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Bi- and trinuclear oxalamidinate complexes of palladium as catalysts in the copper-free Sonogashira reaction and in the Negishi reaction

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Abstract

The binuclear complex [(acac)Pd(*oxam*)Pd(acac)] **1** (*oxam*: tetraphenyl oxalic amidinate) has been prepared from H_2*oxam* and $Pd(acac)_2$ in excellent yield. The complex was characterized by elemental analyses, mass spectroscopy, ^{1}H NMR, ^{13}C NMR spectroscopy and in the solid state by X-ray single crystal diffraction analyses. **1** consists of a bimetallic centrosymmetric unit in which the planar *oxam* ligand acts in a bis-chelating fashion. Each palladium center is in a planar environment.

The complex **1** acts as highly selective pre-catalyst in the copper-free Sonogashira reaction between 4-bromoacetophenone and phenylacetylene. Its long-time catalytic activity is higher than that of the related binuclear complex **2** (*oxam*: tetra-*p*-tolyl oxalic amidinate) or that of the trinuclear compound [(acac)Pd(*oxam*)Zn(*oxam*)Pd(acac)] (**3**), the solid-state structure of which was also determined by an X-ray structural analysis of single crystals. In addition, **2** is an active and extremely selective pre-catalyst for the Negishi reaction between 3,5,6,8-tetrabromophenanthroline and R–C≡C–ZnCl (R: Ph, (^{i}prop)$_3$Si) to form tetra-alkyne-substituted derivatives.
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Keywords: Palladium; Sonogashira reaction; Negishi reaction; Binuclear complexes; *N*-chelate ligands

1. Introduction

Recently we have described the syntheses and structures of oligonuclear nickel(II) and palladium(II) complexes with oxalic amidinates bridging the metal centers. Some of them have proven to be active catalysts in a number of C–C-linking reactions [1–5].

From a general point of view these oligonuclear metal complexes are interesting candidates for homogeneous catalysts due to the following reasons: most of the complexes are air-stable and contain very simple, cheap bis-chelating ligands which are easily accessible. They bear *two* reactive metal centers on the peripheries and therefore, both metals may serve as carriers of catalytic activity. This activity can be tuned by *four* substituents of the nitrogen donor atoms of the ligand. Furthermore, the catalyst metals in these complexes are connected via oxalamidinate bridges which allow electronic communication between the peripheral metals. Due to their twofold anionic nature the oxalic amidinates are poor π-acceptor ligands which do not form stable Ni(0) or Pd(0) complexes. Nevertheless, Ni and Pd complexes with oxalic amidinate bridges are active in the Kumada cross coupling or in the Heck reaction, although, according to the accepted mechanism of these reactions, Ni(0) or Pd(0) species are postulated to be formed in these catalytic reactions [6–11].

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To evaluate the catalytic potential of oligonuclear oxalamidinate complexes in a range of other C–C-bond reactions we now report on the copper-free Sonogashira reaction and show that binuclear complex **1** is most active and highly selective. In addition, **2** is an extremely selective catalyst in the Negishi reaction of tetrabromo-phenanthroline.

N,*N*-chelate ligands for controlling this catalysis as well as bi- and oligonuclear complexes catalyzing this reaction are very rare [12,13].

2. Results and discussion

2.1. Synthesis and structures of the complexes 1–4

Scheme 1 shows the molecular formula of the complexes **1**–**4**. Complex **1** can be obtained by treating tetra(phenyl)oxalamidine (H_2A) with $Pd(acac)_2$ (acac: acetylacetonate) following a general synthesis for binuclear oxalamidinate Ni- and Pd complexes in good yield [1,2]. Complex **2** was already described using the same preparative method [2].

The binuclear complex **1** was characterized by elemental analyses, ^1H NMR, ^{13}C NMR and mass spectroscopy. The solid-state structure of single crystals of **1** was established by an X-ray study (Fig. 1). As expected, the two Pd ions are in a square-planar coordination sphere created by two N atoms of the bridging ligand and two O atoms of the terminal acac ligand. The double chelate ligand moiety containing two CN_2 units is essentially planar, with all C–N bonds being equivalent. The bond C–N distances in this centrosymmetric structure are 1.325(3) and 1.330(3) Å, indicating a partial double bond character due to complete electron delocalization over the CN_2 units. The C1–C1A bond length in the bridging ligand is that of a single bond (1.510(4) Å).

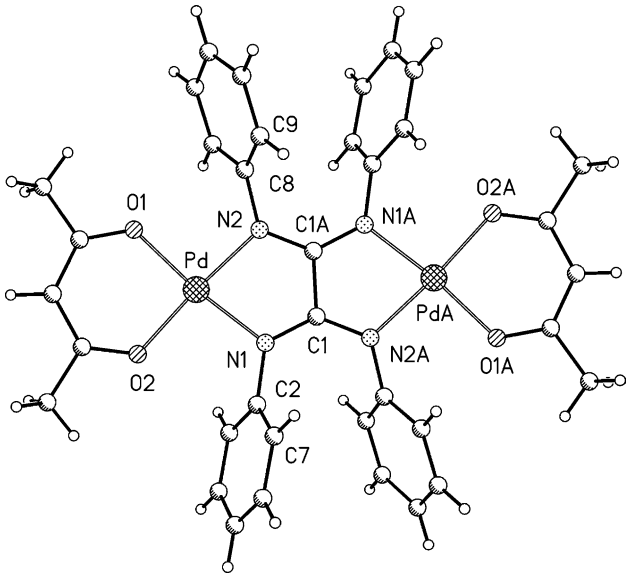
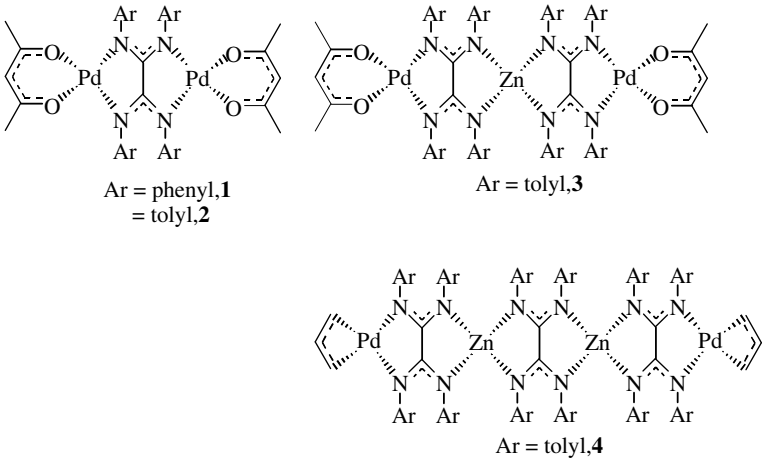


Fig. 1. Molecular structure of complex **1**; selected bond lengths (Å) and bond angles (°) Pd–O1 1.9953(16), Pd–O2 2.0066(15), Pd–N1 2.0117(18), Pd–N2 2.0091(18), N1–C1 1.325(3), N2–C1A 1.330(3), C1–C1A 1.510(4) N1–C1–N2A 131.19(19), O1–Pd–O2 91.54(7), N1–Pd–N2 80.82(7).

