# Complexation of (1-diphenylphosphino)cyclopropanecarbonitrile with palladium(II)

**Natalya M. Vinogradova, Irene L. Odinets,* Konstantin A. Lyssenko, Margarita P. Pasechnik, Pavel V. Petrovskii and Tatyana A. Mastryukova**

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: odinets@ineos.ac.ru*

10.1070/MC2001v011n06ABEH001515

(1-Diphenylphosphino)cyclopropanecarbonitrile **1** was synthesised by the reduction of a phosphine oxide; the interaction of **1** with $(PhCN)_2PdCl_2$ leads to 1:1 or 1:2 complexes depending on the ratio between the reactants.

Functionalised phosphine ligands are of considerable interest because of their unusual complexing properties. Ligands containing phosphorus and nitrogen complexing centres are of special interest, because catalytic systems based on such ligands show high activity in many reactions.[1–5]

Furthermore, palladium organonitrile complexes (with coordination *via* the nitrogen atom of a cyano group) are known as carbonylation catalysts,[5] *e.g.*, for highly selective formation of 1,5-diphenylpentan-3-one from styrene by hydroformylation. Among these complexes are those containing separate phosphine and organonitrile ligands.[5,6]

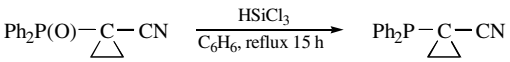
Mono-, bis- and tris-β-cyanoethyl-substituted phosphines were obtained by the cyanoethylation of phosphines.[7] The nickel[8] and molibdenum[9] complexes of tris(β-cyanoethyl)phosphine (CEP) having three-dimensional polymeric structures are known. In these complexes, the metals are coordinated *via* the nitrogen atom of a cyanoethyl group. However, in the crystalline complexes $Mo_2Cl_4(CEP)_2(RCN)_2$ (R = Me, Et and Pr$^i$), coordination of nitrile groups to molybdenum was not observed.[9]

As for α-cyanosubstituted phosphines, a few representatives of the simplest linear cyanomethylphosphines were prepared by the reduction of phosphine oxides with diphenylsilane,[10] or of phosphine sulfide with nickel powder[11] and by the reaction of silylphosphines with chloroacetonitrile.[12] The complexing properties with a variety of metals ($Ni^{II}$, $Fe^0$, $Au^I$, $Pt^{II}$, $Pd^{II}$ and $Rh^{III}$) were investigated only for cyanomethyldiphenylphosphine, and it was found that the nitrogen atom of the cyano group is not involved in the coordination.[12]

It was reasonable to suggest that the replacement of a methylene group in the above cyanomethyldiphenylphosphine by a cycloalkyl moiety would result in a rigid ligand structure, which is suitable for bidentate coordination with the participation of a nitrogen centre. Moreover, the phosphorus atom in such a ligand exhibits higher nucleophilicity due to the positive inductive effect of the cycloalkyl substituent.

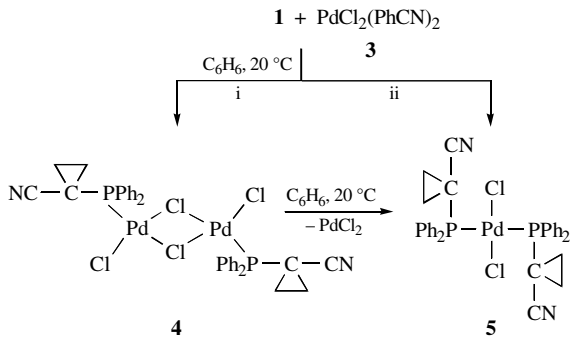
The synthesis of (1-diphenylphosphino)cyclopropanecarbonitrile **1**† (L) was carried out by the reduction of phosphine oxide **2**‡ with an excess of trichlorosilane in quantitative yield according to NMR data and 95% after isolation. Phosphine **1** is a low-melting waxy solid, which is stable in argon for a long time.

Depending on the ratio between reactants, the reaction of **1** with *trans*-dichloro(dibenzonitrile)palladium **3** in a $C_6H_6$ solution leads to the formation of the 1:1 ML or 1:2§ $ML_2$ complex.




