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Synthesis and characterization of the unusual cluster $[Ni_2(GaAr')_2(\eta^1:\eta^1-\mu_2-C_2H_4)]$: Ready addition of ethylene to Ni(COD)(GaAr')_2 at 25 °C and 1 atmosphere

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1. Introduction

The chemistry of transition metal complexes with π -bonds to aromatic rings is of key importance in modern coordination and organometallic chemistry. The discovery of ferrocene, $[Fe(\eta^5 (C_5H_5)_2$], essentially simultaneously by several groups, its structural recognition by Wilkinson, Woodward and Fischer initiated the field of modern organometallic chemistry [1,2]. In addition, the first example of a metal complex of a neutral arene, bis(benzene)chromium, $[Cr(\eta^6-C_6H_6)_2]$, was reported four years later by Fischer and Hafner [2]. Since that time, ionic and neutral metallocenes and bis (arenes) [3,4], including ansa-bridged and half-sandwich type complexes have been studied intensively by experimental and theoretical investigations [5-8]. Recent examples of interesting metal complexes stabilized by π -arene interactions include the first organometallic zinc(I) compound, $[(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(\eta^5-C_5Me_5)Zn-Zn(Q^5-C_5Me_5)Zn-Zn(Q^5-C_5Me_5)Zn-Zn(Q^5-C$ C_5Me_5] [9] containing the first stable Zn–Zn bond in a molecular complex, the sandwich complexes containing monolayer palladium sheets, $[Pd_3(C_7H_7)Cl_3]^+$ and $[Pd_5(naphthanacene)_2(toluene)]^+$ [10], the mixed-valent $[Fe(0)(NHC)(\pi^8-\eta^4,\eta^4-COT)Fe(I)(\pi^6-\eta^5-COT)_2]_2$ species and the tri-iron cluster $Fe_3(COT)_3$ (COT = 1,3,5,7-cyclooctatetraene), which was obtained by the fusion of three molecules of Fe(COT) catalyzed by N-heterocyclic carbenes (NHC) [11].

ABSTRACT

The nickel (0) compound Ni(COD)(GaAr')₂ (Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*-Pr₂)₂), **1**, was synthesized by the reaction of Ni(COD)₂ (COD = 1,5-cyclooctadiene) with (GaAr')₂. Compound **1** reacted with ethylene at 25 °C and at 1 atm pressure to give the bimetallic cluster [Ni₂(GaAr')₂($\eta^1:\eta^1-\mu_2-C_2H_4$)], **2**, through the incorporation of one molecule of ethylene and displacement of COD. The structure of **2** featured an unusual Ni₂Ga₂C₂ core bicyclic structure in which the C₂H₄ moiety bridges the Ga…Ga edge of a Ga₂Ni₂ tetrahedron. The galliums each carry an η^1 -bonded Ar' substituent which complexes the nickel atom by an $\eta^6-\pi$ interaction with one of its flanking Ar' rings.

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However, metal-metal bonded organometallic complexes of neutral aryl rings are rare. A Ni₂(C₆H₆)₃ species has been detected through mass spectroscopy of a mixture of Ni_n(benzene)_m clusters generated in the phase gas by laser vaporization but no stable examples are known [12]. Herein, we describe the unexpected synthesis of the compound [Ni₂(GaAr')₂(η^1 : η^1 - μ_2 -C₂H₄)] which incorporates a (arene)nickel-nickel(arene) entity.

2. Experimental

2.1. Materials and methods

All manipulations were carried out using modified Schlenk techniques under an atmosphere of N₂ or in a Vacuum Atmospheres HE-43 drybox. All solvents were dried and degassed three times prior to use. The compound (GaAr')₂ was prepared according to literature procedures. Ni(COD)₂ was used as received from Strem. ¹H and ¹³C NMR were recorded on Varian 300 spectrometer and referenced to known standards. X-ray quality crystals of **1** and **2** were covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the cold temperature stream. The data were collected near 90 K using a Bruker SMART 1000 diffractometer and Mo K α ($\lambda = 0.71073$ Å) radiation. Absorption corrections were applied using SADABS [13]. The structures were solved by use of Direct Methods in SHELXS [14] and refined by the full-matrix least-squares procedure in SHELXL. All

