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Binuclear titanium(III) complex derived from diphenylphosphanylmalononitrile, $[\mu^2(N,N')\text{-}Ph_2PC(CN)_2TiCp_2]_2$: Synthesis, structure and properties

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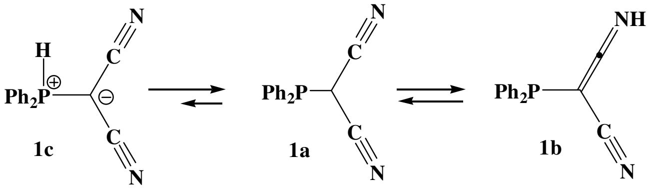
Abstract

Diphenylphosphanyl malononitrile, $Ph_2P–CH(CN)_2$ (**1**) reacts with Cp_2TiCl in the presence of triethylamine in THF to give air sensitive Ti(III) complex $[\mu^2(N,N')\text{-}Ph_2PC(CN)_2TiCp_2]_2$ (**2**), which is centrosymmetric dimer in the solid state, containing nearly planar 12-member metallocycle. Solution of **2** (200 K) exhibits anisotropic EPR spectrum; every spectral component contains splitting on a single phosphorus nucleus.

Keywords: Transition metal complexes; Titanium; Metallocenes; Malononitrile; Phosphinoamides; Imido-complexes; X-ray diffraction

1. Introduction

Hybrid ligands that contain both soft and hard donor atoms are currently receiving increasing attention due to their potentials for generating metal complexes with unusual reactivity as well as bimetallic complexes containing metals of different nature [1]. Diphenylphosphanyl-derivative of malononitrile, $Ph_2P–CH(CN)_2$ (**1**) [2] shows dynamic behavior due to increased mobility of aliphatic hydrogen.



This promising ligand may show so far multiple reactivity, using phosphorus-, carbon- and nitrogen-active centers. However equilibrium concentration of ylide form **1c** is negligibly small. It is known that for the raise the stability of ylide form more bulky substituents at phosphorus (e.g. *t*-Bu) are required [3]. Interestingly, IR spectrum of **1** contains absorption bands in the NH region (our data: 3400 (m), 3185 (w)), which may be assigned to associated and non-associated forms, and two very strong absorptions at 2170 and 2122 cm^{-1} which may be explained by the presence of both cyano (C≡N) and ketimido-groups (=C=N–). To that note, that ^1H NMR spectrum of **1** consists of single resonance at 4.05 ppm (NH), while P–CH fragment should give doublet due to splitting on phosphorus nucleus.

Pure diphenylphosphanylmalononitrile is relatively stable compound while its solutions in THF show limited stability. So, yellow solution of **1** slowly turned deep red for a period of a day at room temperature to give a mixture of products, probably oligomers.

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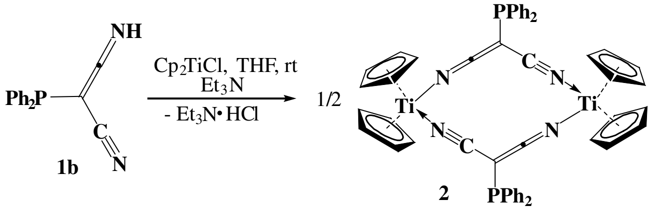
Schwartz reagent $[Cp_2ZrHCl]_n$ is known to react with diphenylphosphanylmalononitrile leading to the corresponding zirconocene ketimide complexes [2]. In this communication we report another remarkable example of fixation of ketimido form of **1** by its interaction with Cp_2TiCl.

2. Results and discussion

Starting diphenylphosphanylmalononitrile was prepared by modified method [2]. Addition of a stoichiometric amount of chlorodiphenylphosphine to $NaHC(CN)_2$ (prepared by the reaction of sodium bis(trimethylsilyl)amide, $(Me_3Si)_2NNa$, with malononitrile) affords the corresponding phosphino-derivative **1** in 90% preparative yield.

Interaction of **1** with η^5-dicyclopentadienyltitanium(III) chloride in THF in the presence of Et_3N (molar ratio 1:1:1) affords binuclear complex **2** in 60% preparative yield:



Triethylamine hydrochloride was filtered and the product (**2**) was separated from concentrated filtrate in the manner of greenish-violet crystals, extremely air sensitive.

