ORGANOMETALLICS

Nickel(0) Complexes of Polyunsaturated Azamacrocyclic Ligands

Sandra Brun, Anna Pla-Quintana, and Anna Roglans*

Department of Chemistry, University of Girona, Campus de Montilivi s/n. E-17071-Girona, Spain

Klaus-Richard Pörschke* and Richard Goddard

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

Supporting Information



ABSTRACT: A series of nickel(0) complexes, **3**, **4**, and **5**, containing unsaturated 15-membered azamacrocyclic ligands have been synthesized. Structural characterization of the complexes is based on NMR spectroscopy, X-ray diffraction analysis, and differential scanning calorimetry. In addition, the catalytic activity of the complexes in the Suzuki–Miyaura cross-coupling of arylboronic acids and aryl halides has been tested.

■ INTRODUCTION

About 50 years ago Wilke made the seminal discovery that transition metal atoms can be stabilized by cyclic polyene ligands to form homoleptic transition metal-alkene complexes such as trigonal-planar Ni(t,t,t-cdt) (t,t,t-cdt = trans,trans,trans-1,5,9-cyclododecatriene) and tetrahedral $Ni(cod)_2$ (cod = *cis,cis*-1,5-cyclooctadiene).¹ Later, by reaction of Ni(t,t,t-cdt)with ethylene, the parent $Ni(C_2H_4)_3$ was also obtained.² The complexes have been termed "naked nickel",³ owing to the ease with which displacement of the alkene ligands in the course of stoichiometric and catalytic reactions can occur. More recently, Pörschke and co-workers⁴ have systematically studied the coordination behavior of acyclic 1,5-dienes, 1,6-dienes, 1,6diynes, and 1,6,11-trienes at Ni(0), Pd(0), and Pt(0), leading inter alia to compounds of type I (Figure 1).^{4h} An important finding of these investigations was that ligands having 1,6- or 1,6,11-sequences of the olefinic functions are much better suited for coordination at the given trigonal-planar metal centers than the corresponding acyclic or cyclic 1,5-dienes and 1,5,9-trienes. While the chair-type, formally C_s -symmetrical conformation of the (1,6-diene)M(0) entity in trigonal-planar complexes seems to be particularly stable, a few tetrahedral (1,6-diene)Ni(0) complexes showing a twist-type, formally C_2 symmetrical conformation have also been reported.⁵ Supplementing previous studies, the ligand properties of c,c,c-1,5,9cyclododecatriene were analyzed in detail.⁶ Nickel is also known to be stabilized inside a macrocyclic scaffold of three alkyne moieties, such as the planar tribenzocyclyne and heterocyclotriynes containing silicon, germanium, or titanium.⁷

In recent years, following the unexpected discovery of an (E,E,E)-1,6,11-triazacyclopentadeca-3,8,13-triene—Pd(0) complex,⁸ the Roglans group has worked intensively on the



Figure 1. Ni(0), Pd(0), and Pt(0) complexes with acyclic diazatriene (I) and cyclic triazatriene (II) and mixed triazaalkene/alkyne ligands (III, IV), having the ene/yne functional groups in 1,6,11-sequence.

synthesis of a series of azamacrocycles with various ring sizes and numbers of C=C and C=C bonds.⁹ The ability of these macrocycles to coordinate at Pd(0), Pt(0), and Ag(I) has been studied, with particular success in the stabilization of palladium(0) (structures II, III, and IV in Figure 1). The resulting palladium(0) complexes are very stable and have been thoroughly characterized, paying special attention to the stereoisomerism arising from the different faces of the olefinic double bonds complexed to the metal. While in principle complexation of the metal at one of the two stereotopic faces of each C=C function present in the macrocycles can give rise to

Received: December 22, 2011 Published: February 24, 2012

Scheme 1. Synthesis of the Ni(0) Complexes 3, 4, and 5



2 4a series of isomers, only the energetically most favorable isomer is actually formed, as shown by NMR and X-ray techniques. It appears that the conformation of the six-membered chelate rings determines the stability of a complex and, hence, whether it is formed. In the case of the Pd(0) complexes II,^{9d} the observed isomers show two azapalladacyclohexanic rings in *chair* conformation and the third ring in *twist* conformation, whereas for Pd(0) complexes III and IV the observed isomers

show only chair-type conformations.^{9e} Of particular interest is the fact that the Pd complexes of the 15-membered trienic macrocycle (type II) have been found to be recoverable and reusable catalysts in C–C bond-forming reactions, such as Suzuki–Miyaura cross-couplings and Heck couplings. This has been particularly successful when using diazonium salts as the electrophilic counterpart.¹⁰

