CAMPHOR–PALLADIUM COMPLEXES AS CATALYSTS FOR CYCLIZATION OF ALKYNES

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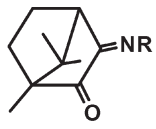
Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

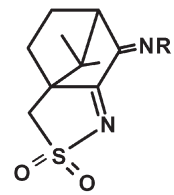
Catalytic properties of the camphor-derived complexes *trans*-[$PdCl_2(L1)_2$], R = Me_2N (**1**), *i*-Pr (**3**), C_6H_5 (**4**), in PhC≡CMe cyclotrimerization are highly dependent on the characteristics of the R group. Their activity decreases in the order **1** > **3** > **4**. The effects of geometric and/or electronic parameters on the catalytic activity of the complexes are evaluated on the basis of X-ray and electrochemical data.

Keywords: Alkyne; Palladium; Catalysis; Camphor; Cyclotrimerization; X-ray analysis.

Search for highly selective catalysts for aromatic ring formation remains an attractive research area due to its relevance to synthetic purposes[1–3]. We have reported that *trans*-[$PdCl_2(L1)_2$] (R = NMe_2 (**1**)), is a highly selective catalyst for the cyclic trimerization of terminal or internal alkynes, but the related *cis*-[$PdCl_2(L2)_2$] (R = NMe_2 (**2**)) is unable to promote it, although it is active in the oligomerization of alkynes[4] (see Fig. 1 for ligands).



L1



L2

FIG. 1
Camphor-type ligands, L1 (R = NMe_2 (**1**), *i*-Pr (**3**), Ph (**4**)); L2 (R = NMe_2 (**2**))

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The considerably different catalytic properties of complexes **1** and **2** were unexpected since they are conceptually analogous, i.e. they have ligands derived from (+)-camphor that coordinate to the palladium centre through the nitrogen atom of an imino group. The geometry of the complexes *trans*-**1** or *cis*-**2** and/or the electronic properties of the ligating groups (=NR (**1**) or $=NSO_2$- (**2**)) account for their different activities. As far as the effect of the imine and sulfonylimine groups on the redox properties of the complexes is concerned, cyclic voltammetry studies[5] showed that **1** is less electron-rich (easier to reduce) than **2**, suggesting the relevance of electronic parameters. However, the *trans* and *cis* geometries render difficult further conclusions. This difficulty can in principle be overcome in complexes with similar geometries, i.e. those with imine-coordinating ligands of L1, where R is expected to be the main parameter influencing the reactivity.

The identification of the parameters that promote and control the catalytic activity of **1** is an important task for optimization of the cyclotrimerization process and the possibility to extend it to other alkynes.

In order to get an insight into the effect of the R group on the catalytic properties of complexes we synthesized *trans*-$[PdCl_2(L1)_2]$ (R = *i*-Pr (**3**), C_6H_5 (**4**)) and studied their properties as catalysts in the cyclotrimerization of PhC≡CMe. The molecular structure of **3** was confirmed by X-ray diffraction analysis.

EXPERIMENTAL

The syntheses of the complexes and catalytic experiments were carried out under inert atmosphere by using vacuum and the Schlenck techniques. The camphor-derived ligands are well-known compounds synthesized with slight modifications[6]. Solvents were purified by conventional techniques[7] and distilled before use. $PdCl_2$ was purchased from Riedel–de Haën and 1-phenylprop-1-yne and solvents from Aldrich. The NMR spectra (δ, ppm; *J*, Hz) were obtained in $CDCl_3$ on a Varian 300 spectrometer. TMS was used as internal reference. The IR spectra (ν, cm^{-1}) were obtained on a Jasco FTIR 430 spectrometer. Cyclic voltammetry experiments were performed with a wave form generator PPRI and a Hi-Tek potentiostat DT2101 in 0.2 M $NBu^t_4BF_4/CH_2Cl_2$ solution using a Pt wire as working electrode. Ferrocene (0.54 V vs ESC) was used as internal reference.