**2** **1**

These complexes precipitated from the reaction solutions after ~10 min as fine orange (ML) or yellow ($ML_2$) crystals.




ratio **1**:**3** = 1:1 (i), 2:1 (ii)

The structure of the complexes was confirmed by IR and $^1$H, $^{31}$P NMR¶ (**5**) spectroscopy and X-ray diffraction analysis.

An insignificant shift of the CN absorption band in the IR spectra of **4** and **5** ($\Delta\nu_{CN}$ 8 cm$^{-1}$ for **4**, $\Delta\nu_{CN}$ 10 cm$^{-1}$ for **5**) means that the nitrogen atom is not involved in the coordination with palladium.

The complexation of phosphine with palladium results in a considerable downfield shift in the $^{31}$P NMR spectra ($\Delta\delta_P$ 18 ppm

† *Synthesis of* **1**: To a solution of (1-diphenylphosphoryl)cyclopropanecarbonitrile **2** (0.48 g, 1.87 mmol) in benzene (120 ml) trichlorosilane (9.35 mmol) was added. After reflux in an argon atmosphere for 15 h, the reaction mixture was cooled and evaporated to dryness. Acetonitrile (50 ml) was added to the residue and the formed precipitate of polymeric siloxane was filtered off. After removing the solvent from the filtrate, 0.45 g (95%) of phosphine **1** was obtained as a low-melting waxy substance, 100% pure according to $^1$H and $^{31}$P NMR. $^1$H NMR (400.26 MHz, $CDCl_3$) $\delta$: 1.33–1.39 (m, 2H, $CH_2$), 1.60–1.64 (m, 2H, $CH_2$), 7.41–7.42 (6H, *o*-H, *p*-H in Ph), 7.53–7.58 (4H, *m*-H in Ph). $^{13}$C NMR (100.68 MHz, $CDCl_3$) $\delta$: 5.64 (d, P–*C*–CN, $^1J_{PC}$ 24.1 Hz), 14.49 and 14.65 (2s, $CH_2$), 121.27 (CN), 128.37 (d, $^3J_{PC}$ 4.8 Hz), 129.26, 132.31, 132.50, 132.63, 134.53 (d, $^1J_{PC}$ 8.8 Hz). $^{31}$P NMR (162.02 MHz, $CDCl_3$) $\delta$: 12. IR (KBr, $\nu$/cm$^{-1}$): 2228 (CN). Analysis of the corresponding phosphonium salt with methyl iodide [mp 162–163 °C, $^{31}$P NMR ($CDCl_3$) $\delta$: 33.3]: found (%): C, 51.84; H, 4.21; N, 3.51; calc. for $C_{17}H_{17}NPI$ (%): C, 51.91; H, 4.33; N, 3.56.

‡ (1-Diphenylphosphoryl)cyclopropanecarbonitrile **2** was obtained by the cycloalkylation of diphenylphosphorylacetonitrile by 1,2-dibromoethane under phase-transfer catalysis conditions.[13] Selected data for **2**: yield 61%, mp 168–169 °C (EtOH–acetone). $^1$H NMR (400.26 MHz, $CDCl_3$) $\delta$: 1.60–1.65 (m, 2H, $CH_2$), 1.81–1.86 (m, 2H, $CH_2$), 7.52–7.54, 7.61–7.66, 7.83–7.89 (10H, Ph). $^{13}$C NMR (100.68 MHz, $CDCl_3$) $\delta$: 6.66 (d, P–*C*–CN, $^1J_{PC}$ 99.5 Hz), 13.19 ($CH_2$), 119.94 (d, CN, $^2J_{PC}$ 9.1 Hz), 129.44 (d, P–C in Ph, $^1J_{PC}$ 107.7 Hz), 128.45, 128.58, 131.28, 131.37, 132,62, 132.64 (CH in Ph). $^{31}$P NMR (162.02 MHz, $CDCl_3$) $\delta$: 27.7. IR (KBr, $\nu$/cm$^{-1}$): 1195 (P=O), 2233 (CN). Found (%): C, 71.94; H, 5.12; N, 5.11. Calc. for $C_{16}H_{14}NOP$ (%): C, 71.91; H, 5.24; N, 5.24.

