

[PdCl₂(PPh₃)(CN-(CH₂)₃-O-C(O)-CH=CH₂)]
and [PdCl₂(PPh₃)(C-N(H)-CH₂-CH₂-N-(CH₂)₃-
O-C(O)-CH=CH₂)]: Prototypes of Novel Organo-

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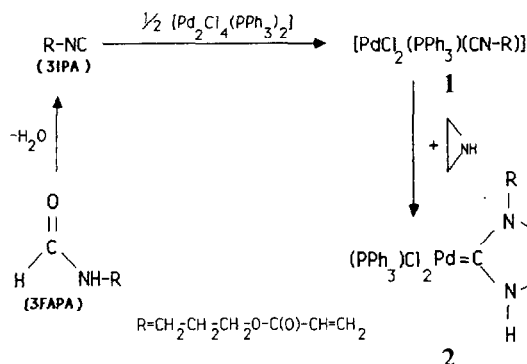
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Among the variety of methods employed to prepare highly dispersed metal-containing supported catalysts [1, 2], homo- and copolymerization of vinyl organometallic monomers has attracted considerable interest in recent years [3]. The known disadvantages of this strategy are the possibility that undesirable reactions with radical, basic or acidic initiators may severely damage the involved complex, or that optimal polymerization behaviour is prevented by interference of the metal center with the propagating chain. We are successfully using γ -ray-initiated copolymerization of vinyl monomers to prepare precursors of highly and regularly porous isocyano macromolecular ligands [4, 5]. A proper choice of comonomer(s) and of the crosslinker is expected to make possible the design of widely solvent and substrate compatible supports [6], suitable for preventing a typical drawback of supported catalysis; *i.e.* slight 'mobility' of reagents and products inside the catalytic materials. In view of the well-established very wide bonding ability and coordination versatility of isocyanides towards most diverse metal centers [7, 8], complexes obtained upon reaction of vinyliso-

cyanides with the desired metal acceptors could be most convenient monomers to synthesize tailored metal-supporting polymers, in which tenths of different metal centers could be ultrafinely dispersed for possible actual hybrid or supported catalysis.

The title compounds embody at least two remarkable requisites to test these potentialities: (i) an expected strong metal–ligand bond; and (ii) the fact that the free isocyano ligand (3-isocyanopropylacrylate, 3IPA) can be successfully polymerized by γ -ray-initiation, with considerable survival of the isocyano functionality [9].

3IPA can be obtained by dehydration of 3-formamidopropylacrylate (3FAPA) [10] with POCl₃ [11] or phosphorus pentoxide in dichloromethane in the presence of diisopropylamine. ¹H and ¹³C NMR data of both acryloil derivatives are collected in Table 1. Reaction of stoichiometric amounts of 3IPA with [PdCl₂(PPh₃)]₂ [12] in benzene at room temperature affords *cis*-[PdCl₂(PPh₃)(3IPA)] (**1**) in about 50% yield. Pertinent spectral data are collected in Table 1. Moreover, addition of aziridine in THF at 0 °C affords the sparingly soluble carbene complex **2** in about 75% yield (Scheme 1).



Scheme 1.

The choice of aziridine was suggested since it is known to give readily cyclic carbenes upon reaction with metal-coordinated isocyanides [13]. In fact, the conversion of monomers such as **1** into their carbene derivatives could afford organometallic monomers (such as **2**) suitable for obtaining copolymers in which the metal–carbon bond is likely to be stabilized towards nucleophilic attack [14].

Complex **1** is thermally stable up to 280 °C under argon (combined DSC and TG analysis). Beyond this temperature, PdCl₂ is left as a residue. Complex **2** behaves similarly and decomposes in the range 285–290 °C.

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TABLE 1. Selected NMR^a and FTIR^b Spectroscopic Data of 3FAPA, 3IPA, **1** and **2**