In the present study we investigate the coordination properties of azamacrocycles 1^{8c} and 2^{9e} (Scheme 1) bonded to nickel(0), with a focus on the different kinds of unsaturation and rigidity of the scaffold. The new Ni(0) complexes have been characterized in solution and the solid state by spectroscopic (NMR, X-ray diffraction) and thermal techniques (DSC) and probed for their reactivity in C–C bond-forming reactions (Suzuki–Miyaura cross-coupling).

RESULTS AND DISCUSSION

Preparation of the Nickel(0) Complexes. Reacting equimolar amounts of $Ni(cod)_2$ and (E,E,E)-1,6,11-tris(4tolylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene $(1)^{8c}$ in THF solution at room temperature for 1 h resulted in ligand exchange. Cooling the solution to 0 °C afforded yellow crystals of 3 in 78% yield (Scheme 1). The crystals of 3 include one molecule of THF solute. Complex 3 readily dissolves in THF, but is insoluble in diethyl ether and n-pentane. It appears unstable in methylene dichloride. Complex 3 represents the lighter homologue of the known derivatives $1 \cdot Pd(0)$ and 1.Pt(0).^{8d} While the crystal structures of these complexes and also of the uncoordinated 1^{8c} are known, the crystals of 3 obtained from THF have so far proved to be unsuitable for an X-ray structural investigation, which unfortunately precludes a comparison of the three homologues. We expect that the structure of 3 will be very similar to that of the $1 \cdot Pd(0)$ and 1.Pt(0) analogues.

A DSC (differential scanning calorimetry) study on crystalline $1 \cdot Pd(0)$ and related compounds revealed vitrification after recooling from the melt as an order-disorder

phenomenon. Most of these compounds remained a glass, although $1 \cdot Pd(0)$, interestingly, recrystallized when reheated.^{9f} This behavior appears not to be paralleled by the Ni(0) analogue 3, which showed a broad endothermic effect between 167 and 195 °C, attributable to unspecified changes in the lattice, and eventually sharp melting at 207 °C, but no change when recooled and reheated (see Supporting Information, SI).

When in a similar reaction Ni $(cod)_2$ was treated with 1 equiv of (E,E)-1,6,11-tris(4-tolylsulfonyl)-1,6,11-triazacyclopentadeca-3,8-diene-13-yne (2),^{9e} a mixture of colorless crystals of 4 and some well-formed orange crystals of 5 precipitated at 20 °C in the course of 1–2 days (Scheme 1). Formation of 5 was avoided by using a 10% excess of 2. This way, pure 4 was isolated in 80% yield. Separation of 4 from 5 is possible by recrystallization from THF, in which 5 is insoluble. The crystals of 4 obtained from THF include five solute molecules, causing substantial disorder (see also SI for structure determination). The solute THF is largely removed when the crystals are dried in a vacuum at ambient temperature. Complex 4 readily dissolves in THF and methylene dichloride, where it appears to be stable, but it is insoluble in diethyl ether and *n*-pentane.

For complex 5 elemental analysis revealed a variable content of up to two Ni atoms per macrocyclic ligand, suggesting the presence of a potentially dinuclear complex $(C_{33}H_{37}N_3O_6S_3)$ -Ni_{1+n} $(C_8H_{12})_n$ ($n \le 1$) in which 4 is associated with n Ni(cod) entities. In fact, reacting isolated 4 with a further equivalent of Ni(cod)₂ afforded orange 5 in 91% yield. An in situ reaction of macrocycle 2 with 2 equiv of Ni(cod)₂ is less suited for the preparation of 5 since here, owing to the slowness of the two reaction steps and insolubility of 5, the crystallizing 5 incorporates a larger amount of 4. Any 4 incorporated in crystalline 5 cannot be removed by treatment with THF. Complex 5 is insoluble in the common organic solvents even when heated, which precludes its solution NMR characterization.

