

Supplementary Information

Metal-mediated coupling of amino acid esters with isocyanides leading to new chiral acyclic aminocarbene complexes

**Tatyana B. Anisimova,^a M. Fátima C. Guedes da Silva,^{*a} Vadim Yu. Kukushkin,^{b,c}
Armando J. L. Pombeiro,^{*a} and Konstantin V. Luzyanin^{*a,b}**

^aCentro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, e-mail: fatima.guedes@tecnico.ulisboa.pt, pombeiro@tecnico.ulisboa.pt

^bInstitute of Chemistry, Saint Petersburg State University, Universitetsky Pr. 26, 198504 Stary Petergof, Russian Federation, e-mail: konstantin.luzyanin@chem.spbu.ru

^cInstitute of Macromolecular Compounds of the Russian Academy of Sciences, V.O. Bolshoi Pr. 31, 199004 Saint Petersburg, Russian Federation

Table S1. Crystal Data and Structure Refinement Details for **9**, **11**, and **12**.

	9	11	12
Empirical formula	C ₂₈ H ₃₁ Cl ₂ N ₃ O ₃ Pd	C ₂₈ H ₃₆ C ₁₅ N ₃ O ₂ Pd	C ₂₆ H ₃₀ Cl ₇ N ₃ O ₂ Pd
Formula weight	634.86	730.25	771.08
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
space group	P 21 21 21	P 21 21 21	P 21
<i>a</i> (Å)	14.3881(4)	12.7792(7)	24.1788(6)
<i>b</i> (Å)	17.1311(6)	16.8591(9)	12.3145(4)
<i>c</i> (Å)	26.0983(10)	17.8453(10)	24.9100(6)
α (deg)	90	90	90
β (deg)	90	90	104.4940(10)
γ (deg)	90	90	90
<i>V</i> (Å ³)	6432.8(4)	3844.7(4)	7180.9(3)
<i>Z</i>	8	4	8
No. rfls.	40590	27200	72209
Rfls Unique/Obs	13994/11853	8552/4971	18319/15342
ρ_{calc} (Mg/m ³)	1.311	1.435	1.426
μ (Mo K α) (mm ⁻¹)	0.773	0.868	1.064
R _{int}	0.0473	0.0717	0.0586
Final R1 ^a , wR2 ^b (<i>I</i> ≥ 2 σ)	0.0439, 0.1335	0.0659, 0.1555	0.0487, 0.1242
GOF	0.684	0.954	1.037

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$

Table S2. Crystal Data and Structure Refinement Details for **13** and **16**.

	13	16
Empirical formula	C ₂₃ H ₃₉ Cl ₂ N ₃ O ₂ Pd	C ₂₃ H ₃₉ I ₂ N ₃ O ₂ Pd
Formula weight	566.87	749.77
Crystal system	Orthorhombic	Monoclinic
space group	P 21 21 21	P 21
<i>a</i> (Å)	9.3639(2)	11.089(3)
<i>b</i> (Å)	14.8451(3)	9.429(4)
<i>c</i> (Å)	18.9144(4)	13.503(7)
α (deg)	90	90
β (deg)	90	93.98(4)
γ (deg)	90	90
<i>V</i> (Å ³)	2629.25(10)	1408.5(10)
<i>Z</i>	4	2
No. rfls.	41297	12473
Rfls Unique/Obs	7564/6755	5145/4850
ρ_{calc} (Mg/m ³)	1.432	1.768
μ (Mo K α) (mm ⁻¹)	0.932	2.873
R _{int}	0.0532	0.0315
Final R1 ^a , wR2 ^b	0.0264, 0.0556	0.0206, 0.0507
(<i>I</i> \geq 2 σ)		
GOF	0.947	0.817

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

Compounds **9** and **12** are crystallized with more than one complex molecule in the asymmetric unit, *viz.*, two molecules in the former case and four in the latter together with four chloroform molecules. Although in **9** the bond distances and angles are similar, the two molecules (denoted by *Pd1* or *Pd2* in accord with their metal atoms) are not superimposable — a fact that results not only from the twisting of the isocyanide moiety but also to the relative orientations of the branches of the carbene ligand (Figure S1 and Table S2).

In what concerns the four complex molecules in **12**, they can differ markedly in the angle between the least-square plane of the phenyl ring of the isocyanide ligand and the least square plane defined by the C_{isocyanide}, the C_{carbene} and the two chloride ligands of the coordination sphere of the metal; that parameter assume values of 59.25, 46.57, 31.98 or 31.11° for Pd1-, Pd2-, Pd3- or Pd4-containing molecules, respectively. Additionally, the C_{pyrrolidine}-C_{ester}-O-C_{tBu} torsion angle in the Pd1 molecule differs greatly from that in the other molecules (-27.59° against an average of 178.51°). The quaternion fit in Figure S2 illustrates the differences in the complex molecules of **12**.

Table S3. Selected comparative angles (°) for the two molecules of **9**.

Parameter *	Pd1	Pd2
∠ plane <i>A</i> and plane <i>B</i>	67.59	46.57
N-C _{carbene} -N-C _{phenyl}	-1.74	5.37
C _{carbene} -N-C-C _{ester}	-162.65	-118.22
C _{carbene} -N-C-C _{methylene}	76.70	118.42
N-C-C _{methylene} -C _{phenyl}	-164.00	67.54

* Plane *A* refers to the least-square plane of the phenyl ring of the isocyanide ligand; plane *B* refers to the least square plane defined by the C_{isocyanide}, the C_{carbene} and the two chloride ligands of the coordination sphere of the metal.