§ *Synthesis of palladium complexes* **4** *and* **5**. To a filtered solution of $PdCl_2(PhCN)_2$[16] **3** (0.38 mmol) in benzene (25 ml) phosphine **1** (0.38 mmol in the case of **4**, 0.76 mmol in the case of **5**) was added under argon at 20 °C. Orange (**4**) or yellow (**5**) crystals of the target complex were precipitated in 30 min. The complexes were filtered off to give solvates with benzene molecules (X-ray data) and subsequently dried *in vacuo* (1 h, 20 °C, 1 Torr) to yield solvent-free complexes.

Selected data for **4**: yield 85%, mp 334–335 ° (decomp.). IR (KBr, $\nu$/cm$^{-1}$): 2236 (CN). Found (%): C, 52.19; H, 4.04; N, 2.87, Cl, 13.98. Calc. for $C_{32}H_{28}Cl_4N_2P_2Pd_2$ (%): C, 52.17; H, 3.95; N, 2.77; Cl, 14.03.

Selected data for **5**: yield 93%, mp 303–305 °C (decomp.). $^1$H NMR ($CDCl_3$) $\delta$: 1.78–1.82 (m, 2H, $CH_2$), 1.90–1.94 (m, 2H, $CH_2$), 7.44–7.54 (m, 6H, *o*-, *p*-H in Ph), 7.77–7.82 (m, 4H, *m*-H in Ph). $^{31}$P NMR (162.02 MHz, $CDCl_3$) $\delta$: 30.5. IR (KBr, $\nu$/cm$^{-1}$): 2238 (CN). Found (%): C, 56.51; H, 4.07; N, 3.98; Cl, 10.33. Calc. for $C_{32}H_{28}Cl_2N_2P_2Pd$ (%): C, 56.55; H, 4.12; N, 4.12; Cl, 10.46.

¶ In the case of **4**, we failed to record NMR spectra because it is insoluble in conventional solvents such as $CH_2Cl_2$, $CHCl_3$, THF, $C_6H_6$ and their perdeutero analogues.

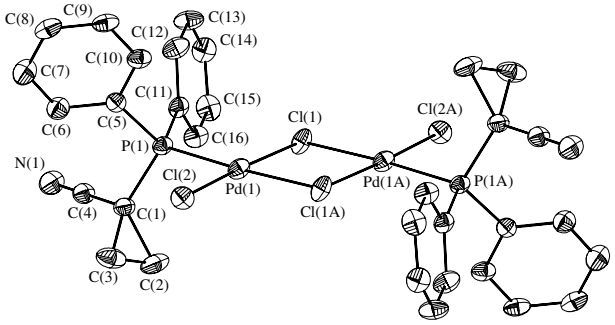



**Figure 1** The general view of **4**. Selected bond lengths (Å): Pd(1)–P(1) 2.229(1), Pd(1)–Cl(1) 2.317(1), Pd(1)–Cl(2) 2.269(1), Pd(1)–Cl(1A) 2.4057(13), P(1)–C(5) 1.793(6), P(1)–C(11) 1.807(5), P(1)–C(1) 1.818(5); selected bond angles (°): P(1)–Pd(1)–Cl(1) 94.65(5), P(1)–Pd(1)–Cl(2) 89.14(5), Cl(1)–Pd(1)–Cl(2) 176.19(5), P(1)–Pd(1)–Cl(1A) 176.86(6), Cl(1)–Pd(1)–Cl(1A) 85.30(5), Cl(2)–Pd(1)–Cl(1A) 90.93(5), Pd(1)–Cl(1)–Pd(1A) 94.70(5), C(1)–P(1)–Pd(1) 113.4(2), C(1)–P(1)–C(5) 109.0(2), C(1)–P(1)–C(11) 102.3(2), C(5)–P(1)–Pd(1) 111.1(1), C(5)–P(1)–C(11) 107.5(2), C(11)–P(1)–Pd(1) 113.0(2).