In addition, the aromatic phenyl groups at the four N atoms are distorted out of the plane of the two CN_2 units (in the average 56°). Other selected bond distances are listed in the caption of Fig. 1.

In comparison with the structure of **2** [2] only small structural differences in the bond lengths and angles are found. The Pd–N distances are equal (average 2.0105 Å); however, the Pd–O distances differ slightly with 2.013(3) Å for complex **2** and 2.001(2) Å for complex **1** . The C1–C1A distances of the bridging ligand lie in the same range for both complexes (1.510(4) Å (complex **1**) and 1.519(9) Å (complex **2**)), just as the C–N bonds of the CN_2 units do (1.330(3) Å (for **1**) and



Scheme 1. The complexes **1**–**4**.

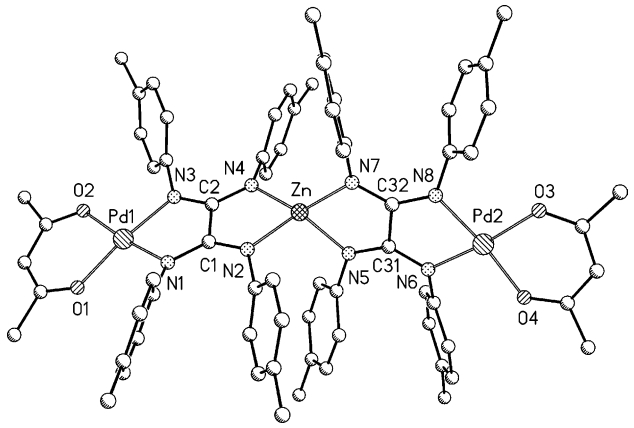


Fig. 2. Molecular structure of complex **3**; selected bond lengths (Å) and bond angles (°) Pd1–O1 1.999(5), Pd1–O2 2.010(4), Pd1–N1 2.003(5), Pd1–N3 2.008(6), Pd2–O3 2.012(4), Pd2–O4 2.000(4), Pd2–N6 1.999(5), Pd2–N8 2.006(5), Zn–N2 1.997(5), Zn–N4 1.990(5), Zn–N5 2.008(5), Zn–N7 1.993(5) C1–C2 1.518(9), C31–C32 1.524(8), C–N bond lengths 1.311(8)–1.341(7) O1–Pd1–O2 91.13(19), O3–Pd2–O4 91.53(18), N1–Pd1–N3 80.5(2), N6–Pd2–N8 80.96(19), N2–Zn–N4 83.2(2), N5–Zn–N7 82.7(2), N4–Zn–N5 126.6(2), N4–Zn–N7 130.7(2), N–C–N angles within the oxalic amidinates 130.8(6)–131.4(6).

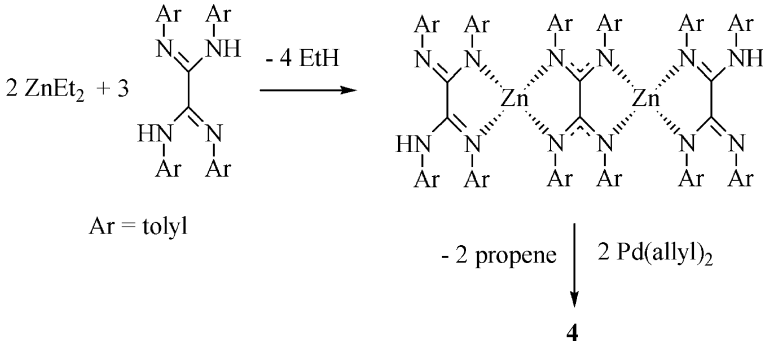
1.335(6) Å (for **2**)). The distortion of the aromatic groups out of the plane of the CN_2 units is about 56° for complex **1** and 60° for complex **2**.

The heterotrinuclear complex **3** (Scheme 1) was already obtained in a two-step reaction [2]. In the first step, a bis(oxalamidinato)Zn(II) complex was formed in situ by treating 1 equiv. of $ZnEt_2$ with a solution of 2 equiv. of the free oxalic amidine H_2B, followed by the addition of 2 equiv. of $Pd(acac)_2$. Upon very careful workup, we succeeded now in isolating single crystals of complex **3**. Its hitherto unknown solid-state structure is depicted in Fig. 2.

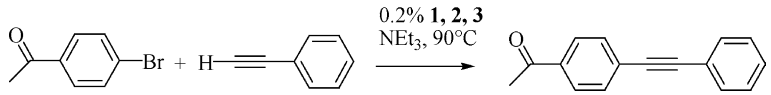
The three metal centres of the heterotrinuclear complex **3** are bridged by two tetra(*p*-tolyl)oxalic amidinates. The two peripheral Pd ions are each coordinated in a square-planar geometry created by two O atoms of the terminal acetylacetonate ligand (O–Pd–O angle 91.13(19)° and 91.53(18)°) and two N atoms of the tetra(*p*-tolyl)oxalamidinate ligand. The inner Zn ion is coordinated in a distorted tetrahedral geometry by four N atoms of two bridging oxalic amidinates. The two N–Pd–N bite angles are only slightly smaller than the two N–Zn–N bite angles. (80.5(2)° and 80.96(19)° compared to 83.2(2)° and 82.7(2)°). The two C–C bond lengths between the CN_2 units of the bridging oxalic amidinates lie in the range of single bonds, as was already noted for the dinuclear Pd-complexes **1** and **2**. Again, the two CN_2 units in the bridging ligand are planar with all C–N bonds being equivalent. Their bond lengths show a high double bond character with bond distances ranging from 1.311(8) to 1.341(7) Å. The *p*-tolyl substituents at the N atoms of the two bridging ligands are distorted out of the plane of the CN_2 units.

