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Journal of Organometallic Chemistry



Synthesis and structure of new compounds with Pt–Ga bonds: Insertion of the bulky gallium (I) bisimidinate Ga(DDP) into Pt–Cl bond

Adinarayana Doddi^a, Christian Gemel^a, Rüdiger W. Seidel^b, Manuela Winter^a, Roland A. Fischer^{a,*}

^a Inorganic Chemistry-II, Organometallics and Materials, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitaetsstrasse 150, D-44780 Bochum, Germany ^b Analytical Chemistry, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, D-44780 Bochum, Germany

ARTICLE INFO

Article history: Received 22 February 2011 Received in revised form 5 April 2011 Accepted 8 April 2011

Keywords: Insertion Cyclooctadiene Platinum complexes Dicylcopentadiene Main-group

ABSTRACT

Reactions of the sterically bulky mono-valent group 13 bisimidinate gallium(I), Ga(DDP) (1) (DDP = 2-{(2, 6-diisopropylphenyl)amino}-4-{(2, 6-diisopropylphenyl)imino}-2-pentene, HC(CMeNC₆H₃-2,6-ⁱPr₂)₂) with olefin supported group 10 complexes, [(diene)PtCl₂] [diene = 1,5-cyclooctadiene (COD), *endo*-dicyclopentadiene (dcy)] and [(COD)Pd(Me)(OTf)] (OTf = 0₃SCF₃) are reported. These reactions afforded [(COD)Pt(Cl){ClGa(DDP)}] (2), [(dcy)Pt(Cl){ClGa(DDP)}] (3) and [(DDP)Ga(Me)(OTf)] (4) in moderate yields. Compounds 2–4 were characterized by elemental analysis, NMR (¹H, ¹³C) spectroscopy and also by single crystal X-ray structural analysis. The solid state structures of complexes 2 and 3 reveal the oxidative insertion of Ga(DDP) into the Pt–Cl bond without altering the π -coordinated double bonds in the olefin.

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1. Introduction

The isolation and structural characterization of low oxidation state group 13 metal (I) chemical entities at room temperature have opened up new horizons in the history of main-group chemistry. The coordination chemistry of these sterically demanding ER type of compounds (E = Al. Ga. In: R = bulky alkyl, arvl, $C_5Me_5^-$, etc.) as ligands to yield a variety of intermetallic transition metal (M) complexes of the kind $[(L_nM)_a(ER)_b]$ (a < b) is a continuously expanding field [1]. Besides fundamental interest in structure and bonding, the chemistry of these complexes and clusters with unsupported M-E bonds is related to the materials chemistry of the respective alloys or intermetallic compounds [1b,d,e]. Early work in this direction targeted MOCVD of CoGa and related materials [2a,b], more recent work deals with soft chemical synthesis of M_xE_v alloy nanoparticles [2c,e] such as NiAl dispersed as colloids [2c]. The substitution or the rearrangement of the labile ligands (i.e, CO, PR₃ and olefins) by ER has proven to be the most fruitful synthetic route for making a variety of such homoleptic and heteroleptic complexes [1,3]. Their reactivity and electronic properties are comparable with the well-known N-heterocyclic carbene (NHC) class of ligands. The NHC analogous ER ligands are thus considered as strong σ -donors due to the presence of a sp hybridized lone pair on the main-group metal (I) centre. However, there is a striking difference between the behaviour of N-heterocyclic carbenes and ER ligands. In addition to its coordinating properties, ER ligands exhibit strong reducing properties and may also yield insertion compounds as intermediates when combined with compounds exhibiting M-X bonds. Among these main-group metal-ligand species, the neutral and bulky six-membered β -diketiminato derivatives [:E{[N(Ar)C(Me)]₂CH}: Ar = C₆H₃ⁱPr₂-2.6; E = Al [4]. Ga [5], In [6], Tl [7]], abbreviated as E(DDP) [DDP = 2-{(2,6-diisopropylphenyl)amino}-4-{(2,6-diisopropylphenyl)imino}-2-pentene], are of special interest due to the bulkiness which can be incorporated into their metal complexes. Another NHC analogous anionic five-membered diazabutadienido ligand $[:Ga{N(R)C(H)}_2]^ (R = {}^{t}Bu, Ar)$ [8] and recently the neutral four-membered guanidinate ligands $[:E{(Ar)NC(NCy_2)N(Ar)}]$ (E = Ga, In, Tl) [9] have been developed during the last five years.

The chemistry of platinum gallyl complexes with these gallium (I) heterocyclic ligands have been explored some extent. Very recently the first homoleptic platinum(0) complex, $[Pt{Ga(Giso)}_3]$ with the neutral four-membered guanidinato gallium(I) heterocycle [:Ga(Giso)] (Giso = { $(2,6-^iPr_2C_6H_3)NC(NCy_2)N(C_6H_3-2,6-^iPr_2)$ }, Cy = cylohexyl) was reported by C. Jones and his coworkers, where they described particularly short Pt–Ga (3-coordinate) bonds [10]. Likewise, few structurally interesting platinum complexes have also been reported with the anionic gallium (I) heterocyle by the salt elimination process [11].

Although the insertion chemistry of Ga(DDP) (1) has been explored to some extent towards transition and main-group metal

^{*} Corresponding author. Tel.: +49 (0) 234 32 24174; fax: +49 (0) 234 32 14174. *E-mail address*: roland.fischer@rub.de (R.A. Fischer).

