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A palladium(II) complex with a chelating (carboxy) phosphanoalkyl ligand

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Abstract

rac-[*SP*-4-2]-{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{[2-(diphenylphosphanyl-κP)ferrocenyl](methoxycarbonyl)methyl-κC} palladium(II) (**1**) was synthesized by deprotonation of [*SP*-4-4]-chloro{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{rac-methyl 2-(diphenylphosphanyl)ferrocenylacetate-κP}palladium(II) with *t*-BuOK. Complex **1** was characterized by spectral methods and its reactivity studied. The structure of **1** was determined by X-ray crystallography and discussed in relation to other complexes with phosphanoalkyl ligands derived from phosphanoacetic esters.

Keywords: Palladium; Phosphinoester ligands; Alkyl complexes; Ferrocene; X-ray crystallography

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Indroduction

Phosphanoalkyl ligands obtained from phosphanocarboxylic ligands often shown interesting coordination behaviour. It has been shown that anions resulting from a deprotonation of phosphanoacetic esters ($[R^1_2PCHCO_2R^2]^-$) can coordinate as chelating enolate (**A** [1], **B** [2]) or phosphanomethanide(1−) (**C**, [2,3]) ligands. These two modes are mutually intercovertible [2] and can even coexist in one molecule (**D**) [4]. Besides, the anion $[Ph_2PCHCO_2Et]^-$ is capable of acting as a μ-1κP:2κC^1 bridge between two palladium(II) atoms bearing additional *ortho*-metallated ligands, the respective bridged dinuclear complex being accessible from **A**-type compounds [1,5]. Complexes **A**–**D** react willingly with polar molecules, affording various insertion and addition products (Chart 1).

We have recently reported about the synthesis of *rac*-[2-(diphenylphosphano)ferrocenyl]acetic acid and coordination chemistry of this acid and its methyl ester in a series of palladium(II) complexes with *ortho*-metallated *N*,*N*-dimethylbenzylamine as an auxiliary ligand [6]. As there is a direct relation between these novel organometallic ligands and the respective (diphenylphosphano)acetic acid derivatives, we have turned, in view of the above results, to study the reactivity of *C*-deprotonated ferrocene phosphanoester.

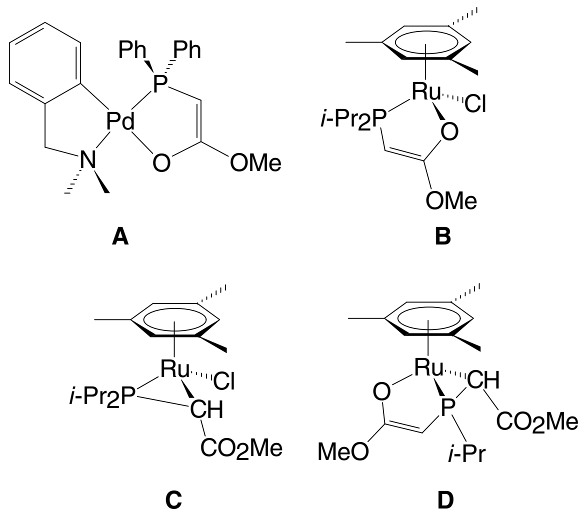

Chart 1.

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Of the two general approaches, i.e., pre-formation of a phosphanomethanide anion followed by the reaction with a transition metal compound [1,5] or a deprotonation of an already coordinated ligand [2–4], the latter one was chosen. Thus, a reaction of complex **4** with excess potassium *tert*-butoxide in tetrahydrofuran followed by crystallization from dichloromethane–hexane afforded bis-chelate compound **1** (see Scheme 1) as a rusty-orange, crystalline solid, which is well soluble in THF and halogenated solvents. The same compound was obtained using sodium hydride as the base or when complex **4** was formed in situ by reacting stoichiometric amounts of the precursors **2** and **3** [6].

NMR spectra of **1** show characteristic signals due to the palladium-bonded methine group [δ_H 3.26 (s), δ_C 41.28 (d, $J_{PC} = 4$ Hz)] and phosphorus coupling patterns ($^4J_{PH}$ [1,6,7] and $^3J_{PC}$ [6]) typical for a *trans*-P,N arrangement. ^{31}P NMR spectrum displays a singulet at $\delta_P + 41.5$, significantly downfield compared to the parent complex **4** (δ_P 28.0, [6]). Another characteristic feature of **1** is a strong $\nu_{C=O}$ band in IR spectra at 1652 cm^{-1}, shifted by ca. 80 cm^{-1} to lower energies from the position observed for **3** and **4** [6]. The shift corresponds well to the trends in the series [Ru(η^6-1,3,5-$Me_3C_6H_3$)$RuCl_2$(*i*-$Pr_2PCH_2CO_2Me$-κP)] ($\nu_{C=O}$ 1719 cm^{-1}), **B** ($\nu_{C=O/C=C}$ 1524 cm^{-1}) and **C** ($\nu_{C=O}$ 1661 cm^{-1}) [2b].