The heterotetranuclear compound **4** containing two peripheral palladium(II) centres and two inner zinc atoms bridged by three tetra(*p*-tolyl)oxalic amidinate ligands (Scheme 1) was synthesized according to Scheme 2. In the first step 2 equiv. of $ZnEt_2$ were reacted with 3 equiv. of the oxalic amidine H_2B at −70 °C to give an instable binuclear oxalamidinate zinc complex (Scheme 2). The cold solution of this intermediate was then added to a THF/toluene solution of $(allyl)_2Pd$ at −70 °C. After work up **4** was isolated as yellow microcrystalline compound in low yield (ca. 25%). Analysis and mass spectrum confirmed its composition. In the mass spectrum the tetranuclear complex ion $[(allyl\text{-}Pd)_2Zn_2(oxam)_3]^+$ (m/z = 1759) was detected as basic peak.

^1H and ^{13}C NMR studies were conducted in $CDCl_3$ at room temperature and showed all expected shifts and splitting patterns associated with the structure of **4**. The ^1H NMR spectrum of **4** shows the expected two singlets for the methyl groups at 2.04 and 2.07 ppm which integrated for 36H when compared with the 48 phenyl protons and the signals of the 10 protons of the allyl groups. The very simple pattern of the ^{13}C NMR spectrum supports the structure of **4**. Only 13 signals were observed, corresponding to the two different CH_3 groups (at 20.5 and 20.6 ppm), two signals for the η^3-bonded allyl groups (at 60.5 and 114.3 ppm),



Scheme 2. Preparation of **4**.



Scheme 3. Catalytic copper-free coupling of 4-bromoacetophenone and phenylacetylene with the catalysts **1**–**3**.

eight phenyl signals and one signal for the quarternary C atoms. We assume that the signal at 160.8 ppm belongs to the latter (see also Section 4).

2.2. Catalytic behaviour of *1*–*3* in the Sonogashira reaction and Negishi reaction

The oligonuclear complexes **1**–**3** are different to those of commonly used homogeneous Pd-pre-catalysts for the Sonogashira reaction [12] or for the Negishi reaction [14,15]. In these catalytic C–C bond forming reactions mononuclear compounds are used, mostly stabilized by phosphines or carbenes or as palladacycles. Much effort has been directed toward the reduction of the amount of Cu salt in the catalytic system preferently running the coupling between an aromatic halide and a terminal alkyne without any such additive. However, only few copper-free catalyst systems for the Sonogashira reactions were described [14,16–26].

In 1993, several Pd(0) complexes such as $Pd(PPh_3)_4$ were found to be active in the Sonogashira reaction without CuI; however, high palladium loading was used [16]. Recently, lower catalyst concentrations and faster reactions with $(Ph_3P)_2PdCl_2$ were achieved by developing an improved methodology [17]. The use of ionic liquids has also been described [18].

Herrmann et al. were successful in developing catalyst systems (such as $(dba)_3Pd_2$/(*t*-butyl)$_3$P) which work even at room temperature [13]. More recently, a number of palladacycles have been used as catalysts for the copper free catalysis with aryl bromides and terminal alkynes [19,20]. Also, aryl chlorides were successfully coupled with phenylacetylene by using pincer complexes containing PCP-type chelate ligands [21]. Astruc and coworkers [22] synthesized chelating and dendrimeric phosphines to stabilize Pd(II) in six-membered chelates for controlling the copper-free Sonogashira reaction at room temperature. Very interestingly, Buchwald and Gelman [23] found that the addition of copper cocatalysts can even inhibit the high activity of a palladium catalyst consisting of a steric bulk phosphine and $(CH_3CN)_2PdCl_2$.

In an initial experiment we used the substrates 4-bromoacetophenone and phenylacetylene in triethylamine as solvent at 90 °C, yielding 1-(4-acetylphenyl)-2-(phenyl)acetylene (Scheme 3) to evaluate the catalytic activity of the oligonuclear palladium complexes **1**–**3**.

Table 1 contains selected results which show, that all three complexes are catalytically active. No CuI is required to couple the two substrates in a very selective manner. The most active pre-catalyst is complex **1**, coupling the substrates almost quantitatively in 36 h (entry 4). The structurally very similar dinuclear Pd complex **2** is less active than **1** (entries 9–11) and the heterotrinuclear Pd/Zn complex **3** in which the palladium atoms are separated by an additional Zn complex moiety, is also less active than **1** (entries 12–14). In addition, complex **1** is also the most selective catalyst (100% selectivity), although the two other complexes are highly selective catalysts as well.

Although the mechanism of the Sonogashira reaction is not well established [14], it is generally accepted that the formation of a Pd(0) species (e.g., by reductive elimination of the product from an Ar–Pd–C≡C–Ar′ intermediate) and the following oxidative addition of Ar–X to regenerate a Pd(II) species are the key steps in the catalytic cycle. Due to their dianionic nature the oxalamidinates are poor π acceptor ligands which are not able to stabilize Pd(0). Not surprisingly, all attempts to form stable palladium(0) complexes with these ligands were therefore unsuccessful. Nevertheless, **1**–**3** are active catalysts. We assume therefore that in the catalytic cycle, for example with **1** or **2** as pre-catalyst, the intermediate **A** could be formed as the product of a reductive elimination reaction (Scheme 4).

A can be represented by two canonical structures. Where the charges should be located, needs, however, further investigations. In the next step of the catalytic cycle this intermediate **A** may undergo oxidative addition of the aryl bromide to generate **B**.

Scheme 4 may also explain the differences in the catalytic activities of the complexes **1**–**3** in long-time reactions. The lower π-acceptor property of the bridging ligand in **2** and **3** compared with that of the ligand in **1** should result in lower thermal stabilities of the intermediate **A** formed from **2** or **3.** This leads to the partial decomposition of **2** and **3** and the observed precipitation of Pd black during the course of the catalytic reaction. In contrast, a decomposition to form elemental palladium was not observed, when **1** was used in the catalytic reaction. This might be the reason for the observed diminished catalytic activity of **2** and **3** in comparison with **1**.

The complexes **1**–**3** belong to the very rare group of Pd-catalysts with *N*,*N*-chelate ligands which are active in the copper-free Sonogashira reaction [12]. Interestingly, addition of CuI even lowers the activity of **1** (entry 6). Further advantages of the oligonuclear complexes of the type **1**–**3** are their stability toward air and moisture, the high variability of the steric and electronic properties of the ligands and their easy access.