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complexes (Fig. 1) (i.e. the insertion behaviour of Ga(DDP) into the M–X (M: Si, Sn, Ga, Hg, Zn, Pb, Rh, ^tBu, X:–Cl, $-O_3SCF_3$) and also M–C (M: Ga) bonds) [12–16], the same chemistry with olefin supported platinum(II) chloro complexes is not explored. To the best of our knowledge, only a very few Ga(DDP) containing platinum complexes have been reported in the literature so far [17]. Following our previous work on the reactivity of zero valent, olefin supported platinum and palladium complexes towards ER [18–23], we got interested in comparing the reactions of **1** with olefin complexes of the group 10 metal centres Pt^{II} and Pd^{II}. Herein, we report the reactions of Ga(DDP) with the olefin supported complexes containing Pt–Cl and Pd–Me bonds, such as [(diene)PtCl₂] [diene = 1,5-cyclooctadiene, (dcy) *endo*-dicyclopetadiene] and [(COD)PdMe(OTf)] in comparison to the reaction of [Pt(COD)₂] with Ga(DDP) which yields a bright orange complex [(1,3-COD)Pt{Ga(DDP)₂] [17].

2. Results and discussion

Unlike GaCp*, Ga^I(DDP) is less reducing and very bulky and thus likely not to yield homoleptic complexes $[Pt(Ga(DDP)_n)]$ ($n \le 4$) such as $[Pt\{Ga(Giso)\}_3]$ [10] or $[Pt(GaCp^*)_4]$ [22] when combined with the selected olefin supported Pt(II) complexes, $[(diene)PtCl_2(diene = 1,5-COD, dcy)]$ and the Pd(II) complex [(1,5-COD)PdMe(OTf)]. These reactions afforded the new platinum complexes $[(COD)Pt(Cl) \{CIGa(DDP)\}]$ (**2**) and $[(dcy)Pt(Cl)\{CIGa(DDP)\}]$ (**3**) as the insertion products of gallium into Pt–Cl bonds, while the palladium(II) complex is reduced to Pd(0) and [(DDP)Ga(Me)(OTf)] (**4**) was obtained as the stoichiometric by-product. All new compounds **2–4** were analytically and structurally characterized, as described in the following.

2.1. Synthesis and characterization of [(COD)Pt(Cl){ClGa(DDP)}] (2) and [(dcy)Pt(Cl){ClGa(DDP)}] (3)

An equimolar mixture of **1** with platinum(II)-olefin complexes $[(1,5-COD)PtCl_2]$ and $[(dcy)PtCl_2]$ in toluene at room temperature, afforded pale yellow crystals of platinum–gallyl complexes in 43% (**2**) and 28% (**3**) yield respectively (Scheme 1). During these reactions, the initial colour of the reaction mixture (yellow) changed to orange after

15–30 min of stirring at room temperature. This colour gradually changed to brown as the final colour of the reaction mixture. Complexes **2** and **3** are stable over several days in their solid–state at room temperature under inert atmosphere (Ar), but prolonged storage in solution and solid–state lead to slow decomposition with formation of a grey substance. They readily dissolve in common organic solvents such as THF, benzene and toluene but are insoluble in hexane and pentane. Elemental analysis of both compounds are in good agreement with the proposed molecular formulae [(COD)Pt(Cl) {ClGa(DDP)}] (**2**) and [(dcy)Pt(Cl){ClGa(DDP)}] (**3**).

To gain further insight into these reactions, we have carried out some experiments using a two fold excess of Ga(DDP) for the possible isolation of Pt(0) complexes, since we expected that ligand **1** can take up to two Cl⁻ ligands from the Pt centre, there by leading to Cl₂Ga(DDP) as an anticipated by-product. However, no other products were isolated, except for **2** and **3** from their respective reactions according to Scheme 1. It is worth mentioning that our previous work on the reaction of [Pt(COD)₂] with **1** forms a bright orange Pt(0) complex [Pt(COD){Ga(DDP)}₂] in hexane, but in the present case no such compounds were observed, but only oxidative insertion of Ga(DDP) into the Pt–Cl bond has occurred [17]. This might be due to the fact that the steric bulk of **1** normally does not favour more substitution at the platinum centre unlike GaCp*, with which a few homoleptic and heteroleptic complexes have been isolated [22].

The ¹H and ¹³C NMR spectra of **2** and **3** exhibit the expected resonances for the DDP ligand. These data is consistent with their proposed structures. The typical ¹H NMR resonances [C₆D₆ for **2** and d₈-THF for **3**] for methine (γ -*CH*) protons of the DDP backbone in both **2** and **3** are observed as sharp singlets at δ 4.94 and 5.15 ppm respectively (Supporting Information Figure S2 and S5) which are in the expected range when compared to the Ga(DDP)-supported metal complexes [12–15]. The resonance due to the olefin protons of COD in **2** appears as two different broad multiplets centred at δ 4.53 and 5.52 ppm, associated with the NMR active ¹⁹⁵Pt satellites, and whereas the –CH– protons of isopropyl groups show two different overlapping septets centred at δ 3.80 and 3.89 ppm. The ²*J*_{Pt-H} couplings to these olefin protons (10–35 Hz) are considerably lower than those for [Cl₂Pt(COD)] (²*J*_{Pt-H} = 65 Hz) [24]. The ¹³C NMR chemical shifts found for DDP and COD moieties



R=2, 6-Diisopropylphenly group

Fig. 1. Examples of main-group and transition metal complexes with insertion of Ga(DDP).