When complex 4 was studied by DSC, an endothermic effect occurred around 164 °C, which can be ascribed to loss of THF. Release of THF has been confirmed by heating solid 4 to 170 °C for one hour, which leaves the solvent-free but otherwise unchanged compound, as evidenced by ¹H NMR. Compounds 4 and 5 suffered exothermic decomposition in DSC at 225 and 213 °C, respectively (see SI). All three nickel complexes proved to be sensitive to air and moisture.

NMR Spectra of 3. The uncoordinated 15-membered cyclotriene **1** shows two broad ¹H signals for the six olefinic

Table 1. Selected ¹H and ¹³C NMR Resonances of the Uncoordinated Cyclotriene 1, the Ni(0) Complex 3, and the Homologues $1 \cdot Pd(0)$ and $1 \cdot Pt(0)$



and 12 methylene protons and two ¹³C signals of equal intensity for the six olefinic and six methylene C atoms (Table 1).^{8b} The spectra not only prove equivalence of all methylene and the olefinic moieties but also show that the geminal methylene protons are enantiotopic on the time average. Assuming that the ground-state structure of the cyclotriene skeleton of 1 in solution is similar to that in the solid state^{8b} and can be conceived as (idealized) C_2 -symmetrical with the C_2 -axis passing through the center of one C==C bond and the opposite N atom, the spectra are consistent with rotations of the other C==C moieties about their vinylic C--C bonds, resulting in 60° jumps of the C_2 -axis. The time-averaged symmetry in solution is D_{3h} .



In contrast, complex 3 shows for the cyclotriene ligand a total of nine ¹H resonances of equal intensity, as there are three signals for olefinic protons (**b**, **c**, and **f**) and three pairs of signals for different methylene groups (**a**, **d**, and **e**) whose geminal protons are now diastereotopic (Table 1). The ¹³C NMR spectrum furnishes six signals of equal intensity (**a**–**f**). Complete resonance assignments were performed on the basis of 2D COSY and HSQC spectra (see SI). Similar to what was found previously for **1·Pd(0)** and **1·Pt(0)**^{8c} (for additional treatises of the structures and NMR spectra of these and related complexes see refs 9a, b, d), the triazacyclotriene ligand in 3 forms three formal azanickelacyclohexanic rings with Ni(0) in a chair—chair—twist conformational combination, resulting in an overall rigid C₂-symmetrical structure and the presence of a pair of enantiomers. The geometry is corroborated by the ¹H NMR spectrum, which exhibits different resonances for the olefinic protons at the asymmetrical azanickelacyclohexanic rings in chair conformation (δ (H) 3.38 and 3.22; **c**, **f**) and the markedly upfield olefinic resonance for the equivalent olefinic protons of the C_2 -symmetrical ring in twist conformation (δ (H) 2.00; **b**). Regarding the methylene groups, for the rings in chair conformation the protons in equatorial (δ (H) 4.52; **d**, **e**) and axial positions (δ (H) 1.34 and 1.38; **d**, **e**) have substantially different chemical shifts, while for the ring in twist conformation the differentiation between the pseudoequatorial and pseudoaxial protons (δ (H) 4.52 and 2.84; **a**) is smaller.

Article

Comparing the ¹³C NMR resonances of 3 with those of $1 \cdot Pd(0)$ and $1 \cdot Pt(0)$ and uncoordinated 1 (Table 1), we note that the upfield shift of the olefinic C atoms (from δ (C) 127.8 for 1) is least for $1 \cdot Pd(0)$ (δ (C) 78.5–82.8), intermediate for 3 (δ (C) 72.3–75.9), and largest for $1 \cdot Pt(0)$ (δ (C) 62.7–69.0), consistent with an increasing metal–alkene back-donation in this order.¹¹ The upfield shift of the methylene C atoms (from δ (C) 51.3 for 1) is much smaller, but for each C atom a, d, and e it strictly follows the sequence $3 < 1 \cdot Pd(0) < 1 \cdot Pt(0)$, apparently reflecting continuous conformational changes in the macrocycle due to the increasing size of the metals.