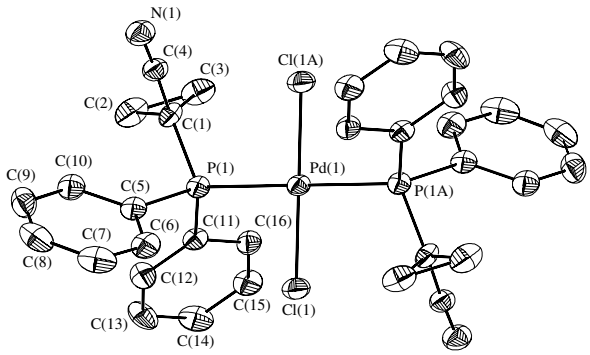
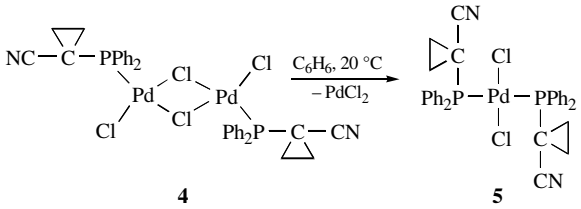



**Figure 2** The general view of **5**. Selected bond lengths (Å): Pd(1)–P(1) 2.321(1), Pd(1)–Cl(1) 2.286(1), P(1)–C(1) 1.839(4), P(1)–C(5) 1.826(4), P(1)–C(11) 1.819(4); selected bond angles (°): P(1)–Pd(1)–Cl(1) 87.54(4), Cl(1)–Pd(1)–Cl(1A) 180.00(7), P(1A)–Pd(1)–P(1) 180.00(6), Cl(1)–Pd(1)–P(1A) 92.46(4), C(1)–P(1)–Pd(1) 115.7(1), C(1)–P(1)–C(5) 103.4(2), C(1)–P(1)–C(11) 104.0(2), C(5)–P(1)–Pd(1) 114.2(1), C(5)–P(1)–C(11) 106.9(2), C(11)–P(1)–Pd(1) 111.6(1).

for **5**). The chemical shift of **5** is close or even greater than that of starting phosphoryl compound **2** ($\delta_P$ 27 ppm), thus indicating rather strong coordination of the phosphorus atom.

According to X-ray diffraction data for **4** and **5**,†† phosphine **1** acts as a monodentate ligand in both complexes and coordinates palladium with only the phosphorus atom (Figures 1 and 2, both complexes in crystals are lying on the centre of symmetry). In contrast to **5**, complex **4** is a rare example[14,15] of relatively stable binuclear palladium complexes with two μ-Cl atoms (in CCDC there are only 14 similar structures). It should be noted that the molecular geometries of phosphine ligands in binuclear and mononuclear complexes are different. Namely, Pd(1)–P(1), P(1)–Ph and P(1)–C(1) bond lengths in **4** are shorter than those in **5** by approximately 0.1, 0.003 and 0.02 Å, respectively. The *trans*-effect apparently causes such alterations, and they are consistent with published data.[6] In addition to changes in the bond lengths, the mutual orientation of the CN group with respect to the Pd–P bond also depends on the complex type. Thus, CN is in an antiperiplanary conformation in **4**, whereas it is in a synclinal conformation in **5**.

Although it is relatively stable, palladium complex *trans*-**4** with bridging chlorine atoms undergoes a gradual transformation to *trans*-**5**. This reaction completed in about two months in a benzene solution (20 °C), and was accompanied by the release of $PdCl_2$. The transformation was monitored by $^{31}P$ NMR spectroscopy.




**4** **5**

Thus, we found that the nitrogen atom of the cyano group in (1-diphenylphosphino)cyclopropanecarbonitrile **1**, as well as in unsubstituted cyanomethyldiphenylphosphine,[12] is not involved in coordination with palladium(II). Ligand **1** forms a stable 1:1 complex with bridging chlorine atoms.

This work was supported by the Russian Foundation for Basic Research (grant nos. 99-03-33014, 00-15-97386 and 00-03-32807). We are grateful to Professor O. V. Gussev for his helpful comments.