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Та	ıble	1		

Selected	crystal	lographic	data fo	or compounds	1 and 2 .
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Compound	1	2	
Formula	C ₇₁ H ₉₃ Ga ₂ Ni	C ₆₂ H ₇₈ Ga ₂ Ni ₂	
Formula weight	1144.6	1080.10	
Crystal color-habit	Red/plate	Green/block	
Crystal system	Triclinic	Orthohombic	
Space group	Pī	Pbca	
a (Å)	12.169(1)	18.875(5)	
b (Å)	12.920(1)	16.526(4)	
c (Å)	21.674(2)	34.479(8)	
α(°)	78.967(2)	90	
β(°)	78.316(2)	90	
γ(°)	70.439(2)	90	
V (Å ³)	3116.1(5)	107.55(4)	
Z	2	8	
Crystal size (mm)	$0.12 \times 0.2 \times 0.03$	$0.44 \times 0.37 \times 0.32$	
Density d(calcd) (g cm ^{-3})	1.220	1.334	
Absorption coefficient μ (mm ⁻¹)	1.197	1.718	
No. Reflns	28683	3441	
No. of obs Rflns $(I > 2\sigma(I))$	11301	2608	
R1	0.034	0.107	
wR2; all data	0.093	0.2157	

non hydrogen atoms were refined anisotropically, while hydrogens were placed at calculated positions and included in the refinement by using a riding model. Some details of the data collection and refinement are given in Table 1. Further details are in the supplementary material.

Synthesis of Ni(COD)(GaAr')2, (1). A deep green benzene solution (15 mL) of Ar'GaGaAr' (0.336 g, 0.36 mmol) was added dropwise to a yellow solution of (10 mL) Ni(COD)₂ (0.098 g, 0.359 mmol). The solution became red immediately and was stirred for 1 h at room temperature, the volatiles were removed under reduced pressure. The red solid was dissolved in hexane, concentrated and cooled to ca. -20 °C. After 3 days the product 1 was obtained as red crystals. Yield: 0.190 g (83%). m.p. = 260 $^{\circ}$ C (decomp). ¹H NMR (C₆D₆): 7.29 (t, 1H, ${}^{3}J_{HH} = 6.6$ Hz, CH_{Ar}), 7.19 (m, 3H, CH_{Ar}), 7.03 (d, 1H, ${}^{3}J_{HH} = 6.6$ Hz, CH_{Ar}), 3.51 (bs, 1H, CH, COD), 3.11 (sept, 2H, ${}^{3}J_{HH} = 6.8$ Hz, CH(CH₃)₂), 2.02 (br. m, 1H, CH₂, cod), 1.85 (br. m, 1H, CH₂, COD),1.21 (d, 3H, ${}^{3}J_{HH} = 7.2$ Hz, CH(CH₃)₂), 1.06 (d, 12H, $J_{HH} = 6.8$ Hz, CH(CH₃)₂). ¹³C NMR (C₆D₆): 168.8 (*i*-C₆H₃), 147.05 (o-Dipp), 143.6, 139.7, 128.9 (CH, Ar), 128.8 (CH, Ar), 123.9 (CH, Ar), 72.1 (CH, COD), 32.3 (CH₂, COD), 30.6 (CH, CH(CH₃)₂), 25.1 (CH₃, CH(CH₃)₂), 23.9 (CH₃, CH(CH₃)₂).