NMR Spectra of 4. The uncoordinated (E,E)-1,6,11triazacyclopentadeca-3,8-diene-13-yne **2** gives rise to five ¹H and six ¹³C NMR signals for the 15-membered ring.^{9e} The methylene protons are enantiotopic, indicating rotation of the C=C moieties about the vinylic C-C bonds. Thus, **2** shows dynamic C_{2y} symmetry in solution.

As for $2 \cdot Pd(0)$,^{9e} the Ni(0) analogue 4 exhibits eight ¹H and a full six ¹³C NMR signals for the macrocyclic ligand (Table 2). Complete resonance assignments were performed from 2D COSY and HSQC spectra (see SI). Thus, the Ni atom is coordinated to the two C=C bonds and the C≡C bond inside the cavity of the macrocycle in a rigid structure, rendering the

		$M = Ni (4), Pd \qquad M = Ni (4), Pd \qquad M = Ni (4), Pd \qquad M = M = M = M = M$	N SO ₂ Ar			
¹ H NMR						
assignation	2 ^{9e} <i>a</i>	$2 \cdot \mathrm{Pd}(0)^{9\mathrm{e}\ a}$	4^b			
a	3.58 (d, J = 5.7 Hz, 4H)	4.72	4.66 (dd, J = 13.2 and 3.2 Hz, 2H),			
		1.72	1.32 (dd, $J = 13.2$ and 10.8 Hz, 2H)			
b	5.44 (m, 2H)	3.93	3.42 (ddd, J = 13.2, 10.8, and 3.2 Hz, 2H	H)		
c	5.60 (m, 2H)	3.68	3.15 (ddd, J = 13.2, 10.8, and 2.4 Hz, 2H	H)		
d	3.69 (d, J = 6.6 Hz, 4H)	4.67	4.58 (dd, $J = 13.2$ and 2.4 Hz, 2H),			
		2.31	2.00 (dd, $J = 13.2$ and 10.8 Hz, 2H)			
e	3.88 (s, 4H)	4.77	4.54 (d, J = 13.6 Hz, 2H),			
		3.76	4.13 (d, J = 13.6 Hz, 2H)			
		¹³ C NMR				
assignation	2 ^{9e} <i>a</i>	2•Pd(0) ^{9e a} 4 ^b			
a	50.9	48.9	9 49.2			
b	131.5	79.0	0 71.3			
c	127.2	80.9	9 74.4			
d	50.1	46.8	8 46.6			
e	37.8	35.7	7 36.5			
f	79.3	82.8	8 97.4			
^a Solvent CDCl ₃ . ^b S	olvent CD ₂ Cl ₂ .					

Table 2. Selected ¹H and ¹³C NMR Chemical Shifts of Macrocycle 2, the Ni(0) Complex 4, and the Pd(0) Homologue 2·Pd(0)

SO₂Ar

SO₂Ar

geminal protons of the three types of methylene groups diastereotopic. While the total number of signals would also be in agreement with C_2 symmetry, C_s symmetry of the complex is substantiated by the large chemical shift difference between the equatorial (δ (H) 4.66) and axial (δ (H) 1.32) diastereotopic protons of methylene group **a**. This is consistent with a chair (as opposed to twist) conformation of the azanickelacyclohexanic ring involving one C atom of each of the two coordinated alkenes,^{9d} leading to a meso combination of the two chiral M– *E*-RCH=CHR substructures. The shift differences of the diastereotopic methylene protons in the asymmetric sixmembered rings involving one alkene and the alkyne functions are less pronounced (δ (H) 4.58, 2.00 (**d**) and δ (H) 4.54, 4.13 (**e**)).

As compared to 2, the signals of the olefinic protons and carbon atoms (**b**, **c**) are markedly shifted upfield upon metal coordination, indicative of partial $sp^2 \rightarrow sp^3$ rehybridization of carbon. This (negative) ¹H and ¹³C coordination shift¹¹ is distinctly larger for the Ni complex 4 than for 2·Pd(0). In contrast, the alkyne carbon atoms (f) are shifted downfield due to partial $sp \rightarrow sp^2$ rehybridization. While this (positive) shift is smaller in magnitude, it is again larger for 4 than for 2·Pd(0), consistent with stronger back-bonding of nickel(0).

