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Platinum(II) and palladium(II) complexes containing 1,3-dimethylcyanurate ligand

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ABSTRACT

New platinum(II) and palladium(II) complexes, *cis*-[PtCl(DMC)(PPh$_3$)$_2$] (**1**·CH$_2$Cl$_2$) and *trans*-[PdCl(DMC)(PPh$_3$)$_2$] (**2**·2CHCl$_3$), where DMC = 1,3-dimethylcyanurate, were synthesized and characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and FAB mass spectroscopy. The structures of complexes are determined by X-ray diffraction and proved to have a distorted square-planar geometry around the metal ions. Both complexes exhibit a high stability in the solid state.

1. Introduction

Cyanuric acid (CYH$_3$) was first synthesized by Wöhler in 1829 [1]. The X-ray structures of its potassium [2–4], calcium [5,6] and rubidium [2] salts have been studied and suggested that the hard metals of these main group elements are coordinated to the cyanurate ligand at the deprotonated enol oxygen. On the other hand, transition metal complexes of cyanurates have also been prepared [7–22], and the donor site of the deprotonated cyanurate anion CYH$_2^-$ is the deprotonated N atom. Furthermore in the case of di- and tri-anionic cyanurate ligands were found to be N,O-chelated [23–28].

Among cyanurates, 1,3-dimethylcyanuric acid (DMCH, also named as 1,3-dimethyl-2,4,6-trioxo-1,3,5-triazine) was known since 1881 [29]. The presence of several potential donor sites such as one amine nitrogen atom and three carbonyl oxygen atoms makes DMCH a very interesting polyfunctional ligand in coordination chemistry. By comparing with CYH$_3$, DMCH has two methyl groups which lower the tendency for making intra and intermolecular hydrogen bonding [30]. This has prompted us to investigate its coordination behavior. Proton loss from the amine N atom to form amide is necessary for the complexation of the 1,3-dimethylcyanurate monoanion (DMC$^-$). The DMC ligand readily forms complexes with many metal ions and earlier work in this field has been reported by Abu-Salem and Kuhn [31–33], most of them have concentrated on the first-row divalent transition metals. However, a literature survey indicates that group d^8 metal complexes of cyanuric acid are rare. In the course of our studies on cyanurate–metal ion interactions, we have succeeded in preparing the first two new platinum(II) and palladium(II) complexes of DMC with ancillary triphenylphosphine ligand. Herein, we report the synthesis, characterization and crystal structures of *cis*-[PtCl(DMC)(PPh$_3$)$_2$] (**1**) and *trans*-[PdCl(DMC)(PPh$_3$)$_2$] (**2**).

2. Experimental

2.1. Materials and measurements

Lithium1,3-dimethylcyanurate (LiDMC) was obtained according to a published procedure [33]. Other chemicals were purchased and used as received. The elemental analysis for C, H and N were performed using a Carlo Erba 1106 elemental analyzer. IR spectra were recorded on a VERTEX 70 FT-IR spectrometer using drift spectroscopy method in the range 4000–200 cm^{-1}. The high resolution NMR spectra were acquired by a Bruker DRX 400 NMR spectrometer (^{1}H 400 MHz; ^{13}C 100 MHz, using *TMS* as external standard; ^{31}P 162 MHz, 85% H$_3$PO$_4$ as external standard). FAB mass spectra were carried out on a TSQ 70 quadrupole mass spectrometer with xenon

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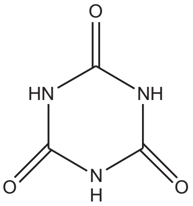
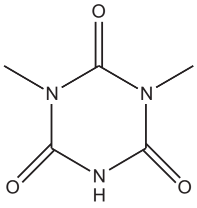
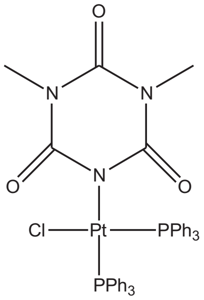


CYH$_3$



DMCH



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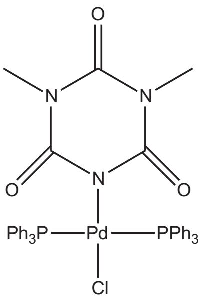

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atoms as bombarding particles (kinetic energy ca. 8 keV). Unless otherwise stated, 3-nitrobenzyl alcohol (3-NBA) was used as matrix material at ion source temperature of ca. 60 °C. In the FAB mass spectra, M represents the solvent-free molecular masses.