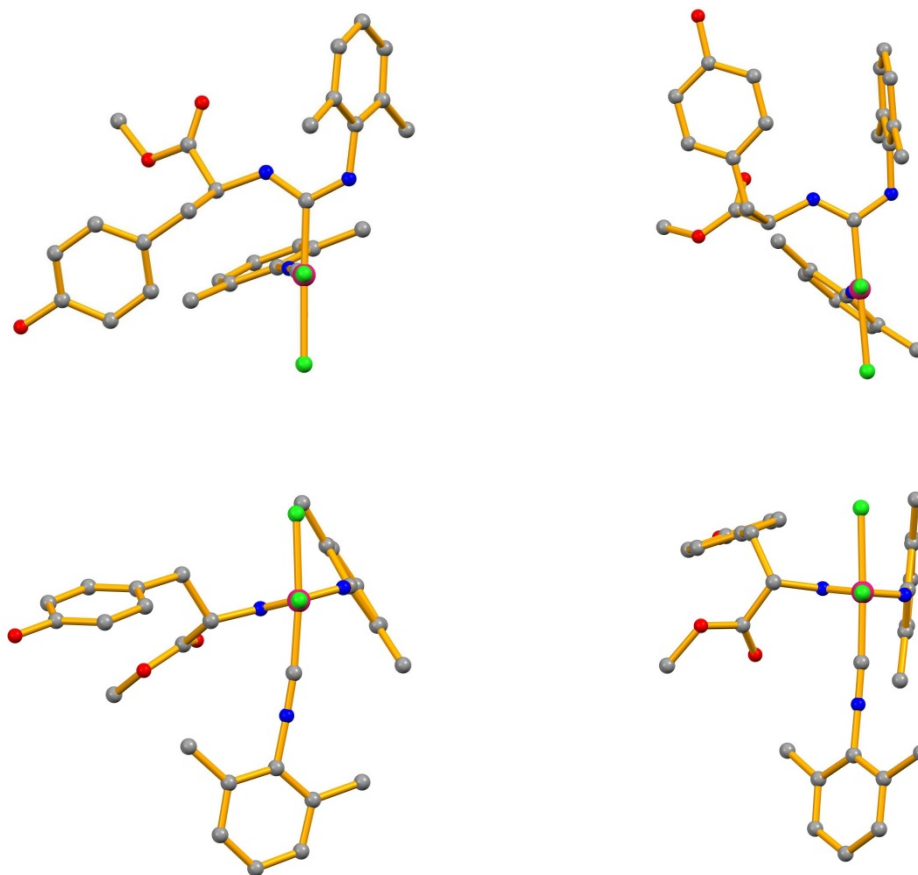


Figure S1. Perspective views of the Pd1- (left) and Pd2- (right) containing molecules of compound **9** oriented along the Cl-Pd-C_{isocyanide} (top) and the Cl-Pd-C_{carbene} axis (bottom).

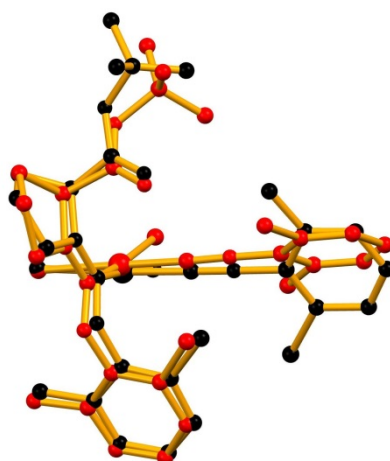


Figure S2. A quaternion fit of the Pd1- (in black) and Pd3- (in red) containing molecules of compound **12** to highlight the relative twisting of the phenyl rings of the isocyanide ligands as well as the torsions of the *t*-butyl ester moieties of the carbenes.

Table S4. Selected bond lengths (Å) and angles (°) in **9** and **11–13**.^(a)

	9	11	12	13	16
Bond lengths:					
Pd1–X1	2.3771(17)	2.359(3)	2.368(3)	2.3561(6)	2.6206(8)
Pd1–X2	2.3012(17)	2.323(3)	2.324(3)	2.3122(8)	2.5992(8)
Pd1–C _{isocyanide}	1.925(7)	1.897(10)	1.900(10)	1.937(3)	2.005(5)
(C–N) _{isocyanide}	1.146(9)	1.150(12)	1.160(12)	1.147(3)	1.151(6)
Pd1–C _{carbene}	1.980(7)	1.974(11)	1.981(10)	1.983(2)	2.007(4)
C _{carbene} –N	1.331(9)	1.336(12)	1.333(13)	1.327(4)	1.334(5)
	1.308(9)	1.318(12)	1.330(13)	1.312(3)	1.322(6)
Bond angles:					
X1–Pd1–X2	91.87(7)	93.54(11)	94.57(10)	92.99(3)	175.030(15)
C _{carbene} –Pd1–C _{isocyanide}	89.5(3)	92.1(4)	92.8(4)	87.84(12)	175.09(19)
X1–Pd1–C _{carbene}	177.8(2)	178.3(3)	176.8(3)	174.34(8)	88.06(13)
Pd1–(C–N) _{isocyanide}	174.3(6)	175.6(9)	176.3(9)	175.1(2)	171.4(4)
(C–N) _{isocyanide} –C	177.1(7)	165.1(10)	178.3(10)	176.4(3)	169.4(4)
Pd1–C _{carbene} –N	122.4(5)	121.6(7)	119.7(7)	117.2(2)	118.4(3)
	118.9(5)	120.9(8)	122.4(7)	123.1(2)	122.4(3)
N–C _{carbene} –N	118.7(6)	117.4(10)	117.5(9)	119.7(3)	119.2(4)

^(a) X refers to chlorine (for **9** and **11–13**) or iodine (for **16**) ligands. For **12**, only data concerning the Pd1 containing molecule are presented.