Crystal and Molecular Structures of 4 and 5. The 1,6,11-triazacyclopentadeca-3,8-diene-13-yne-nickel(0) complexes 4 and 5 were further characterized by means of X-ray crystallography (Table 3). Complex 4 is mononuclear, whereas 5 is a dinuclear complex containing an additional cod ligand.

Monoclinic 4 crystallizes slowly from THF at ambient temperature to give well-formed colorless cubes (space group $P2_1/m$ (No. 11)), containing THF solute. The structure of 4 (Figure 2) resembles a chair, with the 15-membered ring providing the seat, two SO₂-tolyl groups at NCH₂C \equiv CCH₂N representing the front legs, and the other SO₂-tolyl group

forming the back rest. The molecule resides on a crystallographically imposed mirror plane, which passes through the nickel atom, the midpoint of the triple bond and N2 of the ring ligand, and S2, C7, C10, and C11 of one SO₂-tolyl group. There are two identical complexes of 4 in the unit cell, which are related to one another by an inversion center. The remainder of the unit cell is occupied by five disordered THF solute molecules per complex unit.

Article

The Ni atom is trigonal-planar coordinated by the C \equiv C bond and the two trans-substituted C \equiv C bonds, with both carbon atoms of the C \equiv C bond and the midpoints of the C \equiv C bond lying in one plane. This results in the formation of three six-membered rings, each containing Ni and N at the 1,4-positions and four C atoms in between. The central nickelaazacyclohexanic ring involving the ring section between the two C \equiv C bonds and N2 adopts a chair conformation, with the dihedral angles within the ring ranging between 55° and 69°. The other two equivalent pseudonickelaazacyclohexanic rings involving ring sections between one C \equiv C bond and N1 (N1*) adopt "half-chair" conformations, with dihedral angles in one-half of the ring varying between 44° and 71° and in the other merely 15–37°, due to the fact that C2 is constrained to lie in the coordination plane of Ni.

In contrast to 4, the conformation of the 1,6,11triazacyclopentadeca-3,8-dien-13-yne ligand in the Pd(0) homologue $1 \cdot Pd(0)$,^{9e} which crystallized from CH₂Cl₂-ethyl acetate-hexane solution with one CH₂Cl₂ solute molecule in the unit cell (triclinic crystal system, space group $P\overline{1}$ (No. 2)), is asymmetric and more flattened, presumably due to the larger radius of Pd compared to Ni, though a direct comparison with 4 is hampered due to extensive disorder in the ring in $1 \cdot Pd(0)$.

The structure of complex 5 (Figure 3) can be thought of as 4 with an additional Ni(cod) moiety coordinated to the C \equiv C bond. The complex crystallizes solute-free from THF in the

Table 3. Crystal Data for 4 and 5

	4	5
empirical formula	$C_{33}H_{37}N_3NiO_6S_3 \cdot 5(C_4H_8O)$	$C_{33}H_{37}N_3NiO_6S_3 \cdot 0.834(C_8H_{12}Ni)$
color and morphology	colorless prism	yellow plate
fw (g mol ⁻¹)	1087.07	865.77
temp (K)	100	100
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	orthorhombic
space group	$P2_1/m$ (No. 11)	<i>Pnma</i> (No. 62)
unit cell dimens		
a (Å)	11.5404(14)	18.539(3)
b (Å)	17.8908(14)	18.881(3)
c (Å)	13.864(3)	11.2747(15)
α (deg)	90.0	90.0
β (deg)	112.408(11)	90.0
γ (deg)	90.0	90.0
$V(Å^3)$	2646.3(6)	3946.6(9)
Z	2	4
V/Z (Å ³)	1323.2	986.7
calcd density (Mg·m ⁻³)	1.364	1.457
abs coeff (mm ⁻¹)	0.547	1.086
<i>F</i> (000) (e)	1160	1814
cryst size (mm ³)	$0.13 \times 0.12 \times 0.08$	$0.22 \times 0.10 \times 0.04$
θ range for data collecn (deg)	2.78–29.98	2.10-31.45
index ranges	$-16 \le h \le 16$	$-27 \le h \le 27$
-	$-25 \le k \le 25$	$-27 \le k \le 27$
	$-19 \le l \le 16$	$-16 \le l \le 16$
no. of rflns collected	37 802	110 518
no. of indep rflns	7920 ($R_{\rm int} = 0.0802$)	$6679 \ (R_{\rm int} = 0.1310)$
no. of rflns with $I > 2\sigma(I)$	5283	4745
completeness (%)	99.8 (θ = 29.98°)	99.4 $(\theta = 31.45^{\circ})$
abs correction	Gaussian	Gaussian
max./min. transmn	0.92/0.88	0.96/0.83
full-matrix least-squares	F^2	F^2
no. of data/restraints/params	7920/0/394	6679/0/260
goodness of fit on F^2	1.054	1.163
final R indices $(I > 2\sigma(I))$		
R1	0.0730	0.0857
wR2	0.1567	0.2024
R indices (all data)		
R1	0.1228	0.1214
wR2	0.1810	0.2199
largest diff peak/hole (e Å ⁻³)	0.912/-0.829	1.917/-1.214 (Ni2)