2.2. Synthesis of the platinum(II) and palladium(II) complexes

2.2.1. cis-[PtCl(DMC)(PPh$_3$)$_2$] (**1**·CH$_2$Cl$_2$)

To a solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.250 g, 0.316 mmol) in methanol (30 mL) was added LiDMC (0.052 g, 0.319 mmol). The mixture was warmed to 53 °C and stirred for 5 h, whereupon the LiDMC dissolved giving a clear colorless solution. Then the mixture was stirred overnight at room temperature to yield a white precipitate. The mixture was evaporated to dryness under reduced pressure and the product was extracted with dichloromethane (30 mL) and filtered. The filtrate was reduced in volume to ca. 5 mL and light petroleum (25 mL) was added. After 1 day, white crystals at −32 °C were obtained.

Yield: 0.217 g (69%). *Anal.* Calc. for $C_{42}H_{38}Cl_3N_3O_3P_2Pt$ (M = 996.15 g/mol): C, 50.64; H, 3.84; N, 4.22. Found: C, 50.96; H, 4.28; N, 3.82%. ^{1}H NMR (CDCl$_3$): δ 2.96 (s, 6H, NCH$_3$), 7.19–7.84 (m, 30H, Ph), 5.29 (s, 2H, CH$_2$Cl$_2$). ^{13}C NMR (CDCl$_3$): δ 28.93 (CH$_3$), 53.5 (CH$_2$Cl$_2$), 127.87–135.21 (m, Ph), 151.75 (C^2), 152.94 (C^{4,6}), ^{31}P NMR (CDCl$_3$): AB spin system, δ 6.72 (d, PPh$_3$ *trans* to N, ^2J(PP) 19.29), 14.21 (d, PPh$_3$ *trans* to Cl, ^2J(PP) 19.41). IR(DRIFT): ν_{CO} (cm^{-1}) 1726vs, 1681s, 1636vs. MS [FAB, (3-NBA matrix)]: m/z (%) = 912.2 [10, M+H], 875.7 [18, M−Cl], 755.2 [25, M−DMC], 718.7 [100, M−Cl−DMC−1H].

2.2.2. trans-[PdCl(DMC)(PPh$_3$)$_2$] (**2**·2CHCl$_3$)

A suspension solution of *cis*-[PdCl$_2$(PPh$_3$)$_2$] (0.291 g, 0.415 mmol) in 21 mL dichloromethane was added to a stirred solution of LiDMC (0.068 g, 0.415 mmol) in methanol (20 mL) and the mixture was refluxed for 7 h. The resulting red solution was evaporated to dryness under reduced pressure and the product was extracted with chloroform (50 mL). The filtrated solution was reduced in volume to ca. 10 mL and light petroleum (25 mL) was added. After 1 day, yellow crystals at −32 °C were obtained.

Yield: 0.273 g (62%). *Anal.* Calc. for $C_{43}H_{38}Cl_7N_3O_3P_2Pd$ (M = 1061.318 g/mol): C, 48.66; H, 3.61; N, 3.96. Found: C, 48.06; H, 3.24; N, 4.02%. ^{1}H NMR (CDCl$_3$): δ 2.64 (s, 6H, NCH$_3$), 7.28–7.75 (m, 30H, Ph), 7.18 (s, 2H, CHCl$_3$). ^{13}C NMR (CDCl$_3$): δ 28.93 (CH$_3$), 77.20 (CHCl$_3$), 128.09–134.70 (m, Ph), 151.29 (C^2), 152.39 (C^{4,6}), ^{31}P NMR (CDCl$_3$): δ 21.39 (s). IR(DRIFT): ν_{CO} (cm^{-1}) 1721vs, 1649s, 1621vs. MS [FAB, (3-NBA matrix)]: m/z (%) = 823.3 [15, M+H], 786.8 [35, M−Cl], 666.3 [25, M−DMC], 629.8 [70, M−Cl−DMC−1H].