Synthesis of $[Ni_2(GaAr')_2(\eta^{1}:\eta^{1}-\mu_2-C_2H_4)]$, (**2**). A solution of Ni (COD)(GaAr')₂ (0.156 g, 0.25 mmol) in hexane or benzene (15 mL) was treated with excess ethylene at room temperature and atmospheric pressure. Within 10 min the color of the solution changed to deep green and stirring was continued for 1 h. The solution was cooled to ca. $-20 \,^{\circ}$ C, under an atmosphere of ethylene for 3 days which afforded **1** as green plates. Yield: 0.45 g (17%). m.p. = 137 $\,^{\circ}$ C (decomp.). ¹H NMR (C₆D₆, 297 K): $\delta = 0.7$ (d, ³J_{HH} = Hz, 7H), 0.8 (d, ³J_{HH} = Hz, 7H), 1.0 (d, ³J_{HH} = Hz, 7H), 1.1 (d, ³J_{HH} = Hz, 7H), 1.3 (d, ³J_{HH} = Hz, 1H), 1.4 (d, ³J_{HH} = Hz, 7H), 2.5 (sept, ³J_{HH} = Hz, 1H), 2.6 (sept, ³J_{HH} = Hz, 1H), 2.9 (sept, ³J_{HH} = Hz, 2H), 3.1 (sept, ³J_{HH} = Hz, 1H), 5.2 (d, ³J_{HH} = Hz, 1H), 6.07 (d, ³J_{HH} = Hz, 1H), 6.09 (d, ³J_{HH} = Hz, 1H), 6.3 (d, ³J_{HH} = Hz, 1H), 7.2 (18 H). ¹³C NMR (C₆D₆, 297 K): $\delta = 13.9 (CH_2-CH_2)$, 19.8, 21.9, 22.5, 22.9, 24.6, 25.0, 21.1, 25.6, 29.2, 29.5, 29.9, 30.0, 30.1, 83.3, 97.1, 102.0, 121.4, 121.5, 122.1, 122.2, 122.3, 124.8, 125.8, 126.6, 128.2, 140.7, 141.1, 142.2, 145.0, 146.1, 146.4, 146.6, 168.6.

3. Results and discussion

The red complex Ni(COD)(GaAr')₂ (**1**, COD = 1,5-cyclooctadiene) was synthesized by the reaction of the digallene Ar'GaGaAr'



Scheme 1. Synthesis of Ni(COD)(GaAr')₂ (1) and [Ni₂(GaAr')₂(η^{1} : η^{1} - μ_{2} -C₂H₄)] (2).

 $(Ar' = C_6H_3-2,6-(C_6H_3-2,6-i-Pr_2)_2)$ and Ni(COD)₂, Scheme 1. The structure of **1**, was determined by single crystal X-ray diffraction, and shows that it has a distorted tetrahedral coordination geometry in which the nickel atom is complexed by two gallanediyls and a COD ligand, Fig. 1. The Ga(1)-Ni–Ga(2) angle is 101.64(4)° which is similar to that in the bis gallium (I) triazenido derivative Ni(COD) [Ga{(N(Ar)₂)CNR₂}]₂ (Ar= $C_6H_3Pr^i_2$ -2,6; R = cyclohexyl) gallanediyl complex [15]. The Ga–Ni bond lengths 2.201(4) and 2.205(4) Å are among the shortest bond distances reported for gallanediyl nickel species (usual range 2.329(9)–2.476(10) Å) [16], which is presumably due to the two-coordination at gallium and the good σ -donor character of the GaAr' ligand [16,17]. The shortness of the bonds is exceeded by the 2.1700(4) Å observed for the Ga–Ni distance in Ni{GaC(SiMe₃)₃}₄ [18].



Fig. 1. Thermal ellipsoid (30%) plot of Ni(COD)(GaAr')₂ (1). The iso-propyl groups of the flanking aryl rings of the terphenyl substituent and hydrogen atoms are not shown. Selected bonds lengths (Å) and angles (deg): Ni(1)–Ga(2) 2.201(4), Ni(1)–Ga(1) 2.205 (4), C(61)–Ni(1) 2.111(2), C(62)–Ni(1) 2.085(2), C(65)–Ni(1) 2.122(2), C(66)–Ni(1) 2.087(2); Ga(2)–Ni(1)–Ga(1) 101.642(14), C(62)–Ni(1)–C(66) 102.47(10), C(66)–Ni(1)–C(61) 86.61(10), C(62)–Ni(1)–C(65) 86.20(10), C(61)–Ni(1)–C(65) 94.89(9).

Reaction of this compound with excess ethylene in hexane or benzene at room temperature and atmospheric pressure led to an immediate color change from deep red to green. Cooling the solution under an ethylene atmosphere gave **2** as green blocks in moderate yield (Scheme 1). The structure of **2** was determined by X-ray crystallography (Fig. 2).