IR spectrum of **2** in nujol displays two strong absorption bands of CN groups at 2190, 2145 cm^{-1}. These values are shifted for ~20 cm^{-1} as compared with the bands of free ligand **1** (2170, 2122 cm^{-1}). The structure of **2** was confirmed by X-ray diffraction study on a suitable crystal (Fig. 1). Molecule **2** represents centrosymmetric dimer in crystal. Both titanium(III) atoms adopting tetrahedral configuration are coordinated to two cyclopentadienyl rings and two nitrogen atoms of two ketimido-forms of diphenylphosphanylmalononitrile, which are bridge ligands. 12-Member metallocycle is nearly planar, with average deviation of 0.04 Å from the plane. Crystal data and structure refinement for **2** are given in Table 1. Selected bond lengths and angles for **2** are shown in Table 2. Carbon atoms C(1), C(1A) adopt planar sp^2 configuration with sum of angles 360° and C(2)–C(1)–C(3) bond angle 116.95(15)°. The C–N bonds in the molecule {N(1)–C(2) 1.159(2) and N(2)–C(3) 1.154(2) Å} are nearly equivalent. Similar justification of C–N bond distances in the bridge ($M \leftarrow N{\equiv}C–CR{=}C{=}N–M$) is observed in the copper(I) dimer $(Ph_3P)_2Cu[NC–C(CN)–CN]_2Cu(Ph_3P)_2$ [4] (C–N bond lengths are 1.153 Å and 1.145 Å in the bridge and 1.131 Å in terminal CN group). So the found distances

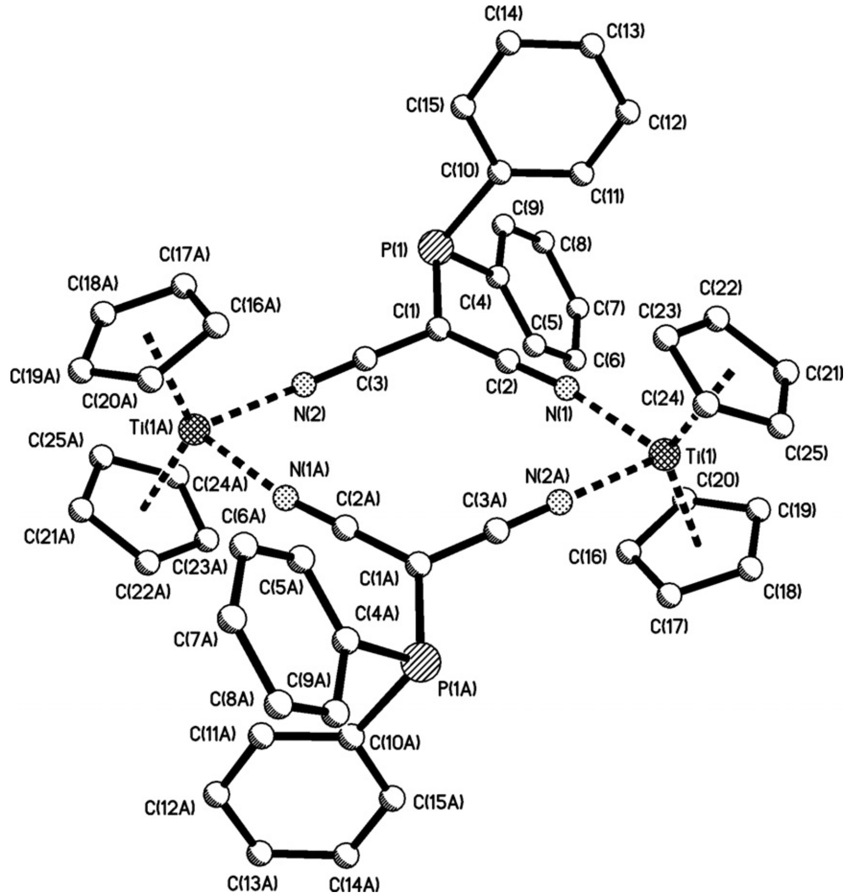


Fig. 1. Molecular structure of **2**, $[\mu^2(N,N')\text{-}Ph_2PC(CN)_2TiCp_2]_2$. Hydrogen atoms omitted for clarity.

Table 1
Crystal data and structure refinement for **2**

Empirical formula	$C_{58}H_{56}N_4O_2P_2Ti_2$
Formula weight	998.81
Temperature (K)	100(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	13.2597(9)
b (Å)	8.7973(6)
c (Å)	21.3829(15)
β (°)	91.145(2)
V (Å^3)	2493.8(3)
$F(000)$	1044
Z	2
D_{calc} (Mg m^{-3})	2493.8(3)
μ (mm^{-1})	0.432
Crystal size (mm)	0.24 × 0.13 × 0.06
θ Range (°)	1.91–26.51
Reflections collected	21211
Reflections unique (R_{int})	5139 (0.0648)
Data/restraint/parameters	5139/5/419
R_1, wR_2 [$I > 2\sigma(I)$]	0.0406, 0.0791
R_1, wR_2 (all data)	0.0724, 0.0890
Goodness-of-fit	1.016
Largest difference in peak and hole (e Å^{-3})	0.406/−0.240