2.3. X-ray crystallography

The crystals of **1**·CH$_2$Cl$_2$ and **2**·2CHCl$_3$ were mounted on a glass fiber with epoxy cement at room temperature, and cooled in a cold stream of liquid nitrogen. The intensity data of the complexes were collected using a STOE IPDS 2 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 and SHELXL-97 programs [34]. All non-hydrogen atoms were found from the difference Fourier map and refined anisotropically. All hydrogen atoms were included using a riding model. The details of data collection, refinement and crystallographic data are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

Complexes **1** and **2** were synthesized by the ligand displacement reaction of *cis*-[MCl$_2$(PPh$_3$)$_2$] with the anhydrous lithium salt of 1,3-dimethylcyanuric acid, Li(DMC) [35], and isolated as air-stable solids in moderate yields (over 50%). The complexes can be isolated in a pure state from the mixture of products by recrystallization from chlorinated solvents-light petroleum, being soluble in most organic solvents at room temperature.

Selected FT-IR spectroscopic data for **1** and **2** are listed in Table 2. The relatively medium and weak bands in the 2835–3002 cm^{-1} range are characteristic of both aromatic and aliphatic ν(C–H) vibrations. The metal complexes of DMC are well characterized by the presence of sharp IR bands due to the absorption of the

Table 1
Crystallographic data and structure refinement for **1**·CH$_2$Cl$_2$ and **2**·2CHCl$_3$.

Complex	**1**·CH$_2$Cl$_2$	**2**·2CHCl$_3$
Formula	$C_{42}H_{38}Cl_3N_3O_3P_2Pt$	$C_{43}H_{38}Cl_7N_3O_3P_2Pd$
M	996.13	1061.25
T (K)	173(2)	173(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	11.9923(8)	11.8784(6)
b (Å)	19.5050(10)	13.8627(7)
c (Å)	19.7441(11)	28.0916(19)
α (°)	90	90
β (°)	104.920(5)	90
γ (°)	90	90
V (Å^3)	4462.6(5)	4625.8(5)
Z	4	4
D_{calc} (g cm^{-3})	1.483	1.524
μ (mm^{-1})	3.434	0.917
F(000)	1976	2144
θ range (°)	5.68–24.71	3.03–26.37
Index range (h, k, l)	$-14 \leqslant h \leqslant 14$, $-22 \leqslant k \leqslant 22$, $-23 \leqslant l \leqslant 23$	$-14 \leqslant h \leqslant 14$, $-17 \leqslant k \leqslant 17$, $-35 \leqslant l \leqslant 35$
Reflections collected	44 004	59 893
Data/parameters	7489/528	9441/685
Goodness-of-fit (GOF) on F^2	1.253	1.056
R_1 [$I > 2\sigma$]	0.0634	0.0450
wR_2	0.0979	0.0833

Table 2
Selected FTIR spectral data[a] for **1**·CH_2Cl_2 and **2**·2$CHCl_3$.

Assignment	**1**	**2**
ν(CH)	3057m, 3026w, 2989w, 2949w	3020m, 2974w, 2931w, 2890w
ν(CO)	1726vs, 1681s, 1636vs	1721vs, 1649s, 1621vs
ν(CC)	1572w, 1527w	1550w, 1526w
ν(CH)	1482s	1460s
ν(CN)	1257s	1260s
ν(M−Cl)	336m	330m
550 ± 5	547vs	535sh

m = medium; w = weak; vs = very strong; s = strong; sh = shoulder.
[a] Frequencies in cm^{-1}.

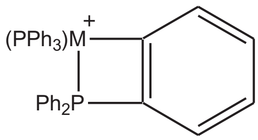
carbonyl groups. The DMC ligand exists in triketo form, three types of strong absorption bands were observed in the frequency range 1621–1726 cm^{-1} characterize vibrations of the carbonyl groups. The weak bands in the frequency range 1526–1572 cm^{-1} can be assigned to the C=C vibrations of the phenyl groups. The bands with medium intensity 1460 and 1482 cm^{-1} correspond to the ν(C–H) deformation vibrations and the strong band centered around 1260 cm^{-1} is attributed to the ν(C–N) stretching vibrations [36]. The appearance of a very strong absorption band at 547 cm^{-1} in complex **1** is important because this band seems to correspond to the absorption which is characteristic for *cis*-$PtXY(PPh_3)_2$ and appears at 550 ± 5 cm^{-1}; the intensity of this band in complex **2** is weak and appears at 535 cm^{-1} as shoulder [37]. The medium intensity bands at 336 and 330 cm^{-1} can be assigned to M−Cl stretching mode for complexes **1** and **2**, respectively. This assignment appears reasonable, because in the case of M−Cl interactions such vibrations are often found in this spectral region [38,39].