This reaction was investigated as part of our studies of the addition of alkenes, alkynes or small molecules (*e.g.* H_2 or NH_3) to Ar'GaGaAr' which have been of interest over the last few years [17]. These have shown that Ar'GaGaAr' added two equivalents of an olefin or alkyne to yield the cycloalkanes or cycloalkenes and hydrogen or ammonia its yield the hydride or amide compounds [Ar'Ga(R)(R')]₂ (R = R' = alkane, alkene or hydride; R = hydride, R' = amide) [17]. For **2** the core structure shows that the cyclooctadiene ligand has been completely displaced and that just one



Fig. 2. Thermal ellipsoid (30%) plot of of $[Ni_2(GaAr')_2(\eta^1:\eta^1-\mu_2-C_2H_4)]$ (2). The isopropyl groups of the flanking aryl rings of the terphenyl substituent and hydrogen atoms are not shown. Selected bonds lengths (Å) and angles (deg): Ni(1)-Ni(2) 2.437 (5), C(61)-C(62) 1.57(4), Ni(1)-Ga(1) 2.421(5), Ni(2)-Ga(1) 2.422(5), Ni(1)-Ga(2) 2.406(5), Ni(2)-Ga(2) 2.411(4); Ga(1)-Ni(1)-Ga(2) 73.20(14), Ga(1)-Ni(2)-Ga(2) 73.09(14).

molecule of ethylene is fixed by the two GaAr' entities to give a Ni₂Ga₂C₂ bicyclic core structure. The ethylene bridges the two Ga atoms, which form an edge of a Ga_2Ni_2 tetrahedron. The C(61)-C(62) (1.568 Å) bond distance is consistent with a single bond [19]. The $Ga \cdots Ga'$ distance of 2.877 Å suggests that the two gallium atoms in 2 are not bonded although a weak interaction is not precluded [20]. The nickel atoms are each η^6 -arene bound by a flanking ring of the Ar' ligand. The Ar' groups are also σ -bonded to a gallium atom. The Ni-Ni bond length (2.44 Å) is consistent with the existence of a single bond [21]. The four Ga-Ni distances are 2.415, 2.421, 2.409 and 2.424 Å, which are also consistent with single bonding [3,16,22]. The Ga–C σ -bonds are 1.907 and 2.024 Å. The Ga–C distances to the flanking are in the expected range. The Ni $-\pi^6$ -arene bond lengths span the range from 2.115 to 2.258 Å, indicating the ring is coordinated nearly symmetrically [23].

¹H and ¹³C NMR spectroscopy of solution of **2** are consistent with the X-ray crystal structure. The two hydrogens of each methylene carbon unit are inequivalent in benzene-D₆ solution at room temperature because of these different magnetic environments. In the ¹H NMR spectrum the compound **2** exhibits two doublet resonances at δ 6.31and 5.33 and a virtual triplet, as a result of overlap of two doublet signals, at 6.19 ppm which was assigned to the four "ethylene" protons. The downfield shifts of these protons are noteworthy and may be a result of the proximity of the flanking aryl rings of the terphenyl ligand. There are four sets of protons signals from the iso-propyl groups which are in the range of 2.4–3.2 ppm. In the ${}^{13}C{}^{1}H{}$ NMR spectrum, one resonance at 13.9 ppm may be assigned to the ethylene group.

All currently known monomeric homoleptic gallanediyl complexes such as $M(GaR)_n$ (M = Fe, Ni, Pd, Pt; R = Cp*, C(SiMe_3)_3, etc) do not react with donor molecules such as CO and PR₃ [22]. However, the dinuclear cluster complexes $M_2(GaCp^*)_5$ (M = Pd, Pt) react with a selection of small molecules (CO, phosphanes, isocyanides) to give substitution products, however, to the best of our knowledge this is the first example of a reaction of an olefin with an $M(GaR)_n(L)_m$ species [24].

In summary, we have shown that a low-valent compound Ni(0)-Ga(I), Ni(COD)(GaAr')₂ (1), readily undergoes addition of one molecule of ethylene at room temperature and 1 atm pressure to give (arene)nickel-nickel(arene) [Ni₂(GaAr')₂(η^1 : η^1 - μ_2 -C₂H₄)] (**2**) complex.

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Appendix A. Supplementary information

CCDC-791693 and 791694 contain the crystallographic data for 1 and 2. These data are available free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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