Scheme 1. Synthesis of platinum–gallyl complexes 2–4 from Ga^I(DDP).

fall in the expected range (Supporting Information S3). Molecule 3 exhibits a non symmetric structure in solution at room temperature, which makes all protons magnetically non-equivalent. We were able to assign all resonances in 3 from the two-dimensional nuclear magnetic resonance spectroscopy [HMBC (Heteronuclear Multiple Bond Coherence) spectrum, see Supporting Information Figure: S7]. The structural complexity in the molecule 3 caused a few broad, partially overlapping signals of DDP and dicyclopentadienyl ligands in the aliphatic region. The proton NMR spectrum of **3** exhibits the characteristic 4 septets of -CH- and 8 sets of doublets associated with 4 and 8 non-equivalent isopropyl and methyl protons of this complex, while the ¹³C NMR spectrum shows the expected twelve resonances of the corresponding carbons. In contrast, ¹H NMR spectrum of **2** shows only 6 resonances (two septets and four doublets) for the same protons, indicative of an over-all more symmetric structure in solution.

Furthermore, complex **3** exhibits the unequal nature of two CH₃ protons on the DDP ring which appear at δ 1.77 and 1.74 ppm. ¹H NMR of 3 at room temperature also exhibits four different broad olefin protons centred at δ 7.88, 6.19, 4.87 and 4.17 ppm, which are associated to the coupling with ¹⁹⁵Pt nuclei. The corresponding ¹³C NMR chemical shifts are assigned as δ 139.4 and 132.6 ppm for the olefin carbons of $-C_3 = C_4$ - and 85.2 and 83.1 for $C_1=C_2$ (atom labelling is shown in Fig. 4, for ¹³C NMR see Supporting Information Figure S6). The methine $(\gamma$ -C₁₂) carbon in **3** resonates at δ 100.4 ppm whereas the same DDP carbon in **2** resonates at 99.4 ppm, which is slightly shifted to up field region. The ¹³C NMR spectrum of 3 also indicates the deshielding nature of imino carbons (-C=N-) occurred in DDP ring (δ 170.9 and 170.7 ppm), when compared with the literature reported complexes [17]. The structure and composition of 2 and 3 are consistent with the elemental, ¹H and ¹³C NMR data.

2.2. Reaction of [(COD)Pd(Me)(OTf)] with Ga^l(DDP)

The reaction of **1** with [(COD)Pd(Me)(OTf)] afforded [(DDP) Ga(Me)(OTf)] (**4**) as a colourless solid in 33% isolated yield. The formation of **4** involves the reduction of Pd^{II} to Pd⁰ followed by the

concomitant oxidation of group 13 metal Ga^I to Ga^{III} by abstracting -CH₃ and triflate groups from the palladium centre. It appears that this reduction is quite fast and yields a black precipitate within few minutes of reaction time. Compound 4 is sensitive to air and moisture and soluble in common organic solvents such as benzene, toluene, fluorobenzene and THF. The ¹H NMR spectrum of **4** shows a sharp singlet at δ 1.57 ppm, corresponding to the presence of methyl protons of DDP ring. The -CH- protons of isopropyl groups appear as broad resonances at 2.84 and 3.84 ppm. In addition to the DDP ligand, the resonance associated with methyl protons of Ga–CH₃ appears at δ : -0.46 ppm in ¹H NMR and that of the methyl carbon resonates at δ ; -13.8 ppm in ¹³C NMR spectrum [5,25,26]. The typical methine (γ -CH) carbon in DDP ring is slightly shifted to the low field region (δ 100.7 ppm) due to the presence of triflate group on the gallium (III) centre. It is noteworthy that the triflate carbon atom was not observed in the ¹³C{¹H} NMR spectroscopic time scale, hence the existence of triflate group is confirmed from the infrared spectrum. A sharp stretching frequency observed at 1013 cm⁻¹ is assigned for the C–F bonds (Supporting Information Figure S11).



Fig. 2. Molecular structure of **2**. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)-Ga(2) 2.417(16), Pt(1)-C(5) 2.155(10), Pt(1)-C(4) 2.211(12), Pt(1)-Cl(1) 2.362(3), Pt(1)-C(8) 2.454(13), C(4)-C(5) 1.385(15), C(1)-C(8) 1.389(16), Ga(2)-Cl(2) 2.249(3), Ga(2)-N(2) 1.983(10), N(1)-Ga(2) 2.019(9), Pt(1)-Cl(1) 2.362(3), Cl(1)-Pt(1)-Ga(2) 85.5(8), Cl(2)-Ga(2)-Pt(1) 110.0(9), N(2)-Ga(2)-N(1) 97.2(4).



Fig. 3. Molecular structure of **3.** Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. The disorder in the dcy carbons has been refined. Selected bond lengths (Å) and angles (deg): Pt(1)–Ga(2) 2.413(7), Pt(1)–C(31) 2.146(11), Pt(1)–C(30) 2.161(11), Pt(1)–C(39), 2.507(12), Pt(1)–C(38) 2.576(10), Ga(1)–Cl(2) 2.214(19), Pt(1)–Cl(1) 2.320(2), Ga(1)–N(1) 1.953(5), Ga(1)–N(2) 1.962(6), C(30)–C(31) 1.372(15), C(38)–C(39) 1.459(15), Cl(1)–Pt(1)–Pt(1)–Ga(1) 85.3(5), Cl(2)–Ga(1)–Pt(1) 111.56(6), N(1)–Ga(1)–N(2) 96.3(2).

2.3. Molecular structures of 2-4

In order to characterise the platinum-gallium bonding, the solid state structures of **2** and **3** were unambiguously determined by the single crystal X-ray diffraction technique. Perspective views of the molecular structures of **2**, **3** with atom numbering schemes are shown in Figs. 2 and 3 respectively. Crystal data and the details of the structure determinations are given in Table 1, whereas selected bond lengths and bond angles are given in corresponding figure footnotes.