The ^1H NMR spectra of complexes **1** and **2** are consistent with their proposed structures. In $CDCl_3$ the signals at 2.96 and 2.64 ppm for complexes **1** and **2**, respectively, were assigned to the methyl groups of the DMC ligand. The phenyl ring protons display two multiplets in the range 7.19–7.84 ppm.

The ^{13}C NMR spectra of complexes **1** and **2** displayed, in addition to the expected resonances for the PPh_3 ligands, three signals one for the methyl groups at 28.93 ppm and two for the carbonyl groups in an approximate 2:1 intensity ratio. The more intense resonance for the two carbonyl groups near the N atom which is the deprotonation site was observed downfield at 152.94 and 152.39 ppm from the smaller signal assigned to the carbonyl group near both the *N*-methyl groups at 151.74 and 151.29 ppm for complexes **1** and **2**, respectively.

The ^{31}P NMR spectrum of the phosphine complex **2** displayed a single resonance at 21.39 ppm consistent with a square-planar geometry with two equivalent *trans* phosphine ligands, while in complex **1** the ^{31}P NMR spectrum show the expected AB patterns for two *cis*-phosphines *trans* to ligands having differing *trans* influences. Thus for complex **1** the two values of 6.72 (^2J(PP) 19.29 Hz) and 14.21 (^2J(PP) 19.41 Hz) ppm were assigned to the phosphines *trans* to 1,3-dimethylcyanurate and chloride ligands, respectively.

Fast-atom bombardment (FAB) mass spectrometry of **1** and **2** by dissolving in 3-nitrobenzylalcohol matrix show a relatively weak parent (protonated) molecular ions $[M+H]^+$ at *m*/*z* 912.2 (10%) and 823.3 (15%), respectively. There are also two additional peaks in common, at *m*/*z* 875.7 (18%) and 786.8 (35%). These are assigned to the complexes $[M-Cl]^+$. The formation of cations by loss of an anionic halide ligand is a common ionization pathway for neutral transition metal halide complexes [40]. The two fragments of weak intensity at *m*/*z* 755.2 and 666.3 (25%) were assigned to $[M-DMC]^+$. The FAB mass spectra are dominated by peaks at *m*/*z* 718.7 (100%) and 629.8 (70%). These are assigned to complex containing an orthometallated triphenylphosphine ligand $[M(C_6H_4PPh_2\text{-}o)(PPh_3)]^+$ (**3**). The cyclometallation of platinum(II) and palladium(II) diphosphine complexes $MCl_2(Ph_2P(CH_2)_5PPh_2)$ based on the gas-phase methodologies has been reported [41,42].



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3.2. Description of crystal structures

The molecular structure of complex **1**·CH_2Cl_2 with the atom labeling is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. Complex **1**·CH_2Cl_2 crystallizes in the monoclinic space group $P2_1/c$. The crystal lattice of complex **1** consists of one dichloromethane molecule of solvation; there are no close contacts between them. The platinum(II) ion has a distorted square-planar coordination arrangement with two *cis* triphenylphosphine ligands, a chloride ligand and a monodentate *N*-bonded 1,3-dimethylcyanurate ligand. The maximum deviation of any atom from the least-squares plane defined by Pt, P1, P2, N40, and Cl3 is only 0.002 Å. The plane of 1,3-dimethylcyanurate ligand is approximately orthogonal to the platinum coordination plane, with a twist angle of 96(1)° between the two planes. This is also illustrated by the torsions angles Cl3–Pt–N40–C45 and Cl3–Pt–N40–C41 which are −85(1)° and 94(1)°, respectively. Presumably, the DMC ligand seems to be out of correct perpendicularity occurs as a result of a steric interaction with a phenyl ring on P1. The Pt–P1 and the Pt–P2 bond distances are different (2.250(2) and 2.265(2) Å), consistent with the amide, *trans* to P2, having slightly larger *trans* influence. The DMC ligand in **1**, appears to have a lower *trans* influence than the corresponding barbiturate analog in *cis*-$[PtCl(debarb)(PPh_3)_2]$ (**4**) (debarb: 5,5-diethylbarbiturate), as evidenced by the slightly longer Pt–P1 2.274(2) Å [43] when compared with that of **1**. The Pt–N40 distance, 2.064(6) Å, is slightly shorter than that in the related complex **4** (2.077(4) Å). The Pt–Cl distance of **1**, 2.357(2) Å, is similar to the Pt–Cl distance in **4** (2.353(2) Å), such Pt–Cl bonds *trans* to a phosphine ligands