orthorhombic crystal system (space group *Pnma* (No. 62)), with four identical molecules in the unit cell.

Each Ni atom is in its zero oxidation state and is trigonalplanar (± 0.1 Å) coordinated by two C=C bonds and the bridging $C \equiv C$ bond. The coordination planes of the two metals, which each contain the two carbon atoms of the $C \equiv C$ bond, make an angle of 92° to one another. Whereas the two C=C bonds of the macrocyclic ligand lie approximately in the coordination plane of Ni1, the two C=C bonds of the cod ligand lie perpendicular to the coordination plane of Ni2. The Ni1···Ni2 distance of 2.684(2) Å indicates a significant $d^{10}-d^{10}$ interaction, which is supported by the observation that the midpoints of the C=C bonds of cod ligand lie slightly out (ca. 0.2 Å) of the plane defined by Ni2, C1, and C1*, away from the Ni…Ni contact. Bond lengths of all the coordinated C=C bonds of the macrocycle (C4-C5 1.388(7) Å) and the cod ligand (C19-C20 1.355(13) Å) are as expected. The C1-C1* distance of the Ni₂(μ -C \equiv C) entity at 1.303(10) Å appears

relatively short for a 2-fold-coordinated $C \equiv C$ bond, but this is likely to be an artifact of the largely anisotropic atomic displacements of these atoms.

The Ni(cod) moiety is present in the crystal with a refined occupancy of 83.4(4)%, indicating the crystal is in fact a mixture of 4 and 5. Several crystals were investigated, and all those studied showed a reduced occupancy of the Ni(cod) group (see SI for details of the structure solution). The molecule resides on a crystallographic mirror plane, as was the case with 4. The plane passes through both nickel atoms Ni1 and Ni2, the midpoint of the triple bond C1–C1*, and the atoms N2, S2, C14, C17, and C18, thereby bisecting the macrocyclic ligand and one SO₂-tolyl group and the cod ligand. The volume per formula unit of 5 at 986.7 Å³ is smaller than that of 4 (1323.2 Å³), which contains the five THF solute molecules.

One of the ethano bridges in the cod ligand is disordered over two positions. The C21A–C21B bond distance at 1.54(3)



Figure 2. Molecular structure of 4 (at 50% probability level). Selected bond distances (Å) and bond angles (deg): Ni1–C1 = 1.940(3), Ni1–C4 = 2.049(3), Ni1–C5 = 2.054(3), C1–C1* = 1.251(7), C1–C2 = 1.479(5), C3–C4 = 1.500(4), C4–C5 = 1.381(4), C5–C6 = 1.509(4), C1*–C1–C2 = 147.5(2), C2–N1–C3 = 114.8(3), C3–C4–C5 = 123.9(3), C4–C5–C6 = 120.0(3), C6–N2–C6* = 112.1(3).



Figure 3. Molecular structure of 5 (at 50% probability level). The (cod)Ni moiety has a partial occupancy of 83.4(4)% in the crystal studied. Selected bond distances (Å) and bond angles (deg): Ni1–C1 = 2.006(5), Ni1–C4 = 2.040(4), Ni1–C5 = 2.035(5), Ni2–C1 = 1.943(7), Ni2–C19 = 2.080(7), Ni2–C20 = 2.093(7), C1–C1* = 1.30(1), C1–C2 = 1.496(7), C3–C4 = 1.501(7), C4–C5 = 1.388(7), C5–C6 = 1.505(7), Ni1···Ni2 = 2.684(2), C1*–C1–C2 = 140.2(3), C2–N1–C3 = 113.8(4), C3–C4–C5 = 123.3(5), C4–C5–C6 = 118.8(5), C6–N2–C6* = 113.2(5).