X-ray Data Analysis

X-ray diffraction analysis was performed on a yellow crystal (0.2 × 0.1 × 0.08 mm) of *trans*-$[PdCl_2(L1)_2]$, R = *i*-Pr (**3**), obtained from a CH_2Cl_2 solution. Data were collected on a MACH-3 apparatus using Mo radiation (λ = 0.71069 Å) and were corrected for Lorentz, polarization, and empirically for absorption effects. Cell dimensions were determined from the setting angles of 25 reflections. Complex **3** crystallizes in the monoclinic non-centrosymmetric space group *P*21. The structure was solved by direct methods using SIR97 [8] and refined using

SHELXL[9] within the WingX suite of programs[10]. Non-hydrogen atoms were refined anisotropically and H atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Crystal data and refinement parameters are summarized in Table I.

CCDC 280300 (for **3**) contains[11] the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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 336033; or deposit@ccdc.cam.ac.uk).

TABLE I
Crystal data and structure refinement for *trans*-[$PdCl_2${3-*i*-PrN=$C_{10}H_{14}O$}$_2$]

Empirical formula	$C_{26}H_{42}Cl_2N_2O_2Pd$
Formula weight	591.92
Temperature, K	293(2)
Wavelength, Å	0.71069
Crystal system, space group	Monoclinic, *P*21
Unit cell dimensions, Å; °	a = 9.895(5), b = 13.698(5), c = 10.486(5); β = 97.620(5)
Volume, Å^3	1408.7(11)
Z	2
Calculated density, Mg/m^3	1.395
Absorption coefficient, mm^{-1}	0.872
F(000)	616
Crystal size, mm	0.2 × 0.1 × 0.08
θ range for data collection, °	1.96–25.96
Limiting indices	$-12 \le h \le 0$, $-16 \le k \le 0$, $-12 \le l \le 12$
Reflections collected/unique	3043/2876 [*R*(int) = 0.0690]
Completeness to θ = 25.96, %	100.0
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2876/1/289
Goodness-of-fit on F^2	1.01
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0502, w*R*2 = 0.0940
R indices (all data)	*R*1 = 0.0782, w*R*2 = 0.1030
Absolute structure parameter	0.00(15)
Largest diff. peak and hole, eÅ^{-3}	0.640 and –0.638

Syntheses of Complexes **3** and **4**

The complexes were prepared from $PdCl_2$ in CH_2Cl_2 by the following typical procedure:

trans-[PdCl$_2$(L1)$_2$] (R = *i*-Pr, (**3**)). A suspension of $PdCl_2$ (0.250 g, 1.40 mmol) and 3-(isopropylimino)bornan-2-one (0.600 g, 2.96 mmol) was heated at reflux in CH_2Cl_2 (30 ml) for 4 h. Filtration and reduction of the volume of CH_2Cl_2 by evaporation to ca. 10 ml followed by slow addition of Et_2O (8 ml) afforded yellow crystals of **3** which were filtered off and washed with Et_2O, yield 0.465 g, 50%. For $C_{26}H_{42}Cl_2N_2O_2Pd \cdot 1/7CH_2Cl_2$ (604.7) calculated: 52.1% C, 7.1% H, 4.6% N; found: 51.7% C, 7.0% H, 4.5% N. IR: 1760 (CO); 1650 (CN); 328 (Pd–Cl). ^{1}H NMR: 4.258 sept, 2 H, *J* = 6.6 (*i*-Pr); 3.093 d, 2 H, *J* = 4.5 (H-4); 2.07–1.46 m, 8 H (H-5,6); 1.87 d, 1.66 d, 12 H, *J* = 6.6 (*i*-Pr); 1.13 s, 6 H (H-8); 0.98, 0.92 s, 12 H (H-9,10). ^{13}C NMR: 201.3 (CO); 177.7 (CN); 60.4 (*i*-Pr); 57.9 (C1); 53.2 (C-4); 44.6 (C-7); 29.7, 23.9 (C-5,6); 23.1, 22.9 (*i*-Pr); 21.1, 17.8, 9.4 (C-8,9,10). (See X-ray structure for labeling.)