CH ₂ =CH-C(O)-O-CH ₂ -CH ₂ -CH ₂ -NH-CHO (3FAPA)
NMR { ¹ H}: δ = 8.17 (H-CO); 6.52–5.77 (vinyl); 4.25 (CH ₂ O); 3.39 (CH ₂ N); 1.91 (CH ₂)
{ ¹³ C}: 130.22, 127.62 (vinyl); 165.50, 161.38 (carbonyls); 61.31 (C-O); 27.81 (C-C-C); 34.22 (C-N)
CH ₂ =CH-C(O)-O-CH ₂ -CH ₂ -CH ₂ -NC (3IPA)
NMR { ¹ H}: δ = 6.56–5.79 (vinyl); 4.31 (CH ₂ O); 3.55 (CH ₂ N); 2.08 (-CH ₂ -); J _{NH} = 3.6 (CN-CH ₂)
{ ¹³ C}: 130.83, 127.62 (vinyl); 165.33 (carbonyl); 60.18 (C-O); 27.48 (C-C-C); 38.13 (C-N); 155.74 (isocyanide);
J _{NC} = 4.9 (CN-); J _{NC} = 5.9 (N-CH ₂)
FTIR: ν(CH) = 2970; ν(CN) = 2149; ν(C=O) = 1717; ν(C=C) = 1618
CH ₂ =CH-C(O)-O-CH ₂ -CH ₂ -CH ₂ -NC-Pd(PPh ₃)Cl ₂ (1)
NMR { ¹ H}: δ = 6.53–5.75 (vinyl); 4.00 (CH ₂ O); 3.32 (CH ₂ N); 1.71 (-CH ₂ -)
{ ³¹ P}: δ = 27.25
{ ¹³ C}: δ = 130.5, 127.70 (vinyl); 165.52 (carbonyl); 60.10 (C-O); 27.48 (C-C-C); 41.52 (C-N); terminal carbon atom in coordinated isocyanide not observed ^c
FTIR: ν(CN) = 2248; ν(CO) = 1716; ν(C=C) = 1608; ν(PdCl) = 293 (broad)
CH ₂ =CH-C(O)-O-CH ₂ -CH ₂ -CH ₂ -N-CH ₂ -CH ₂ -N(H)-C≡Pd(PPh ₃)Cl ₂ (2)
NMR { ¹ H}: δ = 6.40–5.90 (vinyl); 4.23 (CH ₂ O); 3.60–2.80 (N-substituted methylene groups); 2.06 (m, -CH ₂ -)
{ ³¹ P}: δ = 27.68
FTIR: ν(NH) = 3238; ν(C=O) = 1712; ν(C=C) = 1626; ν(C≡N) = 1520; ν(PdCl) = 295

^aVarian FT-80A (³¹P, ¹H) and Jeol FQ-90X (¹³C), CD₂Cl₂, 21 °C; values refer to TMS (¹H, ¹³C) and 85% H₃PO₄; coupling constants *J* in Hz. ^bNicolet 55XC (4000–400 cm⁻¹) and Nicolet 20F (600–50 cm⁻¹), cm⁻¹, Nujol mull between sodium chloride (4000–400 cm⁻¹) and polythene (400–40 cm⁻¹) plates. ^cAs expected according to ref. 15.

The X-ray diffraction study of **1*** (Fig. 1) reveals that Pd is four-coordinated square-planar with small deviations (0.04 Å) of the atoms from the equatorial plane. Apart from some values of the disordered chain of molecule B, all structural details compare well in the two independent molecules. A survey of bond lengths shows that Pd–C and Pd–P bonds are considerably shorter than expected for single bonds on the basis of the sum of the covalent radii, while Pd–Cl are longer. Thus, some double bond character should be attributed to Pd–P and Pd–C, whereas the lengthening of the Pd–Cl bonds should

be attributed to a *trans* influence. It is noteworthy that in both molecules the Pd–Cl distances are not equivalent, the bond *trans* to Pd–P being slightly but significantly longer than that *trans* to Pd–C.

The presence of the triple CN bond at the beginning and the double C=C bond at the end of the chain is also confirmed.

Experimental

Preparation of 3IPA

Dehydration of 3FAPA was performed according to a literature method [11], which was reported to be effective for several other formamides.

Preparation of Complex **1**

[PdCl₂(PPh₃)]₂ (1.15 mmol) was partially dissolved in benzene (100 cm³). A solution of 3IPA (2.35 mmol) in benzene (50 cm³) was added dropwise (room temperature, under nitrogen, 30 min) to the reddish suspension obtained. The reaction mixture was further stirred for 30 min, then filtered and concentrated. **1** was precipitated with ethyl ether and recrystallized from dichloromethane/ethyl ether (yield 50%) after treatment of the dichloromethane solution with activated carbon.