Table 1
Sonogashira- and Negishi reaction with **1**–**3** as pre-catalysts

Entry	Reaction type	Catalyst	mol% cat	Time (h)	Conversion (%)	Selectivity (%)	TON[e]
1	Sonogashira[a]	–	–	36	0	0	0
2	Sonogashira[a]	**1**	0.2	10	36	100	
3	Sonogashira[a]	**1**	0.2	22	54	100	
4	Sonogashira[a]	**1**	0.2	36	98	100	490
5	Sonogashira[a]	**1**	0.2	24	59	100	295
6	Sonogashira[a]	**1**/CuI	0.2	24	11	100	55
7	Sonogashira[b]	**1**	12	47	67	52	22
8	Sonogashira[b]	**1**/$ZnCl_2$	12	47	70	57	23
9	Sonogashira[a]	**2**	0.2	10	13	98	
10	Sonogashira[a]	**2**	0.2	22	26	98	
11	Sonogashira[a]	**2**	0.2	36	47	98	240
12	Sonogashira[a]	**3**	0.2	10	23	97	
13	Sonogashira[a]	**3**	0.2	22	40	97	
14	Sonogashira[a]	**3**	0.2	36	50	97	245
15	Negishi[c]	**2**	20	7	100	100	20
16	Negishi[c]	$(PPh_3)_4Pd$	20	7	47	15	9
17	Negishi[d]	**2**	20	4	100	100	20
18	Negishi[d]	$(PPh_3)_4Pd$	20	4	100	100	20

[a] Conditions for entries 1–6, 9–14: 5 mmol 4-bromoacetophenone and 6 mmol phenylacetylene as substrates; 0.01 mmol Pd pre-catalyst (in entry 1 without a pre-catalyst; in entry 6 with 0.02 mmol CuI); 15 mL triethylamine; reaction temperature 90 °C; yield of the coupling product: determination by GC analysis with diethyleneglycol–dibutylether as internal standard.

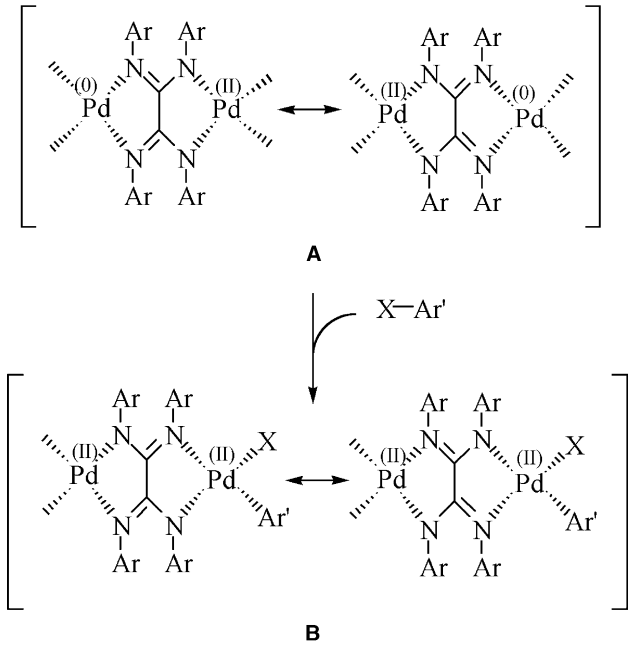
[b] Entries 7–8: 0.46 mmol 3,5,6,8-tetrabromophenanthroline and 2.3 mmol phenylacetylene as substrates, 0.056 mmol pre-catalyst (entry 8: 0.46 mmol $ZnCl_2 * 2THF$), 12 mL dmf/Et_3N (8/4), reaction temperature 150 °C, yield of the coupling product: determination by ^1H NMR spectroscopy.

[c] Entries 15–16: 0.4 mmol 3,5,6,8-tetrabromophenanthroline and 2.8 mmol Ph–C≡C–ZnCl as subtrates, 0.08 mmol pre-catalyst, 15 mL NMP/THF (8/7), reaction temperature 150 °C; yield of the coupling product: determination by ^1H NMR spectroscopy.

[d] Entries 17–18: 0.4 mmol 3,5,6,8-tetrabromophenanthroline and 2.0 mmol (^{i}prop)$_3$Si–C≡C–ZnCl as subtrates, 0.08 mmol pre-catalyst, 14 mL toluene/THF (6/8), reaction temperature 90 °C; yield of the coupling product: determination by ^1H NMR spectroscopy.

[e] TON: mol alkine converted to product/mol catalyst.

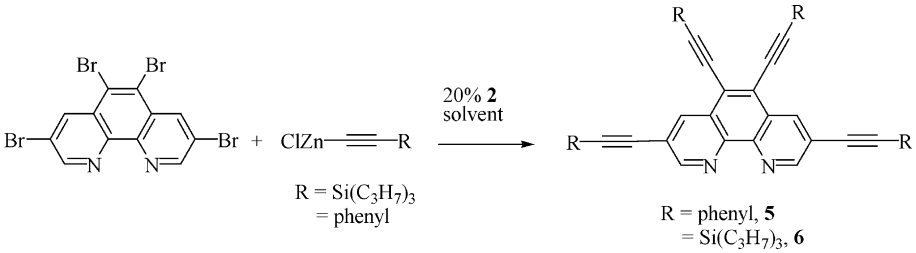
The very high selectivity and good activity of *oxam* based palladium complex **1** in the Sonogashira coupling reaction as well as the moderate reaction conditions without CuI as essential additive prompted us to deploy a more challenging pair of substrates. For the terminal alkyne we used again the phenylacetylene, but for the aromatic halide we chose 3,5,6,8-tetrabromophenanthroline (Br_4phen). Br_4phen represents an easily accessible ligand for ruthenium polypyridyl complexes [27]. Its substitution pattern should allow for the introduction of a wide variety of alkynylated functional groups without interference with the coordination sphere of the phenanthroline unit. Alkyne substituents would enlarge the π-system considerably which has in 3,8-disubstituted phenanthrolines been proven to be extremely useful [28]. It would therefore be highly desirable to be able to transform all four bromo functions in Br_4phen.



Scheme 4. The possible intermediates **A** and **B** in the Sonogashira coupling with **1** and **2** as the catalysts.

3,5,6,8-Tetrabromophenanthroline is difficult to activate due to its extremely low solubility. In addition, it can function as a potential chelating ligand for the Pd or a Cu atom of the catalyst system. It has been suggested that this might suppress the catalytic activity of catalysts in C–C coupling reactions of similar functionalized substrates. Generally, derivatisations of phenanthroline systems have up to now been hampered by low yields [29] and extreme reaction conditions [30].

We used in the catalytic reaction a mixture of dmf and triethylamine as solvent, the amount of pre-catalyst was raised to 12 mol% (3 mol% for each C–Br bond) and the reaction time was prolonged to 47 h (Table 1, entries 7–8). After this time a mixture of products was



Scheme 5. Negishi coupling at Br_4phen catalysed by **2**.

detected containing the desired 3,5,6,8-tetra(phenylacetylene)phenanthroline in less than 15% yield together with species being partially alkynylated.