Compared to the related compounds mentioned above, complex **1** is chemically very robust. It remains unchanged when stored in air for several weeks. The complex does not react with CO_2 but slowly decomposes to metallic palladium when exposed to CO (in CH_2Cl_2 at room temperature and 1 atm). Attempted insertion reactions with internal alkynes [$MeO_2CC\equiv CCO_2Me$ (1 or 3 equiv.), $PhC\equiv CPh$ (1 equiv.) or $EtC\equiv CEt$ (3 equiv.); in CH_2Cl_2 at 50 °C for 20 h] lead to a recovery of the unchanged starting material whereas a reactions with iodine or HBF_4 (both ca. 1 equiv.) gave only intractable mixtures.

The molecular structure of **1** was determined by single-crystal X-ray diffraction and is shown on Fig. 1. The selected geometric data are given in Table 1. The coordination sphere around palladium is almost perfectly planar [the maximum deviation from the least-

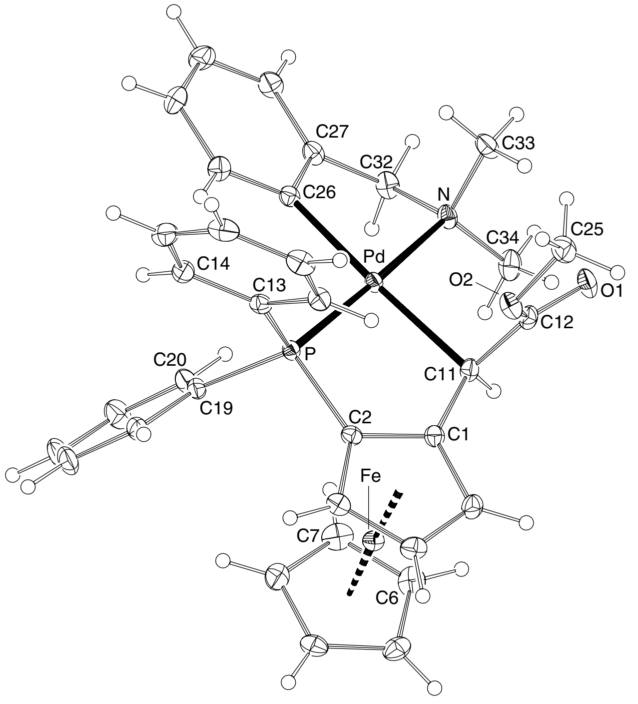
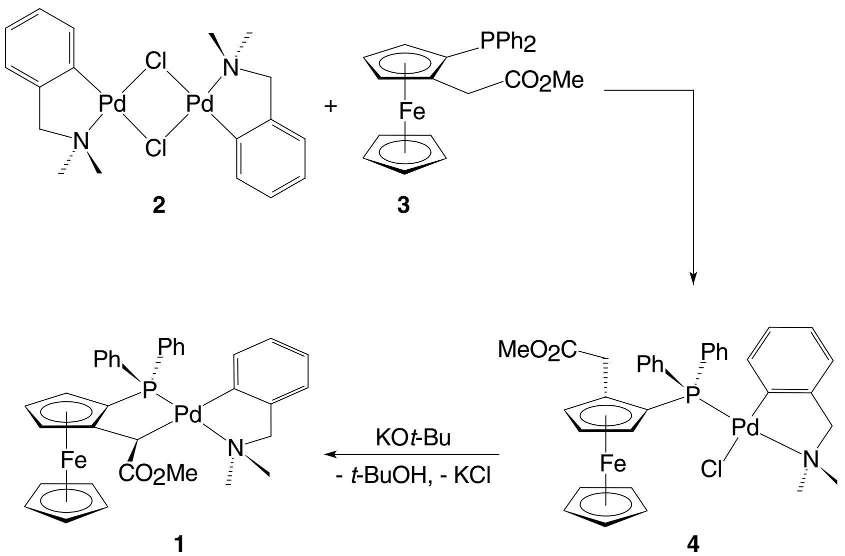


Fig. 1. A perspective view of the molecular structure of **1** showing the atom labelling scheme. Thermal motion ellipsoids are drawn at the 30% probability level.