Single crystals suitable for X-ray structural determination for compounds **2** and **3** were obtained as pale yellow crystals from saturated toluene solutions at -30 °C. For compound **4** colourless crystals were grown from toluene by layering with *n*-hexane at -30 °C. X-ray crystallographic analysis carried out on compound **4** resulted in poor crystallographic data. Therefore, its data and structure are not included here (see in the supplementary data as Figure S1 and Table S1). Nevertheless, the data obtained for **4** are sufficient to get the connectivity of all the atoms, which confirmed the presence of a tetra-coordinated gallium centre bearing one DDP ligand and both, the triflate and methyl groups. These data match with the analytical and spectroscopic characterization of **4**.

Complex **2** crystallized in the space group P-1 with a disordered solvent molecule (toluene), whereas complex **3** crystallized with two solvent (toluene) molecules in the monoclinic system (Space group P21/c). The solid state structures of **2** and **3** shows the insertion of Ga(DDP) into the Pt–Cl bond. The molecular structure



Fig. 4. All carbon atoms are labelled for NMR assignment in complex 3.

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Crystallographic data and collection parameters for compounds 2 and 3.^a

	2	3
Formula	C ₄₄ H ₆₁ Cl ₂ GaN ₂ Pt	C ₅₃ H ₆₉ Cl ₂ GaN ₂ Pt
Mol wt	953.66	1069.81
Data / restraints / parameters	6936 / 120 / 398	8538 / 42 / 483
Data coll, T, K	111(2)	110(2)
Wavelength, Å	0.71073	0.71073
Crystal system, space group	Triclinic, P-1	Monoclinic, P21/c
<i>a</i> , Å	11.0869(12)	20.3741(11)
<i>b</i> , Å	12.4058(11)	18.3324(10)
<i>c</i> , Å	15.6409(16)	12.9208(7)
α, deg	88.722(8)	90.00
β, deg	79.674(9)	90.083(5)
γ, deg	69.390(9)	90.00
<i>V</i> , A ³	1979.0(3)	4826.0(5)
Z, ρ (Calcd) Mg/m ³	2, 1.600	4, 1.472
μ , mm ⁻¹	4.380	3.601
F(000)	964	2176
Crystal size, mm	$0.35\times0.30\times0.25$	$0.31 \times 0.10 \times 0.07$
θ range, deg	3.09 to 25.00	2.90 to 25.05
Reflections collected/unique	12433 / 6936	70499 /8538
	[R(int) = 0.1060]	[R(int) = 0.1515]
Limiting indices	-13<=h<=13,	-24<=h<=24,
	-11 < =k < =14,	-21<=k<=21,
	-18 <= l <= 18	-15 <= l <= 15
Completeness to theta $= 25.00$,	99.6%	99.8 %
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.4073 and 0.3094	0.7866 and 0.4015
Goodness-of-fit on F ²	0.683	0.950
Final R indices [I>2sigma(I)]	R1 = 0.0573,	R1 = 0.0544,
	wR2 = 0.0997	wR2 = 0.1099
R indices (all data)	R1 = 0.1407,	R1 = 0.0962,
	wR2 = 0.1115	wR2 = 0.1177
Largest diff. peak and hole, e.A ⁻³	1.934 and -1.426	0.948 and -1.842

^a refinement method - Full-matrix least-squares on F²

of complexes 2 and 3 depicts that the Pt centres are surrounded by Cl, Ga(DDP) and η^4 -coordinated 1,5-cyclooctadiene (for **2**) and η^4 coordinated dicyclopentadiene (for 3). In both compounds the Cl ligands are arranged in a trans orientation to each other. The Pt–Ga bond distances in **2** and **3** are almost identical [Pt(1)-Ga(2)]2.417(2), Pt(1)-Ga(2) 2.413(7) Å]. These bonds are considerably longer than the Pt-Ga distances in the homoleptic complex [Pt(GaCp*)₄] (2.335(2) Å) or the terminal Pt–Ga distances in the dimeric cluster [Pt₂(GaCp*)₅] (2.326(2) Å and 2.331(1) Å) [22], both featuring Ga(I) ligands. A similar trend can be observed when platinum complexes containing COD and Ga(DDP) are compared, for example [Pt(1,3-COD){Ga(DDP)}2] (Pt-Ga 2.346(1) and 2.342(1) Å) [17] and [Pt{Ga{[N(Ar)C(H)₂]}}₂(COD)] (Pt–Ga 2.383(7) Å) [11]. This elongation is expected because of the tetra-coordinated Ga centre of 2 (also in 3), as compared with lower coordinate Ga centres in the cited reference compounds. Certainly, the bulky Nheterocyclic ligand maintains some steric effect on the Pt–Ga bond distance, too. One should be aware that this kind of Pt-Ga bond lengths, and M-E bonds in general are quite dependent on the type of ligands at both metal centres which influence electronic and steric situations simultaneously. For example, the Pt-Ga distance of $[(Cy_2PCH_2CH_2PCy_2)Pt(GaR_2)(R)]$ (R = CH₂^tBu, Cy = cyclohexyl), exhibiting a tri-coordinate Ga centre, amounts to 2.438(1) Å [27]. The Pt–Cl bond distance in complex **2** [2.362(3) Å] shows a notable deviation when compared to the parent molecule [(1, 5-COD)PtCl₂] (av: Pt–Cl 2.257 Å) [28,29]. As it is observed in other Ga(DDP) supported metal complexes, the bond angles in both compounds suggest that the gallium centre is shifted out from the heterocyclic C₃N₂ plane after coordination with the platinum centre. The bite angles of N–Ga–N in complexes 2 and 3 are 97.2(4)° [N(2)-Ga(2)– N(1)] and 96.3(2)° [N(1)–Ga(1)–N(2)], respectively, which are significantly larger than the same observed in $Ga(DDP)(85.53(5)^{\circ})$ [5]. In complex **2**, the change in the bite angle is approximately 11.47°, whereas in **3**, it is 10.77° which lies in the range of those compounds previously reported [12d, 15,30]. The Ga-N bond lengths are shortened considerably in comparison with the free ligand 1. The average Ga–N bond distances in 1 is reported as 2.054 Å, whereas the average Ga-N bond lengths in 2 and 3 are observed as 2.001 and 1.957 Å respectively. The increased electrophilic nature of **1** upon insertion reaction and coordination to the platinum centre in 2 and 3, has resulted in the shortening of Ga-N bonds and elongation in N-Ga-N bite angles relative to the free Ga(DDP). However, the structural features of the Ga(DDP) backbone in 2 and 3 are similar to those reported metal complexes containing this sterically crowded ligand [15]. At this point we like to note that we refrain from discussing oxidation states of the Ga centres in 2 and **3** for reasons we have extensively explained in numerous previous publications on similar systems [12d,31].