Due to this low yields by converting 3,5,6,8-tetrabromophenanthroline into an acetylenic compound we employed a different type of catalytic reaction that has proven to couple alkynes and aromatic halides, the Negishi type coupling (Scheme 5).

Because of its higher solubility compared to complex **1** we used complex **2** as pre-catalyst in a mixture of NMP/THF as solvent. (Table 1, entry 15). According to mass spectra and ^{1}H NMR spectra of the crude reaction mixture after 7 h at 150 °C the substrates were completely converted into the 3,5,6,8-tetra(phenylacetylene)phenanthroline **5** as the result of an extremely selective reaction. No side products, such as partially substituted species were detected. In contrast, $(Ph_3P)_4Pd$ as catalyst is much less efficient in this reaction. In this case a mixture of di-, tri- and tetra-alkyne-substituted phenanthrolines was isolated (Table 1, entry 16).

Crystals of the $ZnCl_2$ complex of compound **5** could be isolated from toluene after hydrolysis of the reaction mixture, extraction with CH_2Cl_2 and washing with toluene. This complex, being generated during the course of the Negishi-reaction, seems to be very stable, even in water and mineral acids (see Section 4). Fig. 3 displays the molecular structure of single crystals.

In order to evaluate the effect of Zn in such a coordination sphere on the behavior of Br_4phen as substrate in the Sonogashira-reaction we performed this catalysis under addition of one equivalent of $ZnCl_2$ * 2THF (entry 8 in Table 1); however it is quite evident from the results of the catalysis that the coordination of Zn is not sufficient for the improvement of the catalytic performance.

To obtain a 3,5,6,8 alkyne-substituted phenanthroline with four terminal C–H groups which might serve as building block for more extended systems we also reacted 3,5,6,8-tetrabromophenanthroline with the tri(*iso*-propylsilyl)acetylide–ZnCl complex using **2** as catalyst. The reaction was carried out by using a mixture of THF/toluene as solvent and 20 mol% complex **2** as pre-catalyst. After 4 h heating at reflux, all substrate has been converted into the 3,5,6,8-tetrakis[tri(*iso*-propylsilyl)acetylene]phenanthroline **6** according to the mass spectra and ^{1}H NMR spectra of the crude reaction mixture (Table 1, entry 17). After the complete work up (hydrolysis with HCl/water, extraction with CH_2Cl_2 and chromatography on silica gel), the $ZnCl_2$-free compound **6** could be isolated. For compound **6** we were also able to obtain a structural motif by X-ray analysis, shown in Fig. 4.

In contrast to the low efficiency of the Negishi coupling to form **5** by using $(Ph_3P)_4Pd$ as precatalyst, this complex generates the formation of **6** in a very selective reaction (Table 1, entry 18).

In a preliminary investigation of the coordination ability of the synthesised alkinylated phenanthrolines we reacted **6** with [(tbbpy)$_2$ $RuCl_2$] (tbbpy: bis-4-*tert*-butyl-bipyridine).

$$[(tbbpy)_2RuCl_2] + \mathbf{6} \rightarrow [(tbbpy)_2Ru(\mathbf{6})](Cl)_2$$

The reaction carried out under standard conditions proceeded smoothly and resulted in the formation of [(tbbpy)$_2$ Ru(**6**)]$(PF_6)_2$ upon addition of NH_4PF_6 which

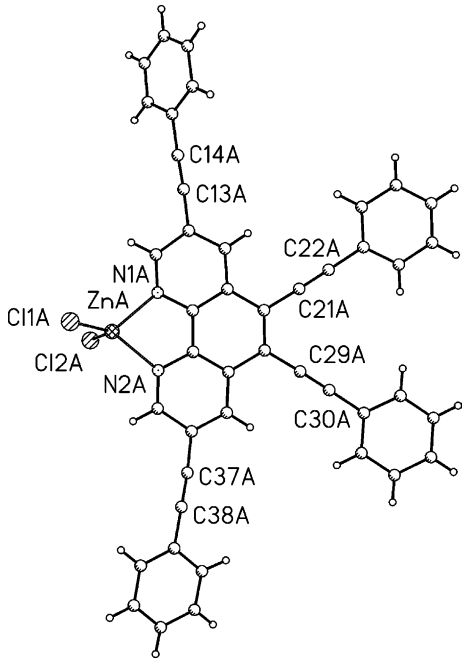


Fig. 3. Molecular structure of **5**, selected bond length (Å) ZnA–Cl1A 2.1896(15), ZnA–Cl2A 2.2047(15), ZnA–N1A 2.082(4), ZnA–N2A 2.096(4), C13A–C14A 1.192(8), C21A–C22A 1.208(6), angles (°) Cl1A–Zn–Cl2A 119.81(6), N1A–Zn–N2A 79.97(15).

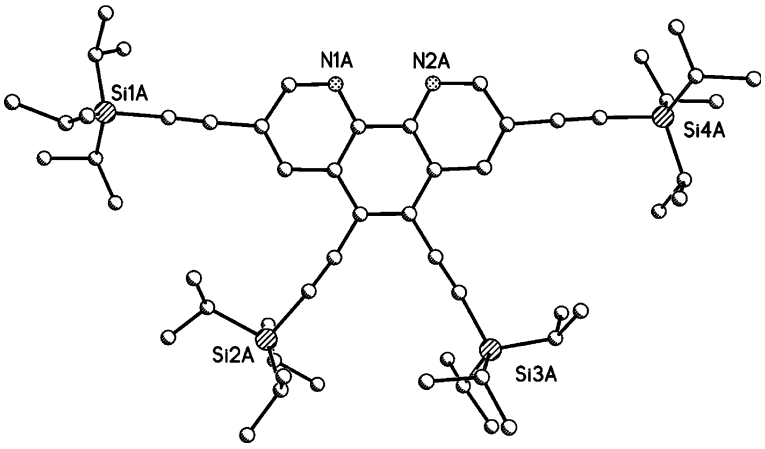


Fig. 4. Molecular structure of **6** as structural motif.

could be isolated in 80% yield. The complex was characterised with ^{1}H and ^{13}C NMR and ESI-MS. The absorption maximum in acetonitril is at 439 nm with a distinct shoulder at 505 nm and the emission maximum at 692 nm. The very red shifted emission wavelength in comparison to the parent ruthenium-phenanthroline complex ($\lambda_{em} = 610$ nm in acetonitrile [27]) probably indicates the increased delocalisation within the π^* system of the coordinated **6**.

3. Conclusions

In conclusion, we have shown that binuclear palladium(II) complexes have an interesting catalytic potential in the copper-free Sonogashira reaction. In this reaction CuI has an inhibiting effect. The highly selective Negishi coupling of tetrabromophenanthroline with terminal alkynes results in interesting new ligands for tuning metal-catalyzed reactions and useful for the formation of oligonuclear organometallics.