Preparation of Complex **2**

Complex **1** (1.40 mmol) was dissolved in distilled tetrahydrofuran (10 cm³) and a yellow, clear solu-

*Complex **1**: a crystal suitable for X-ray diffraction was grown from dichloromethane/ethyl ether: triclinic *P* $\bar{1}$; *a* = 12.937(5), *b* = 13.813(5), *c* = 16.325(5) Å; α = 86.03(3), β = 101.87(3), γ = 115.65(3)°; *V* = 2573 Å³, *D*_c = 1.49 g cm⁻³, *Z* = 4 (there are two independent molecules in the asymmetric unit). A total of 8968 reflections were recorded up to φ = 25° on a Philips PW 1100 diffractometer with Mo Kα radiation (λ = 0.7107 Å). The intensities were corrected for Lp and for absorption. The structure was solved by standard methods using the SHELX76 program and refined to *R* = 0.075 based on the 5060 observed reflections [*I* > 3σ(*I*)]. The ring atoms were refined as rigid bodies. One of the independent molecules is disordered at the chain level, and the seven more peripheral atoms of the chain are statistically distributed in more than two different positions. Refinement of atoms joined by dashed lines in Fig. 1 was carried out with occupancy factors of 0.5. Attempts to interpret in a reasonable model some residual electron density related to other configurations of the chain were unsuccessful.

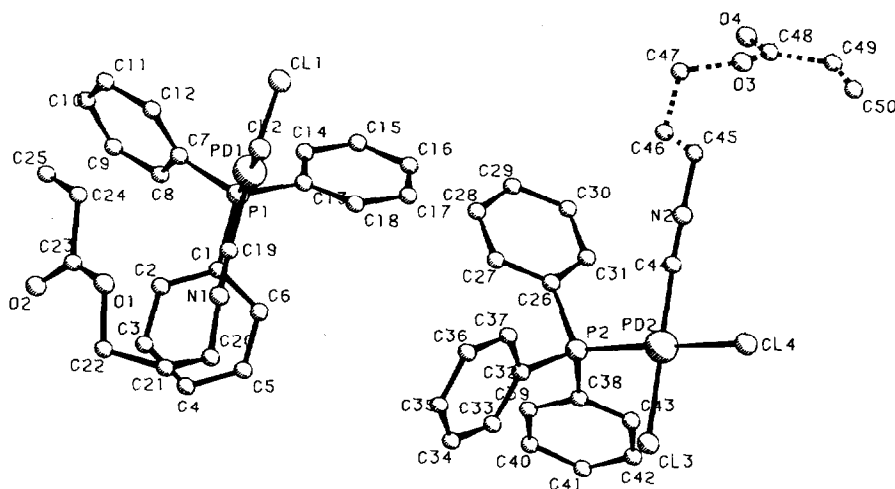


Fig. 1. Crystal structure of 1. Two independent molecules (A and B) of 1 are present in the crystal and, as indicated by the dashed lines, the peripheral part of the chain in molecule B [starting from C(46)] is disordered, being statistically distributed at least in two different orientations. Bond lengths (Å): molecule A: Pd(1)–Cl(1) 2.312(4), Pd(1)–Cl(2) 2.352(4), Pd(1)–P(1) 2.260(4), Pd(1)–C(19) 1.94(1), C(19)–N(1) 1.13(2), N(1)–C(20) 1.45(2), C(20)–C(21) 1.44(2), C(21)–C(22) 1.44(3), C(22)–O(1) 1.51(2), O(1)–C(23) 1.18(3), C(23)–O(2) 1.18(3), C(23)–C(24) 1.56(3), C(24)–C(25) 1.30(3); molecule B [up to C(45)]: Pd(2)–Cl(3) 2.317(4), Pd(2)–Cl(4) 2.350(4), Pd(2)–P(2) 2.256(4), Pd(2)–C(44) 1.91(2), C(44)–N(2) 1.15(2), N(2)–C(45) 1.47(2). Selected bond angles (°): molecule A: Cl–Pd–Cl 93.2(1), P–Pd–Cl 88.0(1), P–Pd–C 91.6(4), Cl–Pd–C 87.3(4), Pd–C–N 177(1), C–N–C 174(1), C–O–C 117(2), O–C–O 128(3), O(1)–C(23)–C(24) 114(3), O(2)–C(23)–C(24) 118(3); molecule B [up to C(45)]: Cl–Pd–Cl 92.5(2), P–Pd–Cl 86.2(1), P–Pd–C 95.0(5), Cl–Pd–C 86.2(5), Pd–C–N 175(2), C–N–C 179(2).

tion was obtained. Subsequently, 32 μl of aziridine was added to the solution kept at 0 °C with an ice-bath. After 10 min, the bath was removed and the reaction mixture was allowed to warm to room temperature, with stirring, and 2 began to precipitate within 45 min. After an overnight stirring (at room temperature), 2 was recovered by filtration and washed with n-hexane. The crude yield was 73%. The complex was further washed with acetone and n-hexane, dried under vacuum, and finally recrystallized from dichloromethane/n-hexane.

Supplementary Material

Atomic coordinates and further details of the crystal structure investigation are available from the authors on request.

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