Scheme 1.

Table 1
The selected geometric data for **1** (in Å and °)[a]

Pd–P	2.2318(6)	P–Pd–C(11)	86.11(6)
Pd–N	2.167(2)	P–Pd–C(26)	96.27(6)
PdC(11)	2.208(2)	N–Pd–C(11)	96.66(7)
Pd–C(26)	2.054(2)	N–Pd–C(26)	81.06(7)
P–C(2)	1.794(2)	C–P–C[b]	101.82(9)–108.99(9)
P–C(13)	1.825(2)	C(1)–C(11)–C(12)	114.1(2)
P–C(19)	1.825(2)	C(11)–C(12)–O(1)	126.8(2)
C(12)–O(1)	1.223(3)	C(11)–C(12)–O(2)	113.1(2)
C(12)–O(2)	1.367(3)	O(1)–C(11)–O(2)	120.1(2)
O(2)–C(25)	1.436(3)	C(12)–O(2)–C(25)	115.4(2)
C(1)–C(11)	1.503(3)	Pd–C(11)–C(12)	102.5(1)
C(11)–C(12)	1.456(3)		
Fe–Cg1	1.6464(9)	Cg1–Fe–Cg2	177.90(5)
Fe–Cg2	1.655(1)		

[a] Plane definitions: Cp1: C(1–5); Cp2: C(6–10); Ar: C(26–31); Ph1: C(13–18); Ph2: C(19–24). Cg1 and Cg2 are the centroids of the cyclopentadienyl rings Cp1 and Cp2, respectively.

[b] The range of C(2)–P–C(13,19), C(13)–P–C(19) angles.

squares plane defined by palladium and the four ligating atoms is 0.049(2) Å for N] with a *trans*-P–N geometry. The Pd-donor distances compare well to similar, structurally characterized compounds [*SP*-4-2]-{2-[(dimethylamino)methyl]phenyl-κ^2C^1,N}[{1,1,2,2-tetracyano-3-ethoxycarbonyl-4-(diphenylphosphanyl)but-1-yl-κ^2C^1,P}]palladium(II) [8] and [*SP*-4-2]-{(*R*)-2-[1-(dimethylamino)ethyl]phenyl-κ^2C^1,N}(3-diphenylphosphanyl-2-diphenylphosphonia-1-methoxycarbonylprop-1-yl-κ^2C^1,P^3)palladium(II) perchlorate [9] (in square brackets for the latter compound): Pd–P 2.221(2) [2.245], Pd–N 2.159(7) [2.150], Pd–C(aryl) 2.027(9) [1.970] and Pd–C(alkyl) 2.211(8) [2.171] Å.

The palladium atom in **1** is a part of two five-membered metallacycles with similar chelate bite angles: P–Pd–C11 86.11(6) and N–Pd–C26 81.06(7)°. The ring of the (aminomethyl)phenyl ligand is twisted with a conformation between an envelope and a half-chair, having the aryl ring rotated from the coordination plane by as much as 18.57(8)° along the C26–C29 axis. The other ring involving the phosphinoferrocenyl ligand is planar due to the rigidity of the conjugated ferrocene unit [the maximum displacement from the ring plane is 0.053(2) Å for C11] and nearly coincides with the coordination plane (dihedral angle 4.32(6)°). A comparison with the structure of **4** [6] indicates that the deprotonation/coordination of *P*-bonded ester does not alter the ligand structure in any significant way (cf. relative bond length changes vs. **4**: Pd–P −2%, Pd–N +0.7%, Pd–C26 +2%, C1–C11 +0.7%, C11–C12 −3%, C12–O1 +1%, C12–O2 +2%, O2–C25 −1%). The phosphanoalkyl ligand is bonded without a torsion at the ferrocene unit (cf. τ(C11–C1–C2–P) of only 0.2(3)°) and any significant contribution of a resonance enol form as indicated by tetrahedral arrangement around C11 and unchanged geometry of the methoxycarbonyl group, which is disposed above the coordination plane. This supports the formulation of **1** as a compound with simple phosphane-modified alkyl ligand, related to **C**-type complexes.