## References

1 O. Loiseleur, M. Hayashi, N. Schmees and A. Pfaltz, *Synthesis*, 1997, 1338.
2 A. Sudo and K. Saigo, *J. Org. Chem*., 1997, **62**, 5508.
3 J. M. Brown, D. I. Hulmes and T. P. Layzell, *J. Chem. Soc., Chem. Commun*., 1993, 1673.
4 J. M. Valk, G. A. Whitlock, T. P. Layzell and J. M. Brown, *Tetrahedron Assymetry*, 1998, **6**, 2593.
5 C. Pisano, G. Consiglio, A. Sironi and M. Moret, *J. Chem. Soc., Chem. Commun*., 1991, 421 (and references therein).
6 A. V. George, L. D. Field, E. Y. Malouf, A. E. D. McQueen, S. R. Pike, G. R. Purches, T. W. Hambley, I. E. Buys, A. H. White, D. C. R. Hockless and B. W. Skelton, *J. Organomet. Chem*., 1997, **538**, 101.
7 M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer and V. P. Wystrach, *J. Am. Chem. Soc*., 1959, **81**, 1103.
8 K. Cheng and B. M. Foxman, *J. Am. Chem. Soc*., 1977, **99**, 8102.
9 F. A. Cotton, L. M. Daniels, S. C. Haefner and E. N. Walke, *Inorg. Chim. Acta*, 1996, **247**, 105.
10 O. Dahl and F. K. Jensen, *Acta Chem. Scand*., 1975, **B29**, 863.
11 P. Braunstein, D. Matt, F. Mathey and D. Thavard, *J. Chem. Research (S)*, 1978, 232.
12 O. Dahl, *Acta Chem. Scand*., 1976, **B30**, 799.
13 P. V. Kazakov, I. L. Odinets, A. P. Laretina, T. M. Scherbina, P. V. Petrovskii, L. V. Kovalenko and T. A. Mastryukova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1873 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1990, **39**, 1702).
14 P. J. Dyson, J. W. Steed and P. Suman, *CrystEngComm*, 1999, 2.
15 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 1969.
16 J. R. Doyle, P. E. Slade and H. B. Jonassen, *Inorg. Synth*., 1960, **6**, 218.

*Received: 24th August 2001; Com. 01/1841*

†† *Crystallographic data for* **4** *and* **5**: at 110 K, crystals of **4** are triclinic, space group $P\bar{1}$, $C_{32}H_{28}Cl_4N_2P_2Pd_2{\cdot}2C_6H_6$, $a$ = 10.186(3)Å, $b$ = 10.495(3) Å, $c$ = 10.679(3) Å, $\alpha$ = 76.933(6)°, $\beta$ = 79.305(6)°, $\gamma$ = 76.891(6)°, $V$ = = 1072.1(5) Å$^3$, $Z$ = 1, $M$ = 1013.32, $d_{calc}$ = 1.570 g cm$^{-3}$, $\mu$(MoKα) = = 11.96 cm$^{-1}$, $F$(000) = 508; crystals of **5** are monoclinic, space group $P2_1/n$, $C_{32}H_{28}Cl_2N_2P_2Pd$, $a$ = 9.182(3) Å, $b$ = 15.008(6) Å, $c$ = 11.478(3) Å, $\beta$ = 107.90(1)°, $V$ = 11505.1(9) Å$^3$, $Z$ = 2, $M$ = 1013.32, $d_{calc}$ = 1.570 g cm$^{-3}$, $\mu$(MoKα) = 11.96 cm$^{-1}$, $F$(000) = 508. Intensities of 6992 and 5831 reflections for **4** and **5** were measured with a Smart 1000 CCD diffractometer at 110 K [$\lambda$(MoKα) = 0.71072 Å, $\omega$-scans with a 0.3° step in $\omega$ and 30 s per frame exposure, $2\theta < 52$ and 55°], and 4147 and 3281 independent reflections ($R_{int}$ = 0.0380 and 0.0285) for **4** and **5**, respectively, were used in a further refinement. The absorption correction for both structures was carried out semi-empirically from equivalents. The structures were solved by a direct method and refined by the full-matrix least-squares technique against $F^2$ in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation in **5** and the riding approximation for **4**. The analysis of the Fourier electron density synthesis in **4** revealed that a solvate benzene molecule is disordered by two positions which were refined as the rigid groups with occupancies 0.75 and 0.25. The refinement converged to $wR_2$ = 0.0993 and GOF = 0.902 for all independent reflections [$R_1$ = 0.0490 was calculated against $F$ for 2322 observed reflections with $I > 2\sigma(I)$] for **4** and to $wR_2$ = 0.1113 and GOF = 1.203 for all independent reflections [$R_1$ = 0.0494 was calculated against $F$ for 2330 observed reflections with $I > 2\sigma(I)$] for **5**. All calculations were performed using the SHELXTL PLUS 5.0 program package on IBM PC AT. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/101.