4. Experimental section

4.1. General procedures

All manipulations were carried out by using modified Schlenk techniques under an atmosphere of argon. Prior to use, THF, diethyl ether, *n*-pentane, *n*-hexane and toluene were dried over potassium hydroxide and distilled over sodium/benzophenone. Triethylamine (Fluka) was distilled over sodium/benzophenone. Methyllithium (1.6 M solution in diethyl ether, Fluka), $ZnCl_2$ (0.5 M solution in THF, Aldrich), $ZnEt_2$ (1.1 M solution in toluene, Aldrich), bis(acetylacetonato)palladium(II) (Alfa Aesar), 4-bromoacetophenone (Fluka), sodium acetate (Aldrich), and tri(*iso*-propyl)silylacetylene (Aldrich) were used as received, diethyleneglycol–dibutylether (Fluka), *N*-methylpyrrolidone (Fluka) and dmf (Aldrich) were dried over molecular sieve and distilled. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 F spectrometer. Mass spectra were recorded on a Finnigan MAT SSQ 710. Values for *m/z* are for the most intense peak of isotope envelope. The measured isotopic pattern for the palladium-containing species are in good agreement with the calculated isotopic pattern using the program ICIS (version 8.2.1, Finnigan). Elemental analyses were performed with Leco CHNS-932. IR measurements were carried out with a Perkin–Elmer System 2000 FT-IR.

The ligands tetra(phenyl)oxalic amidine (H_2A) and tetra(*p*-tolyl)oxalic amidine (H_2B) were were prepared according to described methods [31]; 3,5,6,8-tetrabromophenanthroline was prepared as described recently [27]. $[(tbbpy)_2RuCl_2]$ [32] and the complexes **2**, and **3** [2] were synthesized according to literature methods. Single crystals of **3** crystallizing with five dioxane molecules were isolated by recrystallization of the complex from dioxane.

4.1.1. Complex *1*

One equiv. tetra(phenyl)oxalamidine (H_2A (390 mg, 1 mmol) and two equiv. of bis(acetylacetonato)palladium(II) (610 mg, 2 mmol) were suspended in 30 mL toluene and refluxed for 3 h to give a clear, red solution. After cooling to room temperature red crystals form which can be filtered off, washed twice with toluene and *n*-hexane and dried in vacuum.

Yield: 0.72 g (90%). Single crystals suitable for X-ray analysis could be isolated from toluene. Calcd. for $C_{36}H_{34}N_4O_4Pd_2$: C 54.08, H 4.30, N 7.00. Found: C 54.06, H 3.89, N 6.83%. MS (APCI) *m/z*: 800, $[MH^+]$ (100%), 700 $[M^+ - acac]$ (6%), 594 $[M^+ - Pd\text{-}acac]$ (8%), 389 $[M^+ - 2Pd\text{-}2acac]$ (20%). ^{1}H NMR (200 MHz; $CDCl_3$): δ 1.44 (s, 12H, CH_3, *acac*); 4.99 (s, 2H, CH, *acac*), 6.78–6.67 (m, 20H, CH-aromat, *phenyl*). ^{13}C NMR (100.6 MHz; $CDCl_3$): δ 25.1 (CH_3, *acac*),

100.3 (CH, *acac*), 123.8, 126.8, 127.3, (CH-aromat, *phenyl*), 143.8 (C_{quart}-aromat, *phenyl*), 168.9 (C_{quart}, *oxam bridge*), 185.8 (C_{quart}, *acac*). IR (nujol): *v* 1520, 1543 (CH-aromat), 1581 (C=O) cm^{-1}.

4.1.2. Complex **4**

A clear solution of 1.0 mmol bis(η^3-allyl)palladium in THF was prepared by dissolving 366 mg (1.0 mmol) bis(η^3-allyl)di-μ_2-chlorodipalladium(II) in dry toluene. Upon cooling to −60 °C 1.0 mL of a 2.0-M solution of allyl-MgCl in THF was added and the mixture was warmed to −30 °C to complete the reaction. In a second Schlenk tube 1.5 mmol tetra(*p*-tolyl)oxalamidine (*H_2B*) (670 mg) were dissolved in 36 mL toluene. To 12 mL (0.5 mmol) of this solution additional 25 mL of toluene and 1 mmol of a 1.1-M solution of $ZnEt_2$ (0.91 mL) were rapidly added under vigorous stirring. After 10 min of stirring the remaining 24 mL (1.0 mmol) of the tetra(*p*-tolyl)oxalamidine solution were slowly added at room temperature. The clear yellow solution was then added to the previously prepared solution of 1.0 mmol bis(η^3-allyl)palladium in THF at −70 °C. After warming to room temperature the mixture was filtered, the solvents were removed in vacuo and the remaining solid was extracted three times with 10 mL *n*-pentane. At −18 °C a yellow precipitate formed which was filtered off and dried in vacuo. Yield: 0.22 g (25%). Calcd. for $C_{96}H_{94}N_{12}Pd_2Zn_2$: C 65.56, H 5.39, N 9.55. Found: C 66.11, H 5.29, N 9.47%. MS (APCI) *m/z*: 1759 [MH^+] (100%). ^1H NMR (200 MHz; $CDCl_3$): 2.04, 2.07 (2s, 36H, CH_3, *p-tolyl*); 2.50, 2.55–2.70 (2m, 8H, CH_2, *allyl*), *δ* 5.30 (m, 2H, CH, *allyl*), 6.50, 6.20 (2m, 48H, CH-aromat, *p-tolyl*). ^{13}C NMR *δ* (50.3 MHz; $CDCl_3$): 114.3 (CH, *allyl*), 60.55 (CH_2, *allyl*), 20.6, 20.5 (CH_3, *p-tolyl*); 123.9, 124.2, 127,5, 127.7, 130.5, 131.0. (CH-aromat, *p-tolyl*), 149.9, 143.8 (C_{quart}-aromat, *p-tolyl*), 160.8 (C_{quart} *oxam bridge*). IR (nujol): *v γ* 815 (CH disubst. aromat), 1505 (C–C-aromat, *p-tolyl*), 1609 (C–N, *oxam bridge*) cm^{-1}.