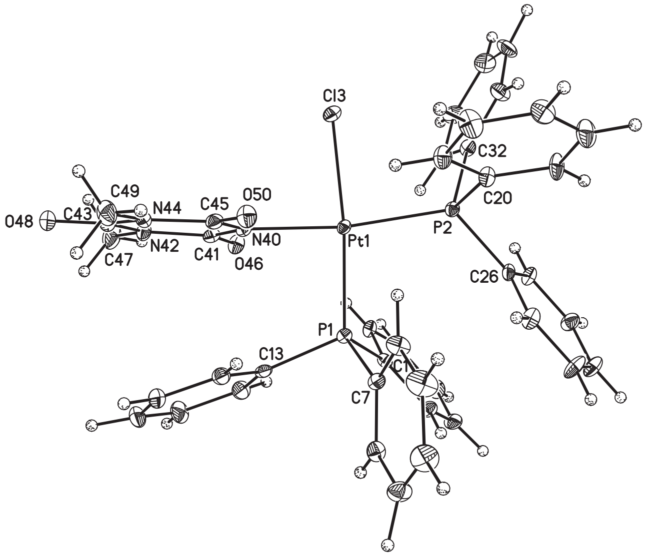


Fig. 1. Molecular structure of the complex *cis*-$[PtCl(DMC)(PPh_3)_2]\cdot CH_2Cl_2$ (**1**), showing the atom numbering scheme. The dichloromethane molecule of crystallization is not shown.

Table 3
Selected bond lengths (Å) and angles (°) for **1**·CH_2Cl_2.

Pt–N40	2.064(6)	Pt–P1	2.250(2)
Pt–P2	2.265(2)	Pt–Cl3	2.357(2)
N40–C45	1.366(10)	N44–C49	1.460(11)
C41–N40	1.327(10)	N42–C47	1.471(11)
N44–C45	1.401(10)	C45–O50	1.231(10)
C41–N42	1.425(10)	C43–O48	1.211(10)
C43–N44	1.383(12)	C41–O46	1.224(9)
N42–C43	1.367(11)	P1–C1	1.814(7)
P1–C7	1.822(8)	P1–C13	1.835(8)
P2–C32	1.826(8)	P2–C26	1.826(7)
P2–C20	1.822(8)		
C41–N40–Pt	119.9(5)	C43–N42–C47	119.2(7)
C45–N40–Pt	116.2(5)	C41–N42–C47	117.4(7)
C41–N40–C45	123.9(7)	C43–N42–C41	123.4(7)
C43–N44–C45	123.5(7)	N40–C45–N44	116.9(7)
N42–C43–N44	115.2(7)	O46–C41–N40	124.1(7)
N40–C41–N42	117.0(7)	O46–C41–N42	118.9(7)
C45–N44–C49	117.0(7)	O48–C43–N42	122.3(9)
C43–N44–C49	119.5(7)	O48–C43–N44	122.5(8)
O50–C45–N40	123.4(7)	O50–C45–N44	119.7(7)
N40–Pt–P1	89.08(18)	N40–Pt–Cl3	85.33(18)
N40–Pt–P2	171.31(18)	P1–Pt–Cl3	173.59(7)
P1–Pt–P2	99.16(7)	P2–Pt–Cl3	86.59(7)
C1–P1–C7	110.0(4)	C13–P1–C1	104.6(3)
C7–P1–C13	100.7(4)	C20–P2–C32	105.1(4)
C20–P2–C26	103.3(3)	C32–P2–C26	103.3(4)
C1–P1–Pt	110.3(3)	C26–P2–Pt	122.4(3)
C7–P1–Pt	116.6(3)	C32–P2–Pt	110.3(3)
C13–P1–Pt	113.7(2)	C20–P2–Pt	110.9(3)