trans-[PdCl$_2$(L1)$_2$] (R = C_6H_5 (**4**)). Obtained from 3-(phenylimino)bornan-2-one. For $C_{32}H_{38}Cl_2N_2O_2Pd \cdot 1/4CH_2Cl_2$ (680.7) calculated: 56.9% C, 5.6% H, 4.1% N; found: 57.2% C, 5.4% H, 4.0% N. IR: 1760 (CO); 1650 (CN); 1590 (C_6H_5); 330 (Pd–Cl). ^{1}H NMR: 7.6–7.2 m, 10 H (C_6H_5); 2.677 d, 2 H, *J* = 4.6 (H-4); 1.91–1.46 m, 8 H (H-5,6); 1.09 s, 6 H (H-8); 0.95 s, 0.88 s, 12 H (H-9,10). ^{13}C NMR: 199.5 (CO); 180.8 (CN); 145.9, 129.1, 127.8, 123.0 (C_6H_5); 58.9 (C-1); 53.6 (C-4); 44.9 (C-7); 29.6, 24.1 (C-5,6); 21.2, 17.5, 9.2 (C-8,9,10).

Catalytic Experiments

All experiments were carried under nitrogen using screw-cap NMR tubes. Typically, the experiments were carried out as follows. The complex (8–10 mg) was dissolved in $CDCl_3$ (ca. 300 μl), and the ^{1}H and ^{13}C NMR spectra measured before the addition of 1-phenylprop-1-yne (50–100 μl) to the NMR tube. The reactions were followed by NMR until full consumption of the alkyne or completion of the reaction (no change in the spectra after at least one week). Workup of the NMR solutions allowed separation and purification of the products.

RESULTS AND DISCUSSION

The molecular structure of *trans*-[PdCl$_2$(L1)$_2$] (R = *i*-Pr (**3**)) shows the complex has square planar geometry with the two camphor ligands in *trans* positions. The basal plane formed by atoms N1, N2, Cl1 and Cl2 is slightly distorted (the Pd atom is just 0.05(4) Å away from the best least-square plane). The ligands L coordinate to the metal through the nitrogen atom of the imino group (=NR) with the ketone oxygen atom of camphor in each ligand pointing to the metal at a close but non-coordinating distance (ca. 2.94 Å) (Fig. 2). These axial interactions impose to the geometry some elongated distorted octahedral character as observed for **1** [5]. The metal-to-oxygen distances (average 2.9 Å) in the two complexes fully agree.

The Pd–N (2.024(8); 2.052(8) Å) and Pd–Cl (2.305(4); 2.308(4) Å) bond lengths are within the expected values. Table II displays selected bond

TABLE II
Selected bond lengths (in Å) and angles (in °) for *trans*-[$PdCl_2${3-*i*-PrN=$C_{10}H_{14}O$}$_2$]

Bond lengths		Angles	
Pd(1)–N(2)	2.024(8)	N(2)–Pd(1)–N(1)	78.6(3)
Pd(1)–N(1)	2.052(8)	N(2)–Pd(1)–Cl(2)	90.5(2)
Pd(1)–Cl(2)	2.305(4)	N(1)–Pd(1)–Cl(2)	90.6(2)
Pd(1)–Cl(1)	2.308(4)	N(2)–Pd(1)–Cl(1)	88.6(3)
Pd(1)···O(1)	2.945(8)	N(1)–Pd(1)–Cl(1)	90.4(2)
Pd(1)···O(2)	2.942(9)	Cl(2)–Pd(1)–Cl(1)	179.0(17)
N(1)–C(3)	1.289(9)	O(1)···Pd(1)–N(1)	71.4(8)
N(2)–C(23)	1.274(10)	O(1)···Pd(1)–Cl(2)	89.7(8)
N(1)–C(11)	1.473(11)	O(1)···Pd(1)–N(2)	109.5(7)
N(2)–C(31)	1.493(12)	O(1)···Pd(1)–Cl(1)	90.4(8)
C(2)–O(1)	1.223(18)	O(1)···Pd(1)–O(2)	179.0(8)
C(22)–O(2)	1.168(16)	O(2)···Pd(1)–N(1)	108.6(8)
C(2)–C(3)	1.52(2)	O(2)···Pd(1)–Cl(2)	91.3(8)
C(22)–C(23)	1.525(17)	O(2)···Pd(1)–N(2)	70.5(7)
C(1)–C(2)	1.540(11)	O(2)···Pd(1)–Cl(1)	88.6(8)
C(21)–C(22)	1.515(12)		
C(1)–C(7)	1.486(19)	Between planes	
C(21)–C(27)	1.570(13)	O1–C2–C3–N1–C11 and O2–C22–C23–N2–C31	9.7(1)
C(1)–C(6)	1.571(14)	Cl2–Pd1–Cl1 and O2–C22–C23–N2–C31	82.0(4)
C(21)–C(26)	1.569(19)	Cl2–Pd1–Cl1 and O1–C2–C3–N1–C11	89.6(4)
C(4)–C(3)	1.480(12)	C1–C2–C3–C4 and C1–C6–C5–C4	72.5(5)
C(23)–C(24)	1.539(12)	C21–C22–C23–C24 and C24–C25–C26–C21	72.1(4)
C(4)–C(5)	1.541(14)		
C(24)–C(25)	1.517(13)	Torsion	
C(4)–C(7)	1.550(11)	O(2)–C(22)–C(23)–N(2)	2(2)
C(27)–C(24)	1.528(13)	C(21)–C(22)–C(23)–N(2)	–177.4(9)
C(6)–C(5)	1.524(15)	C(22)–C(23)–N(2)–C(31)	–177.1(10)
C(26)–C(25)	1.550(17)	C(11)–N(1)–C(3)–C(2)	–179.2(10)
C(10)–C(7)	1.535(11)	O(1)–C(2)–C(3)–N(1)	0(2)
C(7)–C(9)	1.507(13)	C(1)–C(2)–C(3)–N(1)	–178.9(9)
C(1)–C(8)	1.528(14)		