Å is as expected for a C–C single bond. The disorder in the second ethano bridge could not be resolved, but is clearly

present and results in an unrealistically short C22–C22* bond distance of 1.45(2) Å. The cod ring is thus similarly puckered to that in Ni(cod)₂.¹² Bond lengths of the coordinated bonds at 1.36(1) Å are slightly shorter than expected (Ni(cod)₂: 1.391(2) Å, mean), but this may be a consequence of the relatively high atomic displacement parameters of the C atoms of the cod.

Dinuclear trigonal-planar Ni(0) complexes of type $(L_2Ni)_2(\mu$ -RC \equiv CR'), in which the two Ni atoms are complexed by a bridging alkyne ligand and additional donor ligands L such as phosphines,¹³ amines,¹⁴ cod,¹⁵ and alkyne (L_2) ,^{14,16} or as a combination of these ligands, are quite common. Typical Ni···Ni distances range between 2.45 and 2.65 Å, and a typical C \equiv C bond length falls in the range 1.30–1.39 Å (cf. {(cod)₂Ni}₂(μ -PhC \equiv CPh): Ni···Ni = 2.617 Å, C–C = 1.386 Å).^{15a} The C \equiv C bonds of the cod ligands always lie perpendicular to the corresponding C \equiv C–Ni plane. Complex 5, with its macrocyclic diene-yne ligand, is so far the only structurally characterized $(L_2Ni)_2(\mu$ -RC \equiv CR')-type complex in which two C \equiv C bonds of an olefinic ligand lie in the C \equiv C–Ni plane.

Chemical Properties of 3, 4, and 5. To test their reactivity, the 16-electron complexes 3, 4, and 5 were treated with unsaturated substrates such as neat butadiene $(-10 \ ^{\circ}C)$ and neat 1,3,5,7-cyclooctatetraene (20 $\ ^{\circ}C$). None of the reactions took place, and in all cases the starting complexes were recovered. Treating 3, 4, and 5 in THF solution with the smaller CO led readily to displacement of all ligands and formation of Ni(CO)₄.

In order to explore whether the new macrocyclic atoms exhibited possible catalytic activity, we chose to study the Suzuki-Miyaura cross-coupling¹⁷ of arylboronic acids with aryl halides to give biphenyl derivatives as a test reaction. While Suzuki-Miyaura cross-coupling is routinely performed with palladium catalysts,¹⁸ in reactions involving aryl chlorides and aryl bromides, as well as aryl tosylates and aryl mesylates, some nickel catalysts proved to be even more active than palladium complexes. As Ni(0) is more nucleophilic than Pd(0), nickel complexes attack aryl halides more easily in the oxidative addition step, thus favoring the cross-coupling process. An additional advantage, in particular for industrial applications, is that nickel is much cheaper than palladium. In their pioneering study Percec et al.¹⁹ used (dppf)NiCl₂/Zn (dppf = 1,l'bis(diphenylphosphino)ferrocene) in THF in the presence of K₃PO₄ as the catalytic system for the cross-coupling between arylboronic acids and aryl sulfonates or aryl mesylates. Significant progress has since been made in the Ni-catalyzed version of Suzuki-Miyaura aryl-aryl cross-coupling,²⁰ although most applications started with a Ni(II) source and added a reducer for reduction to Ni(0).

Since complexes 3, 4, and 5 contain nickel already in the zero oxidation state and nevertheless appear thermally rather stable, we envisaged their use in Suzuki–Miyaura cross-couplings of arylboronic acids and aryl halides with a base as the only additive. After some experimentation, a 5% molar solution of 3, 4, or 5 with 3 equiv of K_3PO_4 in refluxing 1,4-dioxane was able to cross-couple several organoboronic acids with aryl bromides with different electronic demands in moderate to good yields (Scheme 2). For example, coupling of phenylboronic acid (6a) with 4-bromoanisole affords 4-methoxybiphenyl (10b) in 76% yield. A full description of the optimization process and the experimental details of the catalysis, including Tables S5 and S6, are presented in the SI.