3. Conclusions

In summary, we have prepared two new Pt-Ga containing compounds and showed that Ga(DDP) selectively inserts into the Pt–Cl bonds of [(1,5-COD)PtCl₂] and [(dcy)PtCl₂] to yield exclusively products **2** and **3**. Unlike the GaCp*, Ga(DDP) does not reduce the Pt(II) centre and trap the Pt(0) by substituting the olefin ligands even when used in excess [17]. In contrast, the reaction of Ga(DDP) with Pd(II) precursor yields Pd(0) as precipitate and the oxidized gallium(III) product [(DDP)Ga(Me)(OTf)] (4). This behaviour is in accordance with the steric bulk of Ga(DDP), which hinders the efficient trapping of Pd(0) as $[Pd(Ga(DDP)_n)]$, the weaker coordination properties of the hard triflate at the soft Pd in comparison to Cl and the well-known over-all enhanced susceptibility of organometallic Pd(II) complexes for reduction to Pd(0) in comparison to Pt(II). The ambivalent reactivity of Ga(DDP), depending on the transition metal centre and the ancillary ligands, i.e. coordination, insertion and reduction, may allow the synthesis of unusual transition metal compounds and clusters as we have recently found for main-group elements [13,14].

4. Experimental

All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Hexane and toluene were dried using an MBraun Solvent Purification System. The final H₂O content in all solvents was checked by Karl Fischer titration and did not exceed 5 ppm. Compounds [(1,5-COD) PtCl₂] [32], [(COD)Pd(Me)(OTf)] [33] and Ga(DDP) [5] were prepared as previously described procedures. [(dcy)PtCl₂] is purchased from ABCR. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr University Bochum. NMR spectra were measured on a Bruker Avance DPX-250 and DRX-600 MHz spectrometers in C₆D₆ and d₈-THF at 298 K. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Chemical shifts are described in parts per million, downfield shifted from TMS, and are consecutively reported as position (δ_H or δ_C), relative integral, multiplicity (s = singlet, d = doublet, sept = septet, m = multiplet), couplingconstant (J in Hz) and assignment. IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer.

4.1. Preparation of [(COD)Pt(Cl){ClGa(DDP)}] (2)

To a stirred suspension of $[(1,5-COD)PtCl_2](0.05 \text{ g}, 0.133 \text{ mmol})$ in toluene (2 mL), **1** (0.065 g, 0.133 mmol) was added at room temperature. In few minutes the pale yellow slurry became orange then to brown. The resultant reaction mixture was stirred for 24 h

and then filtered to remove the black solid. The filtrate was concentrated to half of its volume and stored at -30° C for one week to afford pale yellow needles of 1. These crystals were filtered and quickly washed with *n*-hexane $(2 \times 2 \text{ mL})$ and dried in vacuo. Yield: 43% (0.05 g, based on [(1,5-COD)PtCl₂]). Mp: > 185 °C (decomp). ¹H NMR(C₆D₆, 250.1 MHz, ppm): δ = 7.16–7.14 (m, 6H, phenyl), 5.57–5.47 (m, ${}^{2}J_{Pt-H} = 10$ Hz, 2H, H–C=C, COD), 4.94 (s, 1H, CH, Ga(DDP)), 4.66–4.36 (m, ²*J*_{*Pt-H*} = 35 Hz, 2H, *H*–C=C, COD), 3.94–3.75 (m, 4H, merged with each other, CH(CH₃)₂), 1.62 (s, 6H, CH₃), 1.58–1.52 (m, 12H, merged with CH(CH₃)₂ and 2H from H-C-C, COD) 1.34–1.27 (m, 4H, H-C-C, COD), 1.23 (d, ${}^{2}I_{HH} = 7$ Hz, 6H, $CH(CH_3)_2$), merged with 2H from H-C-C, COD), 1.14 (d, $^{2}J_{HH} = 6.5$ Hz, 6H, CH(CH₃)₂). 13 C NMR (C₆D₆, 62.8952 MHz): $\delta = 169.6$ (C=N), 145.3 (C(Dipp)-N), 145.1 (C(Dipp)-N, Dipp = 2, 6-diisopropylphenyl), 142.2 (o-C(Dipp)), 127.3 (m-C(Dipp)), 125.0 (m-C(Dipp)), 124.6 (*p*-*C*(Dipp)), 124.3 (*p*-*C*(Dipp)), 99.4 (*γ*-*C*), 77.6 (C=C; COD), 32.1 (C-C, COD], 28.8 (CHMe2), 28.5 (CHMe2), 26.5 (CMe), 25.8 (CMe), 25.2 (CHMe₂), 25.1 (CHMe₂), 25.0 (CHMe₂), 24.1 (CHMe₂) ppm. IR $(\nu, \text{ cm}^{-1})$: 2938(m), 2844(w), 1517(vs), 1449(m), 1424(m), 1371(vs), 1348(m), 1304(vs), 1252(m), 1242(s), 1165(s), 1091(w), 1048(w), 1010(s), 990(w), 931(w), 856(s), 787(vs), 749(vs), 703(w), 524(w), 437(s). Anal. Calcd (%) for C₃₇H₅₃N₂Cl₂GaPt (861.53 g/mol): C, 51.58; H, 6.20; N, 3.25; found: C, 51.15; H, 6.67; N, 4.25.

