.34615(67)	−0.23188(95)	−0.12663(98)	0.124(6)
O(1)	0.37581(47)	−0.25280(61)	−0.01106(74)	0.092(3)
C(25)	0.46397(76)	−0.2543(12)	−0.0204(12)	0.071(5)
O(2)	0.51777(60)	−0.2595(11)	−0.1329(10)	0.131(5)
C(26)	0.48258(91)	−0.2684(13)	0.1014(14)	0.168(7)
C(27)	0.5721(10)	−0.2546(14)	0.01069(14)	0.203(7)

TABLE 5. Bond angles (°) for $[PdCl_2(PPh_3)(\overline{C-NH-(CH_2)_2-N}-(CH_2)_3-O-C(O)-CH=CH_2)]$

Cl(1)–Pd–Cl(2)	92.73(9)	C(4)–C(5)–C(6)	120.3(8)
P–Pd–Cl(1)	178.1(1)	C(5)–C(4)–C(3)	119.4(8)
P–Pd–Cl(2)	89.06(9)	C(4)–C(3)–C(2)	121.3(8)
Pd–P–C(1)	112.4(2)	C(1)–C(2)–C(3)	119.3(7)
Pd–P–C(7)	111.5(2)	C(8)–C(7)–C(12)	120.5(6)
Pd–P–C(13)	116.7(2)	C(7)–C(8)–C(9)	119.1(7)
P–C(1)–C(2)	119.9(5)	C(8)–C(9)–C(10)	121.5(7)
P–C(1)–C(6)	120.5(5)	C(11)–C(10)–C(9)	119.0(7)
P–C(7)–C(8)	121.5(5)	C(12)–C(11)–C(10)	120.5(7)
P–C(7)–C(12)	117.1(5)	C(18)–C(13)–C(14)	121.0(6)
P–C(13)–C(14)	120.5(5)	C(7)–C(12)–C(11)	119.2(7)
P–C(13)–C(18)	118.4(5)	C(13)–C(14)–C(15)	118.9(7)
C(1)–P–C(7)	109.7(3)	C(14)–C(15)–C(16)	121.4(8)
C(1)–P–C(13)	102.8(3)	C(17)–C(16)–C(15)	119.0(8)
C(13)–P–C(7)	102.7(3)	C(18)–C(17)–C(16)	119.3(7)
C(6)–C(1)–C(2)	119.4(7)	C(13)–C(18)–C(17)	120.0(6)
C(1)–C(6)–C(5)	119.9(7)		

(continued)

TABLE 5. *(continued)*

Cl(1)–Pd–C(19)	87.0(2)	C(19)–N(2)–C(22)	125.6(6)
Cl(2)–Pd–C(19)	178.1(2)	C(21)–N(2)–C(22)	120.3(5)
P–Pd–C(19)	91.1(2)	N(2)–C(22)–C(23)	107.9(6)
Pd–C(19)–N(1)	124.2(5)	C(22)–C(23)–C(24)	109.0(7)
Pd–C(19)–N(2)	126.8(5)	O(1)–C(24)–C(23)	103.4(7)
N1–C(18)–N(2)	108.9(6)	C(24)–O(1)–C(25)	120.2(6)
C(19)–N(1)–C(20)	112.8(5)	O(1)–C(25)–O(2)	117(1)
N(1)–C(20)–C(21)	102.7(6)	O(1)–C(25)–C(26)	114(1)
N(2)–C(21)–C(20)	101.2(6)	O(2)–C(25)–C(26)	127(1)
C(19)–N(2)–C(21)	114.0(6)	C(25)–C(26)–C(27)	116(1)

TABLE 6. Bond distances (Å) for $[PdCl_2(PPh_3)(\overline{C{-}NH{-}(CH_2)_2{-}N}{-}(CH_2)_3{-}O{-}C(O){-}CH{=}CH_2)]$

Pd–Cl(1)	2.355(2)	C(13)–C(14)	1.404(9)
Pd–Cl(2)	2.366(3)	C(14)–C(15)	1.38(1)
Pd–P	2.244(2)	C(16)–C(15)	1.40(1)
P–C(1)	1.805(6)	C(17)–C(16)	1.43(1)
P–C(7)	1.811(6)	C(18)–C(17)	1.39(1)
P–C(13)	1.8257(8)	C(18)–C(13)	1.40(1)
Pd–C(19)	1.942(9)	N(1)–C(19)	1.344(9)
C(1)–C(2)	1.432(8)	N(1)–C(20)	1.51(1)
C(2)–C(3)	1.41(1)	C(20)–C(21)	1.556(9)
C(4)–C(3)	1.38(1)	N(2)–C(21)	1.50(1)
C(4)–C(5)	1.39(1)	N(2)–C(19)	1.344(9)
C(6)–C(5)	1.43(1)	N(2)–C(22)	1.474(9)
C(1)–C(6)	1.392(9)	C(22)–C(23)	1.595(9)
C(8)–C(7)	1.415(8)	C(23)–C(24)	1.55(1)
C(8)–C(9)	1.403(9)	O(1)–C(24)	1.47(1)
C(10)–C(9)	1.41(1)	O(1)–C(25)	1.27(1)
C(11)–C(10)	1.410(9)	O(2)–C(25)	1.16(1)
C(12)–C(11)	1.422(9)	C(26)–C(25)	1.41(2)
C(12)–C(7)	1.415(9)	C(26)–C(27)	1.30(2)

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