Table 2
Selected distances (Å) and angles (°) for **2**

Ti(1)–N(1)	2.143(2)	N(1)–Ti(1)–N(2)#1	79.56(5)
Ti(1)–N(2)#1	2.144(2)	C(1)–P(1)–C(4)	105.24(8)
Ti(1)–C(16)	2.347(2)	C(1)–P(1)–C(10)	103.98(8)
Ti(1)–C(24)	2.386(2)	C(4)–P(1)–C(10)	98.97(8)
P(1)–C(1)	1.797(2)	C(2)–N(1)–Ti(1)	169.7(1)
P(1)–C(4)	1.831(2)	C(3)–N(2)–Ti(1)#1	170.3(1)
N(1)–C(2)	1.159(2)	C(2)–C(1)–C(3)	117.0(2)
N(2)–C(3)	1.154(2)	C(2)–C(1)–P(1)	124.9(1)
C(1)–C(2)	1.392(2)	C(3)–C(1)–P(1)	117.8(1)
C(1)–C(3)	1.403(2)	N(1)–C(2)–C(1)	179.6(2)
		N(2)–C(3)–C(1)	179.2(2)

Symmetry transformations used to generate equivalent atoms: #1: $-x, -y-1, -z$.

are much less than those usually observed for iminato groups C(sp^2)–C=N– (1.29–1.35 Å) [2].

Bond angles N(1)–C(2)–C(1) and N(2)–C(3)–C(1) are linear {179.6(2) and 179.2(2)°, respectively}. Carbon–carbon bond distances in malononitrile fragment {C(1)–C(2) 1.392(2) and C(1)–C(3) 1.403(2) Å} are close to that observed in aromatic compounds.

Both diphenylphosphino-groups do not take part in coordination to metal. Phosphorus–carbon bond distance P(1)–C(1) 1.797(2) Å corresponds to ordinary P–C bond.

EPR spectrum of **2** in CH_2Cl_2/toluene (2/1) solution at ambient temperature (290 K) is a single broad line (~10 G, $g_{iso} = 1.984$) without hyperfine structure. At the same time, frozen solution of **2** (200 K) exhibits anisotropic EPR spectrum with main parameters of g-tensor: $g_1 = 2.025$; $g_2 = 1.987$; $g_3 = 1.942$ (Fig. 2). Every spectral component contains splitting on a single phosphorus nucleus (^{31}P, $I = 1/2$, 100%): $A_1 = 24.2$ G; $A_2 = 16.7$ G; $A_3 = 6.9$ G ($A_{av} = 15.9$ G). Calculated average g-factor $g_{av} = 1.985$ is in a good accordance with experimental $g_{iso} = 1.984$. Titanium satellites are not observed probably due to large line width. In general, g-factor values are typical for Ti^{3+} species [5]. Apparently, complex **2** dissociates in solution and we observe its monomeric form. Coordination mode of ligand **1** in solution cannot be unambiguously determined by EPR method. It should note however, that similar phosphorous isotropic hyperfine coupling constant (10.8 G) was observed in Cp_2TiPMe_2, containing direct phosphorus–metal σ-bond [6]. High value of hyperfine coupling constant for **2** may be attributed to the π-conjugation in this system and electron–acceptor properties of the ligand.

Since Ph_2P– group of phosphanylmalononitrile ligand remains free of coordination, molecule **2** may be considered as a synton or building block for synthesis of bimetallic complexes and extended structures.

3. Experimental

3.1. General procedures

The Cp_2TiCl and $(Me_3Si)_2NNa$ reagents are purchased from Aldrich and used as received. All manipulations were performed with rigorous exclusion of oxygen and moisture, in vacuum or under an argon atmosphere using standard Schlenk techniques. Infrared spectra were recorded on a Perkin–Elmer 577 spectrometer from 4000 to 400 cm^{-1} in nujol. EPR spectra were recorded on a Bruker ER 200 D-SRC spectrometer with ER041 MR microwave bridge, ER 4105 DR double resonator and ER 4111 VT variable temperature unite.

The data for single crystal X-ray structure determination of **2** were collected on a SMART APEX diffractometer (graphite-monochromated, Mo K_α-radiation, ω–θ-scan technique, $\lambda = 0.71073$ Å). The structures were solved by direct methods and were refined on F^2 using SHELXTL [7] package. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms in **2** were found from fourier syntheses of electron density and were refined isotropically. SADABS [8] was used to perform area-detector scaling and absorption corrections. One solvate THF molecule was found in asymmetric unit.