lengths and angles for **3** as well as the angles between planes and torsion angles that fully corroborate the pseudo-octahedral geometry described above.

In the packing structure, a short distance (2.925 Å) between the hydrogen atom at C4 (camphor skeleton) and the chloride atom of a neighbor molecule is observed.

No suitable crystals for X-ray analysis were obtained in the case of **4** (R = Ph); however, the IR spectrum displays a single band at 330 cm^{-1}, attributable to the Pd–Cl stretching frequency, which indicates two equivalent metal–halogen bonds as expected for a *trans* geometry.

Full spectroscopic and analytical characterization of complexes **3** and **4** is available in Experimental.

From a former study[4], *trans*-$[PdCl_2(L1)_2]$ (R = NMe_2) is known as a highly efficient and selective catalyst for cyclic trimerization of alkynes. The conversion of 1-phenylprop-1-yne into 1,3,5-trimethyl-2,4,6-triphenylbenzene (T) catalyzed by **1** was accomplished in 2 h (activity $A = 1.1 \times 10^4$ gT/(mol [Pd] × [(C≡C)] × h) with the formation of less than 1% of secondary products (Scheme 1).

In view of the geometric analogies of the complexes *trans*-$[PdCl_2(L1)_2]$, R = NMe_2, (**1**), *i*-Pr (**3**) and Ph (**4**), we expected that their catalytic activities would be similar.

In order to compare the catalytic properties of complexes **1**, **3** and **4**, we studied the reactions of **3** and **4** with PhC≡CMe under experimental condi-

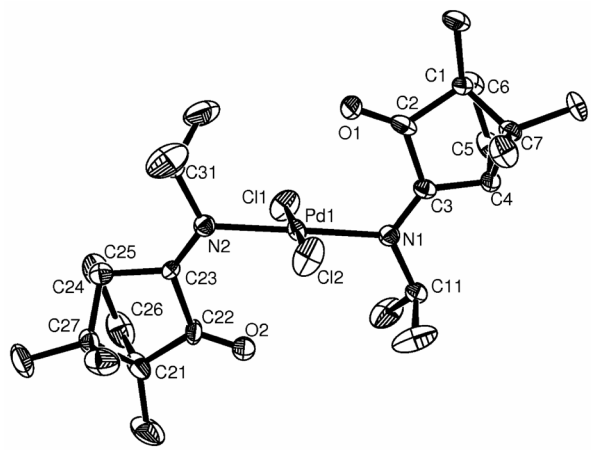
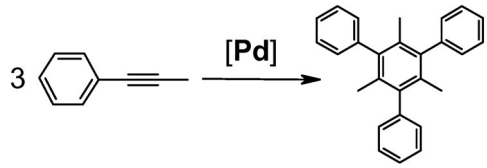


FIG. 2
ORTEP [12] structure of *trans*-$[PdCl_2\{3\text{-}i\text{-}PrN{=}C_{10}H_{14}O\}_2]$ with the atomic labeling scheme



SCHEME 1

tions similar to those previously used with **1** [4] and followed the reactions by NMR.