4.2. Preparation of [(dcy)Pt(Cl){ClGa(DDP)}] (3)

To a stirred solution of [(dcy)PtCl₂] (0.08 g, 0.20 mmol) in toluene (4 mL), 1 (0.097 g, 0.20 mmol) was added at room temperature. The colour of the reaction mixture turns pale vellow to brown. The resultant reaction mixture was stirred for 20 h and then filtered to remove the insoluble black solid. The filtrate was concentrated to 2 mL and stored to -30° C for one week to afford pale yellow crystalline substance. Crystals formed were filtered, quickly washed with *n*-hexane $(2 \times 3 \text{ mL})$ and dried in vacuo. Yield: 28% (0.05 g, based on $[(dcy)PtCl_2]$). Mp: $> 180^{\circ}C(decomp)$. ¹H NMR (d₈-THF, 600.13 MHz): $\delta = 7.92 - 7.83$ (m, ²J_{Pt-H} = 27 Hz, 1H, H–C₄, dcy), 7.22-7.14 (m, 6H, aromatic protons, Ga(DDP)), 6.19 (br, 1H, H–C₃, dcy), 5.15 (s, 1H, methine, Ga(DDP)), 4.87 (m, 1H, H–C₁, dcy), 4.10-4.23 (m, 1H from H-C₄, and 1H from H-C₃₄), 3.93 (sept, 1H, ${}^{2}J_{\text{HH}} = 7$ Hz, H–C₃₇), 3.49 (sept, 1H, ${}^{2}J_{\text{HH}} = 6.8$ Hz, H–C₁₈, Ga(DDP)), 3.34–3.38 (m, 1H from H–C₉ and 1H from H–C₂₉), 3.28 (br, 1H, H–C₇, dcy), 2.86 (br, 1H, H–C₆, dcy), 2.59–2.62 (br, 1H, H–C₈, dcy), 1.81–1.86 (m, 2H, H–C₅, dcy), 1.77 (s, 3H, CH₃, H–C₁₅, Ga(DDP)), 1.74 (s, 3H, H-C₁₄, Ga(DDP)), 1.71-1.73 (m, 2H, H-C₁₀, dcy), 1.59 (d, 3H, ${}^{2}J_{\text{HH}} = 6$ Hz, H-C_{35,} Ga(DDP)), 1.56 (d, 3H, ${}^{2}J_{\text{HH}} = 6.4$ Hz, H–C_{34,} CHCH₃), 1.32 (d, 3H, ${}^{2}J_{HH} = 7$ Hz, H–C₃₉ CHCH₃), 1.30 (d, 3H, ${}^{2}J_{HH} = 6$ Hz, H–C₃₈, CHCH₃), 1.23 (d, 3H, ${}^{2}J_{HH} = 6.7$ Hz, H–C₁₇, CHCH₃), 1.20 (d, 3H, ${}^{2}J_{HH} = 7.4$ Hz, H–C₁₆, CHCH₃), 1.12 (d, 3H, ${}^{2}J_{HH} = 6$ Hz, H–C₂₆, CHCH₃), 1.07 (d, 3H, ${}^{2}J_{HH} = 6.5$ Hz, H–C₂₇, CHCH₃) ppm. ¹³C NMR (d₈-THF, 150.90 MHz): $\delta = 170.9(C_{13}-N, C_{13}-N)$ DDP), 170.7(C₁₁-N, DDP), 146.3(C₂₈(Dipp)-N), 146.1(C₂₄(Dipp)-N), 145.6(o-C₃₃(Dipp)), 145.4(o-C₂₃(Dipp)), 142.6(o-C₂₉(Dipp)), 141.9(o-C₁₉(Dipp)), 139.4(C₄=C, dcy), 132.6(C₃=C, dcy), 127.9(*p*-C₃₁(Dipp)), 127.7(o-C₂₁(Dipp)), 125.2(*m*-C₃₀(Dipp)), $125.0(m-C_{32}(Dipp)),$ 124.9(*m*-C₂₂(Dipp)), 124.8 (*m*-C₂₀(Dipp)), 100.4(γ-C₁₂, Ga(DDP)), 85.2(C₁=C, dcy), 83.2(C₂=C, dcy), 59.1(C₅, dcy), 57.5(C₉, dcy), 52.7(C₇, dcy), 48.0(C₆, dcy), 43.5(C₈, dcy), 33.8(C₁₀-C=C, dcy), 29.6(C₃₄H(CH₃)₂), 29.5(C₃₇H(CH₃)₂), 29.4(C₁₈H(CH₃)₂), 28.8(C₂₅H (CH₃)₂), 27.8(C₃₅H(CH₃)₂), 26.8(C₃₆H(CH₃)₂), 25.7(C₃₉H(CH₃)₂), 25.6 (C₃₈H(CH₃)₂), 25.4 (C₁₇H(CH₃)₂), 25.3(C₁₆H(CH₃)₂), 25.2(C₂₆H (CH₃)₂), 24.8(C₂₇H(CH₃)₂), 24.6(C₁₅-C), 24.3(C₁₄-C) ppm. IR (cm⁻¹): 2939(s), 2901(w), 1517(vs), 1449(w), 1426(s), 1371(vs), 1305(vs), 1251(s), 1167(s), 1010(s), 929(s), 857(s), 790(vs), 753(s), 728(vs). Anal. Calcd (%) for C₃₉H₅₃Cl₂N₂GaPt (885.58 g/mol): C, 52.90; H, 6.03; N, 3.16; found: C, 53.50; H, 6.45; N, 2.93.