4.2. Sonogashira reaction

Variant a: The catalytic reaction was run under an argon atmosphere. About 5.0 mmol of 4-bromoacetophenone were placed into a Schlenk tube together with 0.01 mmol of the precatalyst and a stirring bar and the mixture was degassed and purged with argon. Through a septum 6.0 mmol of phenylacetylene, 0.5 g of the internal standard and 15 mL of triethylamine as solvent and base were added. In order to determine the long-term stability of the catalysts we employed following reaction procedure. The reaction mixture was heated to 90 °C and held at this temperature for 7 h, after cooling for 17 h at room temperature heating and cooling was repeated for four times (last heating periode 8h) resulting in a total reaction time of 36 h. Samples of 0.5 mL were taken after appropriate time intervals, hydrolyzed with 2 mL of distilled water and extracted with diethylether. The organic phase was dried over sodium sulfate and stored at 4 °C until GC-analysis for determination of yield and turnover number could be performed. Results are shown in Table. *Variant b:* The catalytic reaction was run under an argon atmosphere. 0.46 mmol of 3,5,6,8-tetrabromophenanthroline were placed into a Schlenk tube together with 0.056 mmol (12 mol%) of complex **1** and a stirring bar and the mixture was degassed and purged with argon. Through a septum 2.3 mmol of phenylacetylene, 4 mL of triethylamine as base and 8mL dmf as solvent were added. If it was desired a solution of 0.46 mmol $ZnCl_2$ * 2THF (130 mg) in 2 mL dry THF were added as well. The reaction mixture was heated to 150 °C and held at this temperature for 47 h. Following this reaction time the mixture was hydrolyzed with water and halfconcentrated HCl, extracted with CH_2Cl_2 and the organic phase was dried over potassium carbonate. After removal of all solvents, the product was analyzed by mass spectroscopy and ^1H NMR spectroscopy.

4.3. Negishi coupling

4.3.1. Compound **5**

The preparation of the Cl–Zn-phenylacetylide was performed under an argon atmosphere. About 2.8 mmol of phenylacetylene were dissolved in 1 mL of dry THF and cooled to −78 °C. About 2.8 mmol (1.8 mL) of methyllithium as 1.6 M solution in diethylether were added and the solution was immediately warmed to room temperature under formation of methane. The color changed to orange. About 5.6 mL of a 0.5-M solution of $ZnCl_2$ (2.8 mmol) in THF were added to this solution of Li-phenylacetylide and stirred for 1 h at room temperature. 0.4 mmol of 3,5,6,8-tetrabromophenanthroline were placed into a Schlenk-tube together with 0.08 mmol of complex **2** and the reaction tube was degassed and purged with argon. Eight mL of NMP (*N*-methylpyrrolidone) were added to the Schlenk tube and the mixture was stirred. To this suspension the THF solution of the Cl–Zn-phenylacetylide was added and the mixture was stirred in an oil bath for 7 h at 150 °C. After cooling down to room temperature, the reaction mixture was hydrolyzed with 20 mL of half concentrated HCl and extracted with CH_2Cl_2. The organic phase was dried over potassium carbonate, filtered and the solvent was removed completely. The residue was washed with toluene and dried in vacuo. Single crystals of the $ZnCl_2$ complex crystallizing with 1.5 mol toluene suitable for X-ray analysis could be obtained from toluene. The 3,5,6,8-tetra(phenylacetylene)phenanthroline was recrystallized from $CHCl_3$.

Yield: 0.34 g (60%) $C_{44}H_{24}N_2$: MS (EI) *m/z*: 580 [M^+] (100%), 480 [MH^+–C≡C–C_6H_5] (25%). ^1H NMR (400

MHz; $CDCl_3$): δ 7.39 (t), 7.46 (m), 7.66 (d), 7.75 (d) (20H, CH-aromat, *phenyl*); 8,90, 9.00 (2s, 4H, CH-aromat, *phen*). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 83.9, 84.7, 98.7, 104.3 (C_{quart}, $C{\equiv}C$), 123.6, 123.5 (C_{quart}-aromat, *phenyl*), 121.4, 121.8, 127.9, 137.4 (C_{quart}-aromat, *phen*), 129.0, 129.2, 130.3, 130.5, 132.7, 132.8 (CH-aromat, *phenyl*), 139.7 152.6 (CH-aromat, *phen*). IR (KBr): ν 2210 cm^{-1}($C{\equiv}C$), 3057 cm^{-1} (*CH-aromat*), δ, γ 912, 756, 688 cm^{-1} (*CH-phenyl*)

4.3.2. Compound 6

The preparation of the Cl–Zn-tri(*iso*-propyl)silylacetylide was performed under an argon atmosphere. About 2.0 mmol of tri(*iso*-propyl)silylacetylene were dissolved in 2 mL of dry THF and cooled to −78 °C. 2.0 mmol (1.25 mL) of methyllithium as 1.6 M solution in diethylether were added and the solution was immediately warmed to room temperature under formation of methane. 2.0 mmol of $ZnCl_2$ * 2THF were put in a Schlenk tube under an argon atmosphere and dissolved in 3 mL of dry THF. The $ZnCl_2$-solution was then added to the solution of the Li-tri(*iso*-propyl)silylacetylide and stirred for 1 h at room temperature. 0.4 mmol of 3,5,6,8-tetrabromophenanthroline were placed in a Schlenk-tube together with 0.08 mmol of complex **2** and the reaction tube was degassed and purged with argon. 6 mL of toluene were added to the substrates and stirred. To this suspension the THF solution of the Cl–Zn-tri(*iso*-propyl)silylacetylide was added and the mixture was heated under reflux in an oil bath for 4 h. After cooling down to room temperature, the clear and dark reaction mixture was hydrolyzed with 15 mL of halfconcentrated HCl and extracted with CH_2Cl_2. The organic phase was dried over potassium carbonate, filtered and the solvents were removed completely. The residue was then chromatographed on silica gel (toluene/ethylacetate: 99/1). Single crystals suitable for X-ray analysis could be obtained from acetone/water. Yield: 0.22 g (60%) $C_{56}H_{88}N_2Si_4$: MS (EI) *m/z*: 902 [M^+] (18%), 858 [$M^+ - C_3H_7$] (10%), 816 [$M^+ - 2C_3H_7$] (40%), 774 [$M^+ - 3C_3H_7$] (28%), 731 [$M^+ - 4C_3H_7$]. ^1H NMR (400 MHz; $CDCl_3$): δ 1.21 (m, 84H, CH + $CH_3Si(^iProp)_3$), 8.85, 9.11 (2s, 4H, CH-aromat, *phen*). ^{13}C NMR (100.6 MHz; $CDCl_3$): δ 11.3, 11.4 (CH, $Si(^iProp)_3$), 18.8, 18.7 (CH_3,$Si(^iProp)_3$), 96.9, 101.7, 103.4, 104.9 (C_{quart}, C≡C), 120.6. 123.2, 127.9, 143.7 (C_{quart}-aromat, *phen*), 138.1, 153.1 (CH-aromat, *phen*). IR (KBr): ν 2153 (C≡C), 2943, 2865 (*CH-aromat*) cm^{-1}.