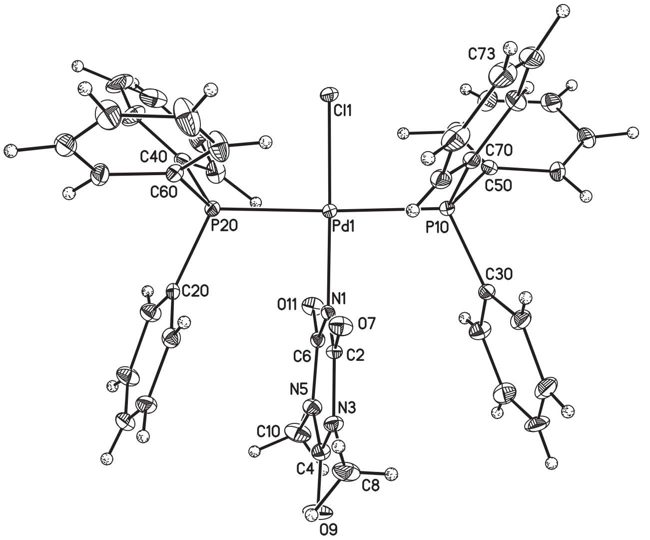


Fig. 2. Molecular structure of the complex *trans*-[PdCl(DMC)$(PPh_3)_2$]·$2CHCl_3$ (**2**), showing the atom numbering scheme. The chloroform molecules of crystallization are not shown.

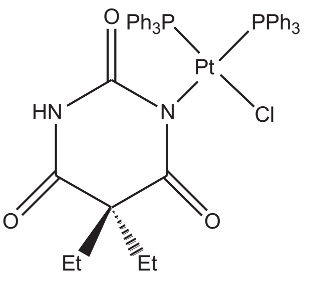
typically lie within this range [41,42]. The C–N bond distances at the deprotonation site C41–N40 1.327(10), N40–C45 1.366(10) Å are as expected for sp^2 C–N bonds [44] and clearly indicate that the double bond is localized between C41 and N40. The remaining structural features are unexceptional. DMCH acid has strong tendency to associate through hydrogen bonding [32,33]. However, examination of the packing diagram for **1** did not reveal any apparent three-dimensional superstructure. This is possibly as a result of the steric bulk imposed by the two triphenylphosphine ligands.

The molecular structure of complex **2**·$2CHCl_3$ with the atom labeling is shown in Fig. 2. Selected bond distances and angles are listed in Table 4. Complex **2**·$2CHCl_3$ crystallizes in the orthorhombic space group $P2_12_12_1$. The complex is composed of two chloroform molecules of solvation; there are no close contacts between them. The palladium(II) ion is coordinated by a monodentate *N*-bonded 1,3-dimethylcyanurate ligand, a chloride ligand and two *trans* triphenylphosphine ligands forming a distorted square-planar coordination arrangement. The deviation of palladium(II) ion from the mean coordination plane is 0.06 Å over the plane. The DMC ligand is twisted away from the coordination plane 80(1)° in order to minimize steric repulsions with the bulky triphenylphosphine ligands. The torsions angles Cl1–Pd–N1–C6 and Cl1–Pd–N1–C2 which are 34(1)° and −143(1)°, respectively. The Pd–P10 and Pd–P20 distances are similar in length (2.321(2) and 2.319(2) Å)) to those found in *trans*-[PdCl{$EtO_2CNC(O)CH_2CN$}$(PPh_3)_2$] (**5**) (Pd–P1 and Pd–P2 (2.311(2) and 2.324(2) Å)), which also has the amide *trans* to a chloride ligand [45]. The two Pd–N1 and Pd–Cl1 bond distances (2.023(3) and 2.294(2) Å) in complex **2** are close to the Pd–N1 and Pd–Cl1 bond distances in N-cyanoacetylurethane complex **5** (2.039(5) and 2.306(2) Å) [45]. All the bond lengths and angles in the DMC ligand are in the normal range, and match the reported value [32,33].