4.3. Reaction of [(COD)Pd(Me)(OTf)] with 1 and the formation of [(DDP)Ga(Me)(OTf)](4)

Ga(DDP) (0.09 g, 0.184 mmol) in toluene (1 mL) was added to a Schlenk tube containing [(COD)Pd(Me)(OTf)] (0.07 g, 0.184 mmol) in fluorobenzene (3 mL) at -40 $^{\circ}$ C. The resultant reaction mixture was immediately turned to dark brown with formation of a grevblack solid. It was slowly warmed to room temperature over a period of 30 min and stirred for another 30 min. The grey-black precipitate formed was filtered off and the filtrate was completely evaporated under reduced pressure, dissolved in toluene (2 mL) and stored at $-30\degree$ C. Colourless crystals formed in 3 days were filtered, quickly washed with *n*-hexane $(2 \times 4 \text{ mL})$ and dried in vacuo. Yield: 33% (0.04 g, based on [(COD)Pd(Me)(OTf)]. Mp: 169–171 °C. ¹H NMR $(C_6 D_6, 250 \text{ MHz}): \delta = 7.15 - 7.00 (m, 6H, Ar CH), 5.16 (s, 1H, \gamma - CH), 3.84$ (broad, 2H, CH(Me)₂), 2.84 (broad, 2H, CH(Me)₂), 1.57 (s, 6H, CH₃), 1.34–1.32 (broad, 12H, CH(Me)₂), 1.07–0.98 (broad, 12H, CH(Me)₂), -0.46 (s, 3H, Ga-CH₃) ppm; ¹³C NMR (C₆D₆, 62.8952 MHz): $\delta = 172.1$ (C=N), 146.4 (C(Dipp)-N), 145.4 (C(Dipp)-N), 143.1 (o-C(Dipp)), 139.2 (*o*-*C*(Dipp)), 124.1 (*m*-*C*(Dipp)), 125.5 (*p*-*C*(Dipp)), 100.7 (γ-*C*), 28.7 (CHMe2), 27.4 (CHMe2), 25.2 (CMe), 24.5 (CMe), 23.6 (CHMe2), -13.8 (Ga–CH₃) ppm. The ¹³C NMR resonance of the triflate group could not be detected. IR (ν , cm⁻¹): 2940(s), 2906(vw), 1507(vs), 1450(w), 1428(w), 1364(vs), 1335(w), 1306(vw), 1280(w), 1250(s), 1226(vs), 1193(vs), 1174(vs), 1090)(w), 1013(vs), 994(vs), 938(w), 867(vw), 794(vs), 754(s), 624(vs), 514(vw), 497(vw), 447(w). Anal. Calcd (%) for C₃₁H₄₄F₃GaN₂O₃S (651.4862 g/mol). C, 57.15; H, 6.81; N, 4.30; S, 4.92; found: C, 55.91; H, 6.87; N, 4.03; S, 7.29.

4.4. X-ray crystallography

The X-ray crystal structures were measured with an Oxford Excalibur 2 diffractometer using Mo_{K α} radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97 [34].

Acknowledgement

We are thankful to Mr. Martin Gartmann, Biomolecular NMR facility at Ruhr University Bochum for 2D NMR measurements.

Appendix

CCDC-801252(2), -801253(3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

Appendix Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.04.008.

References

- [1] (a) M. Asay, C. Jones, M. Driess, Chem. Rev. 111 (2011) 354-396;
- (b) S.G. Gallardo, G. Prabusankar, T. Cadenbach, C. Gemel, M. Hopffgarten, G. Frenking, R.A. Fischer, Structure and Bonding (Book Series), vol. 136, Springer Berlin / Heidelberg, 2010, pp. 147-188; (c) J.B. Robert, J. Cameron, Coord. Chem. Rev. 249 (2005) 1857-1869;

(d) C. Gemel, T. Steinke, M. Cokoja, A. Kempter, R.A. Fischer, Eur. J. Inorg. Chem. (2004) 4161-4176;

(e) R. Murugavel, V. Chandrasekhar, Angew. Chem. 111 (1999) 1289-1293 Angew. Chem. Int. Ed. 38(1999) 1211-1215.

[2] (a) R.A. Fischer, J. Behm, T. Priermeier, W. Scherer, Angew. Chem. Int. Ed. 32 (1993) 746-748;

(b) R.A. Fischer, W. Scherer, M. Kleine, Angew. Chem. Int. Ed. 32 (1993) 748–750; (c) M. Cokoja, H. Parala, A. Birkner, O. Shekhah, M.W.E. van den Berg, R.A. Fischer, Chem. Mat. 19 (2007) 5721-5733;

(d) M. Cokoja, H. Parala, A. Birkner, R.A. Fischer, O. Margeat, D. Ciuculescu, C. Amiens, B. Chaudret, A. Falqui, P. Lecante, Eur. J. Inorg. Chem. (2010) 1599-1603:

(e) M. Cokoja, B.R. Jagirdar, H. Parala, A. Birkner, R.A. Fischer, Eur. J. Inorg. Chem. (2008) 3330-3339.