In summary, complex **1** represents a new entry among complexes with functionalized organyl ligands. Notably, its is available in a stereodefined form since racemic **4** (or **3**) gives (*S*,*R*$_p$)/(*R*,*S*$_p$)-**1** as the only diastereoisomer detected by NMR spectra. Further studies on the reactivity of **1** and the carboxy(phosphanoferrocenyl) methanide anion are currently underway.

Experimental

Materials and methods

The syntheses were carried under argon atmosphere with an exclusion of the direct day light. Tetrahydrofuran was dried over potassium and freshly distilled from potassium-benzophenone ketyl under argon. Dichloromethane was dried over potassium carbonate. Hexane for crystallizations was used without purifica- tion. Di-μ-chlorobis{2-(dimethylaminomethyl-κN)phenyl-κC^1}dipalladium(II) (**2**) [10], *rac*-methyl [2-(diphenylphosphanyl) ferrocenyl]acetate (**3**) and [*SP*-4-4]-chl oro{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{*rac*-methyl [2-(diphenylphosphanyl)ferrocenyl]acetate-κP}palladium(II) (**4**) [6] were prepared as described previously.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58; ^{31}P, 161.90 MHz) at 298 K. Chemical shifts (δ/ppm) are given relative to an internal tetramethylsilane (^{1}H and ^{13}C) or an external 85% aqueous H_3PO_4 (^{31}P). IR spectra were recorded on an FT IR Nicolet Magna 650 instrument in the range of 400–4000 cm^{-1}.

Synthesis of rac-[SP-4-2]-{2-[(dimethylamino-κN)methyl]phenyl-κ^1C}{[2-(diphenylphosphanyl-κP)ferrocenyl](methoxycarbonyl)methyl-κC}palladium(II) (**1**)

Di-μ-chlorobis{2-(dimethylaminomethyl-κN)phenyl-κC^1}dipalladium(II) (**2**) (276 mg, 0.50 mmol) and *rac*-methyl [2-(diphenylphosphanyl)ferrocenyl]acetate (**3**) (443 mg, 1.0 mmol) were dissolved in THF (30 mL). The resulting, clear orange solution was stirred for 30 min. Potassium *tert*-butoxide (337 mg, 3.0 mmol) was added and the mixture was stirred for 24 h. Then, the solvent was removed under reduced pressure and the solid residue extracted into dichloromethane-hexane (1:1, v/v; 50 mL in several portions). The extract was filtered, evaporated to dryness, redissolved in dichloromethane, and re-crystallized by a careful addition of hexane and crystallization by liquid-phase diffusion over several days at room temperature to give solvate $\mathbf{1}\cdot 1/2CH_2Cl_2$ as a rusty orange crystalline solid (427 mg, 59%; two crops).

A similar reaction but with defined complex **4** gave an identical product. Recrystallization of crude **1** from dichloromethane solutions gives solvates with varying solvent content depending on the crystallization conditions. Crystals of unsolvated **1** used for X-ray diffraction analysis were obtained by recrystallization from THF-hexane.