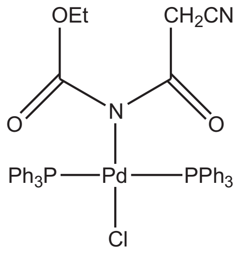
Table 4
Selected bond lengths [Å] and angles [°] for **2**·$2CHCl_3$.

Pd–N1	2.023(3)	N5–C10	1.455(6)
Pd–P20	2.319(2)	C2–O7	1.207(5)
Pd–P10	2.321(2	C6–O11	1.229(5)
Pd–Cl1	2.294 (2)	C4–O9	1.213(6)
N1–C2	1.372(5)	C2–N3	1.401(5)
N1–C6	1.355(5)	N3–C4	1.357(6)
C4–N5	1.389(6)	N3–C8	1.468(6)
N5–C6	1.389(6)	P10–C30	1.821(4)
P20–C60	1.816(5)	P10–C50	1.813(5)
P20–C40	1.815(5)	P10–C70	1.820(4)
P20–C20	1.824(4)		
C2–N1–Pd	118.2(3)	N1–C6–O11	121.8(4)
C6–N1–Pd	118.9(3)	N1–C2–O7	122.5(3)
N1–C2–N3	116.5(3)	N3–C4–O9	122.6(5)
N1–C6–N5	117.6(4)	N5–C4–O9	121.7(5)
C2–N3–C4	124.0(4)	N5–C6–O11	120.6(4)
C2–N3–C8	117.4(4)	O11–C6–N1	117.6(4)
N3–C4–N5	115.7(4)	N3–C2–O7	121.0(4)
C8–N3–C4	118.6(4)	C4–N5–C10	118.3(4)
C4–N5–C6	123.0(4)	C10–N5–C6	118.6(4)
N1–Pd–Cl1	178.36(10)	P20–Pd–P10	172.52(4)
N1–Pd–P20	90.27(9)	P20–Pd–Cl1	88.67(4)
N1–Pd–P10	92.28(9)	P10–Pd–Cl1	88.93(4)
C60–P20–C40	109.3(2)	C30–P10–C50	104.3(2)
C40–P20–C20	105.8(2)	C50–P10–C70	105.7(2)
C20–P20–Pd	114.47(14)	C70–P10–C30	107.3(2)
C40–P20–Pd	110.33(16)	C30–P10–Pd	114.31(15)
C60–P20–Pd	112.73(16)	C50–P10–Pd	118.77(16)
C20–P20–C60	103.8(2)	C70–P10–Pd	105.70(15)

The triazine ring, the two methyl groups and the three carbonyl groups in both complexes are near planar from the mean plane of their attached triazine ring.



4



5

4. Conclusions

Commonly, kinetics and thermodynamics of square-planar d^8 metal complexes are best understood in terms of *trans*-effect and *trans*-influence [46]. As expected, the platinum complex (**1**) is formed by substitution of chloride from *cis*-$[PtCl_2(PPh_3)_2]$ as the kinetically stable product while, starting from the palladium precursor *cis*-$[PdCl_2(PPh_3)_2]$, the *cis*-isomer could not be detected even as an intermediate apparently owing to its highly labile nature. Comparable ligand properties of DMC^{-1} and pyridine in their pentacarbonylmetal complexes have been reported by us formerly [31]. Assuming similar atomic radii of palladium and platinum and following the arguments discussed for the *trans*-influence, additional arguments for the ligand properties may be found here. The *trans*-influence predicts bond weakening in the *trans*-L-M-L′ in case that the ligands compete with the same metal orbitals. In fact, in the palladium complex (**2**), the M–P distances are the longest ones (see Tables 3 and 4) though steric interaction should be minimum. The marked difference in the M–N distances of the complexes (**1**) and (**2**) may also figure the stronger *trans*-influence of the PPh_3 ligand compared with Cl^{-1} and DMC^{-1}, for which similar, i.e. medium σ-donor and weak π-donor properties, may be discussed here.

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Appendix A. Supplementary data

CCDC 838104 and 838103 contain the supplementary crystallographic data for ($\mathbf{1}\cdot CH_2Cl_2$) and ($\mathbf{2}\cdot 2CHCl_3$), respectively. These 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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