- T. Cadenbach, C. Gemel, T. Bollermann, R.A. Fischer, Inorg. Chem. 48 (2009) [3] 5021-5026
- [4] C. Cui, H. Roesky, H.G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, Angew. Chem. 112 (2000) 4444-4446 Angew. Chem. Int. Ed. 39(2000) 4274-4276
- [5] N.J. Hardman, B.E. Eichler, P.P. Power, Chem. Commun. (2000) 1991–1992.
- M.S. Hill, P.B. Hitchcock, Chem. Commun. (2004) 1818-1819.
- [7] M.S. Hill, P.B. Hitchcock, R. Pongtavornpinyo, Chem. Commun. (2006) 3720-3722
- (a) E.S. Schmidt, A. Jokisch, H. Schmidbaur, J. Am. Chem. Soc. 121 (1999) [8] 9758-9759:
 - (b) R.J. Baker, R.D. Farley, C. Jones, M. Kloth, D.M. Murphy, J. Chem. Soc. Dalton Trans. (2002) 3844-3850.
- [9] C. Jones, P.C. Junk, J.A. Platts, A. Stasch, J. Am. Chem. Soc. 128 (2006) 2206-2207.
- [10] (a) S.P. Green, C. Jones, A. Stasch, Inorg. Chem. 46 (2007) 11-13; (b) G.J. Moxey, C. Jones, A. Stasch, P.C. Junk, G.B. Deacon, W.D. Woodul, P.R. Drago, Dalton. Trans. (2009) 2630-2636.
- [11] C. Jones, D.P. Mills, R.P. Rose, A. Stasch, Dalton. Trans. (2008) 4395-4408.
- (a) A. Kempter, C. Gemel, R.A. Fischer, Inorg. Chem. 47 (2008) 7279-7285; [12] (b) A. Kempter, C. Gemel, N.J. Hardman, R.A. Fischer, Inorg. Chem. 45 (2006) 3133-3138: (c) A. Kempter, C. Gemel, T. Cadenbach, R.A. Fischer, Inorg. Chem. 46 (2007) 9481-9487:

(d) G. Prabusankar, S.G. Gallardo, A. Doddi, C. Gemel, M. Winter, R.A. Fischer, Eur. J. Inorg. Chem. (2010) 4415-4418.

- [13] G. Prabusankar, C. Gemel, P. Parameswaran, C. Flener, G. Frenking, R.A. Fischer, Angew. Chem. Int. Ed. 48 (2009) 5526-5529.
- [14] G. Prabusankar, A. Kempter, C. Gemel, M.K. Schröter, R.A. Fischer, Angew. Chem. Int. Ed. Engl. 47 (2008) 7234-7237.
- [15] G. Prabusankar, C. Gemel, M. Winter, R.W. Seidel, R.A. Fischer, Chem. Eur. J. 16 (2010) 6041-6047.
- [16] M. Cokoja, C. Gemel, T. Steinke, F. Schröder, R.A. Fischer, Dalton. Trans. (2005) 44-54.
- [17] A. Kempter, C. Gemel, R.A. Fischer, Chem. Eur. J. 13 (2007) 2990-3000.
- [18] D. Weiß, M. Winter, R.A. Fischer, C. Yu, K. Wichmann, G. Frenking, Chem. Commun. 24 (2000) 2495-2496.
- [19] R.A. Fischer, D. Weiß, T. Steinke, M. Winter, G. Frenking, N. Froehlich, J. Uddin, Organometallics 19 (2000) 4583-4588.
- [20] T. Steinke, C. Gemel, M. Winter, R.A. Fischer, Chem. Eur. J. 11 (2005) 1636-1646. B. Buchin, C. Gemel, T. Cadenbach, I. Fernández, G. Frenking, R.A. Fischer, [21] Angew. Chem. Int. Ed. Engl. 45 (2006) 5207-5210.
- [22] C. Gemel, T. Steinke, D. Weiss, M. Cokoja, M. Winter, R.A. Fischer, Organometallics 22 (2003) 2705-2710.
- [23] T. Cadenbach, C. Gemel, R.A. Fischer, Angew. Chem. Int. Ed. 47 (2008) 9146-9149.
- [24] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 47-49.
- S. Singh, V. Jancik, H.W. Roesky, R.H. Irmer, Inorg. Chem. 45 (2006) 949-951. [25] B. Nekoueishahraki, A. Jana, H.W. Roesky, L. Mishra, D. Stern, D. Stalke, [26]
- Organometallics 28 (2009) 5733-5738. [27]
- R.A. Fischer, H.D. Kaesz, S.I. Khan, H.J. Muller, Inorg. Chem. 29 (1990) 1601–1602.
- [28] A.B. Goel, S. Goel, D.V.D. Veer, Inorg. Chim. Acta 65 (1982) L205-L206. [29] A. Syed, E.D. Stevens, S.G. Cruz, Inorg. Chem. 23 (1984) 3673-3674.
- [30] G. Prabusankar, A. Doddi, C. Gemel, M. Winter, R.A. Fischer, Inorg. Chem. 49
- (2010) 7976 7980
- [31] (a) T. Cadenbach, C. Gemel, D. Zacher, R.A. Fischer, Angew. Chem. Int. Edit. 47 (2008) 3438-3441; (b) T. Cadenbach, C. Gemel, T. Bollermann, I. Fernandez, G. Frenking,
 - R.A. Fischer, Chem. Eur. J. 14 (2008) 10789-10796; (c) T. Bollermann, G. Prabusankar, C. Gemel, R.W. Seidel, M. Winter,
 - R.A. Fischer, Chem. Eur. J. 16 (2010) 8846-8853.
- [32] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521-6528.
- [33] P. Burger, J.M. Baumeister, J. Organomet. Chem. 575 (1999) 214-222.
- [34] (a) G.M. Sheldrick, SHELXS-97, Program for Structure Solution:, Acta Crystallogr. A46 (1990) 467-473; (b) G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement. Universität Göttingen, Göttingen, 1997;
 - (c) A.L. Spek, Acta Crystallogr. Sect. A: Found.Crystallogr 46 (1990) C34.