NMR ($CDCl_3$): δ_H 2.61 (d, $^4J_{PH} = 1.8$ Hz, 3H, N*Me*), 3.06 (s, 3H, O*Me*), 3.21 (d, $^4J_{PH} = 2.9$ Hz, 3H, N*Me*), 3.26 (s, 1H, C*H*Pd), 3.57 (dd, $^2J_{HH} = 13.1$, $^4J_{PH} = 4.0$ Hz, 1H, NCH_2), 3.86 (s, 5H, C_5H_5), 3.97 (apparent dt, $J = 2.6$, 1.3 Hz, 1H, C_5H_3), 4.25 (apparent dt, $J = 1.1$, 2.1 Hz, 1H, C_5H_3), 4.43 (apparent t, J approx. 2.4 Hz, 1H, C_5H_3), 4.77 (d, $^2J_{HH} = 13.1$ Hz, 1H, NCH_2), 6.69–7.92 (m, 14 H, aromatics); δ_C 41.28 (d, $J_{PC} = 4$ Hz, *C*HPd), 48.23 (d, $^3J_{PC} = 3$ Hz, N*Me*), 49.52 (s, O*Me*), 52.19 (d, $^3J_{PC} = 2$ Hz, N*Me*), 67.40 (s, *C*H of C_5H_3), 69.38 (d, $J_{PC} = 15$ Hz, *C*H of C_5H_3), 70.04 (s, C_5H_5), 74.92 (d, $J_{PC} = 6$ Hz, *C*H of C_5H_3), 75.34 (d, $^3J_{PC} = 2$ Hz, NCH_2), 86.71 (d, $^1J_{PC} = 62$ Hz, *C*P of C_5H_3), 102.38 (d, $^2J_{PC} = 31$ Hz, *C*CHPd of C_5H_3), 121.98 (s, *C*H of C_6H_4), 123.62 (s, *C*H of C_6H_4), 125.27 (d, $J_{PC} = 4$ Hz, *C*H of C_6H_4), 127.80 (d, $J_{PC} = 10$ Hz, *C*H of PPh_2), 128.04 (d, $J_{PC} = 10$ Hz, *C*H of PPh_2), 129.57 (d, $^4J_{PC} = 2$ Hz, CH_p of PPh_2), 130.35 (d, $^1J_{PC} = 54$ Hz, C_{ipso} of PPh_2), 130.67 (d, $^4J_{PC} = 2$ Hz, CH_p of PPh_2), 133.02 (d, $J_{PC} = 12$ Hz, *C*H of PPh_2), 134.75 (d, $^1J_{PC} = 46$ Hz, C_{ipso} of PPh_2), 135.13 (d, $J_{PC} = 12$ Hz, *C* H of PPh_2), 139.93 (d, $J_{PC} = 9$ Hz, *C*H of PPh_2), 149.04 (d, $J_{PC} = 1$ Hz, C_{ipso} of C_6H_4), 160.38 (d, $J_{PC} = 6$ Hz, C_{ipso} of C_6H_4), 178.39 (s, $C{=}O$); δ_P +41.5 (s). IR (Nujol) for $\mathbf{1}\cdot 1/2CH_2Cl_2$: $\bar{\nu}$/cm^{-1} $\nu_{C=O}$ 1652vs, 1235s, 1207s, 1177m, 1263m, 1039s, 1026m, 923m, 844s, 824m, 803m, 748m, 739vs, 733vs, 701s, 695s, 541s, 509s, 469s. *Anal.* Calc. for $C_{34}H_{34}FeNO_2PPd \cdot CH_2Cl_2$: C, 54.82; H, 4.73; N, 1.83. Found: C, 55.14; H, 4.97; N, 1.75%.

X-ray crystallography

Crystallographic data for **1**: $C_{34}H_{34}FeNO_2PPd$ ($M = 681.84$ g mol^{-1}), orange block, $0.43 \times 0.43 \times 0.45$ mm^3; triclinic, space group $P\bar{1}$ (no. 2), $T = 150$ K, $a = 9.5707(2)$ Å, $b = 10.6603(2)$ Å, $c = 16.1091(3)$ Å; $\alpha = 107.3043(6)°$, $\beta = 97.0567(6)°$, $\gamma = 107.1371(8)°$, $V = 1459.04(5)$ Å^3, $Z = 2$, $\rho_{calc} = 1.552$ g cm^{-3}, $F(000) = 696$; $2\theta_{max} = 27.5°$, 23 792 total, 6665 unique, 6094 observed [$I > 2\sigma(I)$] diffractions (Nonius KappaCCD diffractometer); 368 parameters. Cell parameters were determined by least-squares analysis from 6162 partial diffractions with $1.0 \leqslant \theta \leqslant 27.5°$. The intensity data were numerically corrected for absorption (μ(Mo Kα) = 1.20 mm^{-1}), transmission coefficient range: 0.704–0.790.

The structure was solved by direct methods (SIR92, [11]) and refined by weighted full-matrix least-squares on F_2 (SHELXL97, [12]). All non hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atom at C11 was identified on a difference density map and isotropically refined (C–H 0.96(2) Å). All other hydrogen atoms were included in calculated positions [C–H bond lengths: 0.96 (methyl), 0.97 (methylene) and 0.93 (aromatic) Å] and assigned $U_{iso}(H) = 1.2U_{eq}(C)$ (methylene and aromatic) or 1.5 $U_{eq}(C)$ (methyl). Final R indices; observed (all) diffractions: R 2.41% (2.82%), wR 5.89% (6.07)%. Extremes on the final difference electron density map: +0.42, −0.67 e Å^{-3}.

Crystallographic data excluding the structure factors have been deposited with the Cambridge Crystallographic Data Centre [deposition No. CCDC-222593]. Copies of the data may be obtained upon request to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; http://www.ccdc.cam.ac.uk, e-mail: deposit@ccdc.cam.ac.uk.

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