3.2. Synthesis

3.2.1. $NaHC(CN)_2$

An equivalent of $(Me_3Si)_2NNa$ (0.66 M solution in THF, 3.0 mL) was added to the solution of malononitrile in THF (0.13 g, 2.0 mmol) at −78 °C. The resulting mixture was stirred and allowed to warm slowly to room temperature. The crystalline precipitate of sodium salt ($NaHC(CN)_2$) was filtered, washed with cold solvent and dried in vacuum. Yield 0.16 g (92%). IR (nujol), ν (cm^{-1}): 3511 (w), 3303 (w), 3073 (m, CH), 2142 (vs, CN), 1357

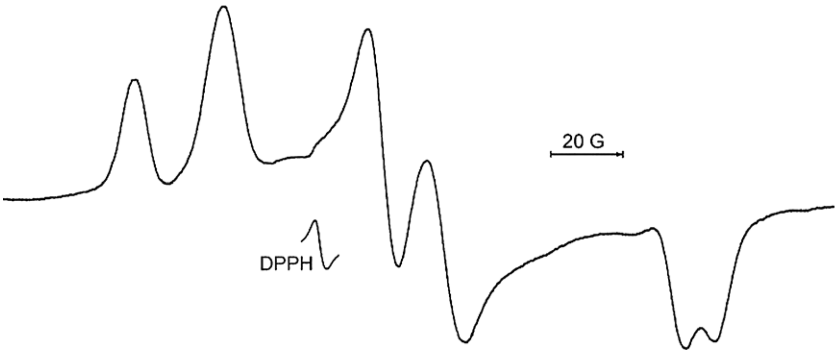


Fig. 2. EPR spectrum of **2** [CH_2Cl_2/PhMe (2:1), 200 K].

(m), 1250 (w), 1138 (s), 1073 (s), 910 (m), 842 (w), 723 (w), 634 (m), 545 (vs), 470 (s).

3.2.2. *Ph_2P–CH(CN)$_2$ (or Ph_2P–C(CN)=C=NH) (**1**)*

A solution of Ph_2PCl (1.10 g, 5.0 mmol) in THF (8 mL) was added dropwise to the suspension of $NaHC(CN)_2$ (0.44 g, 5.0 mmol) in the same solvent at −20 °C. The reaction mixture turned clear, and then precipitate (NaCl) was formed (ca. 15 min). The mixture was slowly warmed to room temperature over 0.5 h, filtered, and the solvent was evaporated. The resulting solid residue was washed with Et_2O and pumped in a vacuum line over 1 h at 20 °C to give **2** as a bright-yellow non-crystalline solid. Yield: 90% (1.13 g). $^{31}P\{^1H\}$ NMR (THF): $\delta = -6.0$ ppm. ^1H NMR (THF-d_8): $\delta = -7.00$ to -8.00 (m, 10H, Ph) ppm; 4.05 (1H, NH) ppm. ^{13}C NMR (THF-d_8): $\delta = 7.0$–7.4 (m, P–CH); 126.8 (s, *p*-Ph); 127.4 (d, $^3J_{C,P} = 6.4$ Hz, *m*-Ph); 128.0–128.6 (m, CN); 132.1 (d, $^2J_{C,P} = 19.3$ Hz, *o*-Ph), 142.1 (d, $^1J_{C,P} = 11.2$ Hz, *i*-Ph) ppm. IR (nujol), ν (cm^{-1}): 3400 (m, NH), 3185 (w, NH), 2170 (vs, C≡N), 2122 (vs, C=N), 1653 (w), 1585 (m), 1432 (m), 1307 (w), 1240 (m), 1182 (m), 745 (s), 698 (s), 567 (s), 550 (s), 528 (m), 470 (w), 432 (w).

3.2.3. *[[μ^2(N,N′)-$Ph_2PC(CN)_2TiCp_2$]$_2$ (THF solvate) (**2**)*

A freshly prepared solution of **1** (0.25 g, 1.0 mmol) in THF (10 mL) was added to the mixture of Cp_2TiCl (0.21 g, 1.0 mmol) and excess of Et_3N (0.15 g, 1.5 mmol) in the same solvent (5 mL) at 20 °C. The resulting mixture was stirred 2 h at room temperature. The crystalline precipitate of triethylammonium hydrochloride was filtered; the solution was concentrated to 5 mL and maintained at 0 °C. Dark green-violet crystals of **2** was filtered and dried in vacuum line. Yield 0.27 g (60%). Anal. Calc. for $C_{54}H_{48}P_2N_4OTi_2$: C, 69.98; H, 5.22; P, 6.68, Ti, 10.34. Found: C, 70.12; H, 5.18; P, 6.73; Ti, 10.28%. IR (nujol), ν (cm^{-1}): 2190 (m, CN), 2146 (s, CN), 1253 (m), 1068 (m), 1012 (m, Cp), 913 (m), 803 (s, Cp), 743 (m), 696 (m), 562 (w), 548 (m), 530 (w).

4. Supplementary material

CCDC 644157 contains the supplementary crystallographic data for **2**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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