In the reaction of *trans*-[$PdCl_2(L1)_2$] (R = *i*-Pr (**3**)) with PhC≡CMe, two days were necessary to detect traces of the cyclic trimer and, after two weeks, just 20% conversion into 1,3,5-trimethyl-2,4,6-triphenylbenzene was observed.

The reaction with **4** is even less effective since, after five days, the conversion of PhC≡CMe into the cyclic trimer was ca. 10%. Moreover, after 20 days at 40 °C, just 20% conversion was achieved. In this process, the coordination of the alkyne to palladium is presumed on the basis of signals detected in the ^{1}H NMR spectrum at 2.15 ppm (Me) and δ 7.2–7.4 ppm (Ph), and supported by the presence of the free camphor ligand in solution with no signs of $PdCl_2$ precipitation. The formation of a palladium–alkyne species was reported in related processes[4]. The stability of the complex formed by the reaction of the alkyne with **4** possibly accounts for the lack of reactivity in the formation of the cyclic trimer.

The results herein demonstrate that complexes **3** and **4** are much less efficient catalysts than **1**. Since the geometries of **1** and **3** and the steric requirements of the corresponding R groups are identical as verified by X-rays, their catalytic properties must be based on the electronic characteristics of the R group. In an attempt to evaluate this effect, we measured the redox properties of the complexes by cyclic voltammetry.

The complexes display one cathodic and one anodic redox process. The cathodic process is attributed to the Pd(II) → Pd(I) reduction, whereas the anodic process is attributed to the oxidation of the coordinated camphor ligand. The potentials of the cathodic processes were used to evaluate the electron density at the metal site.

In all cases, the cathodic processes were irreversible and occurred at the potential values (E_p^{red} = –1.2 V (ref.[5]) (**1**), –1.2 V (**3**), –1.0 V (ref.[13]) (**4**). The anodic process was quasi-reversible in **3** ($E_{1/2}^{ox}$ = 1.76 V) or irreversible in **4** (E_p^{ox} = 1.96 V (ref.[13])) or **1** (E_p^{ox} = 1.80 V (ref.[5])).

The electrochemical data indicate that phenyl in the PhN= group of **4** renders the metal site less electron-rich (easier to reduce) than NMe_2 in **1** or *i*-Pr in **3**.

Extensive electron delocalization through the aromatic imino and ketone groups of the camphor skeleton in **4** can account for a lower electron density at the coordinating nitrogen atom, this trend being responsible for the poorer electron-donating properties of =NPh compared to the amine and isopropyl groups in **1** and **3**, respectively. The ^{13}C NMR chemical shifts of the imine (C2: 180.8 in **4**, 177.7 in **3**, 175.0 in **1**) and ketone carbon atoms (C3: 199.5 in **4**, 201.3 in **3**, 201.5 in **1**) support the lower electron density at the aromatic imino (C2) and higher electron density at the ketone group (C3). The lower catalytic activity of *trans*-$[PdCl_2(L1)_2]$, R = Ph, compared with **1** and **3** can then be attributed to a weak nitrogen–palladium bond that renders the camphor ligand labile and easily substitutable with the alkyne substrate affording a more stable Pd–alkyne complex, as detected by NMR.

The analogy of the redox and ^{13}C NMR spectroscopic properties of **1** and **3** suggest their identical electronic properties. Since no significant differences were detected in geometric and electronic characteristics of complexes **1** and **3**, the parameters that cause their catalytic activities remain unclear. The results herein show that the complexes *trans*-$[PdCl_2(L1)_2]$ (R = Me_2N, *i*-PrN, PhN) catalyze cyclic trimerization of PhC≡CMe, although the kinetics of the process is much faster in the case of *trans*-$[PdCl_2(L1)_2]$, R = Me_2N. In all cases, the selectivity of the formation of 1,3,5-trimethyl-2,4,6-triphenylbenzene (>99%) is remarkable.

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