4.3.3. Preparation of [(tbbpy)$_2$Ru(6)](PF$_6$)$_2$

The complex was prepared using slightly modified standard procedures [33] with [$(tbbpy)_2RuCl_2$] 52 mg (0.073 mmol), and **6** 66 mg (0.073 mmol) dissolved in 50 mL DMF/H_2O and irradiated in a microwave (microwave set-up: 30 s, 600 W; 45 min, 200 W, 10 min, ventilation). After evaporation of the solvent the remaining solid was dissolved in 30 mL EtOH. The product was precipitated by addition of an aqueous solution of NH_4PF_6, removed by filtration, washed with Et_2O and dried on air. Yield: 107 mg, 80%. MS (EI) m/z 1684.5 ($M - PF_6$), 769.2 ($M - 2PF_6/2$). ^1H NMR (400 mHz, d_6-DMSO): δ 1.02–1.04 (42H), 1.14–1.16 (42H), 1.37 (s, 18H), 1.39 (s, 18H), 7.31 (d, 2H), 7.69 (m, 6H), 7.78 (d, 2H), 8.64 (d, 4H). ^{13}C NMR (200 MHz, d_6-DMSO): δ 10.46, 10.63, 18.27, 18.41, 29.92, 35.34, 35.47, 99.20, 101.6, 107.0, 121.8, 123.5, 124.4, 130.0, 136.1, 146.2, 151.0, 152.2, 153.3, 155.8, 156.7, 1561.9, 162.4. UV/Vis (Acetonitrile): λ = 439 nm, shoulder at 505 nm; emission (Acetonitrile, λ_{ex} = 439 nm): λ = 692 nm.

5. Crystal structure determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [34,35].

The structures were solved by direct methods (SHELXS [36]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [37]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. Since the quality of the data of compound **6** is insufficient, we will only publish the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. All non-hydrogen atoms were refined anisotropically [37]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **1** [38]: $C_{36}H_{34}N_4O_4Pd_2$, Mr = 799.47 g mol^{-1}, yellow-brown prism, size $0.02 \times 0.02 \times 0.02$ mm^3, monoclinic, space group $P2_1/c$, a = 11.2417(4), b = 9.0294(2), c = 15.8736(5) Å, β = 95.256(2)°, V = 1604.49(8) Å^3, T = −90 °C, Z = 2, $\rho_{calcd.}$ = 1.655 g cm^{-3}, μ(Mo Kα) = 11.67 cm^{-1}, F(000) = 804, 9475 reflections in h(−14/14), k(−10/11), l(−20/17), measured in the range 2.90° ⩽ Θ ⩽ 27.48°, completeness Θ_{max} = 99.3%, 3655 independent reflections, R_{int} = 0.025, 3145 reflections with $F_o > 4\sigma$ (F_o), 208 parameters, 0 restraints, $R1_{obs}$ = 0.028, $wR2_{obs}$ = 0.073, $R1_{all}$ = 0.035, $wR2_{all}$ = 0.078, GOOF = 1.034, largest difference peak and hole: 0.556/−0.902 e Å^{-3}.

Crystal Data for **3** [38]: $C_{70}H_{70}N_8O_4Pd_2Zn$ * $5C_4H_8O_2$, Mr = 1806.03 g mol^{-1}, yellow-orange prism, size $0.03 \times 0.03 \times 0.02$ mm^3, triclinic, space group $P\bar{1}$, a = 15.9614(5), b = 18.6093(7), c = 18.9105(6) Å, α = 115.719(2)°, β = 96.270(2)°, γ = 90.307(2)°, V = 5021.5(3) Å^3, T = −90 °C, Z = 2, $\rho_{calcd.}$ = 1.194 g cm^{-3}, μ(Mo Kα) = 6.49 cm^{-1}, F(000) = 1880, 34,021 reflec-

tions in $h(-20/20)$, $k(-22/24)$, $l(-24/22)$, measured in the range $1.65° \leqslant \Theta \leqslant 27.47°$, completeness Θ_{max} = 97.1%, 22,351 independent reflections, R_{int} = 0.045, 14,001 reflections with $F_o > 4\sigma(F_o)$, 970 parameters, 1 restraints, $R1_{obs}$ = 0.082, wR^2_{obs} = 0.224, $R1_{all}$ = 0.136, wR^2_{all} = 0.2665, GOOF = 1.043, largest difference peak and hole: 2.362/−1.155 e Å^{-3}.

Crystal Data for **5** [38]: $C_{44}H_{24}Cl_2N_2Zn * 1.5C_7H_8$, Mr = 855.12 g mol^{-1}, colourless prism, size 0.03 × 0.03 × 0.02 mm^3, triclinic, space group $P\bar{1}$, a = 14.410(3), b = 16.890(3), c = 18.871(4) Å, α = 85.93(3)°, β = 89.18(3)°, γ = 77.62(3)°, V = 4475.0(16) Å^3, T = −90 °C, Z = 4, $\rho_{calcd.}$ = 1.269 g cm^{-3}, μ(Mo Kα) = 7.07 cm^{-1}, F(0 0 0) = 1764, 19,948 reflections in h(0/18), $k(-21/22)$, $l(-24/23)$, measured in the range $4.33° \Theta \leqslant 27.84°$, completeness Θ_{max} = 93.9%, 19519 independent reflections, R_{int} = 0.040, 12,830 reflections with $F_o > 4\sigma(F_o)$, 1029 parameters, 0 restraints, $R1_{obs}$ = 0.080, wR^2_{obs} = 0.190, $R1_{all}$ = 0.136, wR^2_{all} = 0.229, GOOF = 1.055, largest difference peak and hole: 1.415/−0.697 e Å^{-3}.

Crystal Data for **6**: $C_{56}H_{88}N_2Si_4$, Mr = 901.64 g mol^{-1}, colourless prism, size 0.03 × 0.03 × 0.02 mm^3, monoclinic, space group $P2_1/n$, a = 22.5147(6), b = 15.4592(4), c = 33.4707(10) Å, α = 90.00°, β = 93.679(1)°, V = 11625.8(6) Å^3, T = −90 °C, Z = 8, $\rho_{calcd.}$ = 1.030 g cm^{-3}, μ(Mo Kα) = 1.36 cm^{-1}, F(0 0 0) = 3952, 50,570 reflections in $h(-29/28)$, $k(-17/19)$, $l(-43/26)$, measured in the range $1.60° \leqslant \Theta \leqslant 27.49°$, completeness Θ_{max} = 86.6%.

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