Scheme 2. Suzuki–Miyaura Reactions Catalyzed by Ni(0) Complexes 3, 4, or 5



CONCLUSIONS

We have reported on the synthesis, structure, and properties of Ni(0) complexes 3, 4, and 5 having macrocyclic (E,E,E)-1,6,11-triazacyclopentadeca-3,8,13-triene (1) and (E,E)-1,6,11-triazacyclopentadeca-3,8-dien-13-yne (2) ligands with 4-tolylsulfonyl substituents at nitrogen. The high thermal stability of the complexes can be attributed to the repetitive 1,6-sequences of C=C bonds or C=C and C≡C bonds, allowing the formation of six-membered azametallacyclohexanic substructures, which can optimally stabilize the metal—ene or metal—yne interactions by adopting chair-type (as opposed to twist-type) conformations.

In detail, in 3 the cyclotriene ligand adopts a chair-chairtwist conformation of C_2 symmetry, due to the geometric constraints imposed by the three E-RHC=CHR bonds, as evidenced by NMR. In 4 the cyclodiene-yne ligand adopts a chair-chair-chair-type conformation having C_s symmetry. Here, the symmetrical azametallacyclohexanic ring formed with one carbon of each of the two E-RHC=CHR bonds prefers to adopt a chair conformation, as do the two flattened rings, each containing a carbon atom of one E-RHC=CHR unit and the C \equiv C bond. As a consequence, while in both 3 and 4 the ligands are flexible enough to ensure good coordination to the metal, the coordination is at the same time rigid enough to exert high stability to the complexes. Complex 5 is derived from 4 by coordination of a Ni(cod) entity to the C \equiv C bond. The structures of 4 and 5 have been confirmed by single-crystal X-ray analysis.

Complexes **3–5** proved to be catalysts for Suzuki–Miyaura cross-coupling of aryl/heteroaryl boronic acids and functionalized aryl bromides, and reaction examples suggest a quite broad scope of the process.

EXPERIMENTAL SECTION

THF was dried by distillation from NaAlEt₄. 1,4-Dioxane was distilled from sodium under nitrogen. Reaction mixtures were chromatographed on a silica gel column (230-400 mesh). Ni(cod)₂,^{1c} 1 $(C_{33}H_{39}N_3O_6S_3, \text{ fw} = 669.9)$,^{8c} and 2 $(C_{33}H_{37}N_3O_6S_3, \text{ fw} = 667.9)^{9e}$ were prepared as published. Microanalyses were performed by Mikroanalytisches Labor Kolbe, Mülheim (Germany). EI mass spectra were recorded at 70 eV. ¹H NMR spectra were measured at 300 and 400 MHz, and ¹³C NMR spectra at 75 and 100 MHz with Bruker instruments. ¹H and ¹³C chemical shifts (δ) were referenced to internal solvent resonances and are reported relative to SiMe₄. Melting points were recorded with a Büchi 510 instrument. DSC experiments were performed using Mettler Toledo DSC820e and DSC822e instruments under inert conditions (continuous flow of 40 mL/min of high-purity N_2). Aluminum crucibles (40 μ L) were used; sample masses were between 4.5 and 7 mg. All handlings of nickel(0) complexes were done with Schlenk-type glassware under an argon atmosphere. For a detailed description of the Ni(0)-catalyzed Suzuki-Miyaura couplings, see the Supporting Information.

(*E,E,E*)-1,6,11-Tris(4-tolylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene-nickel(0) (3). A solution of 1 (268 mg, 0.40 mmol) in THF (15 mL) was combined with a solution of Ni(cod)₂ (110 mg, 0.40 mmol) in THF (10 mL) at room temperature. After standing for 1 h, the mixture was cooled to 0 °C to obtain yellow crystals. These were isolated by filtration, washed with diethyl ether, and dried under vacuum: yield 250 mg (78%). Mp: 210–212 °C (dec). IR (ATR): ν 2848, 1333, 1160 cm⁻¹. For NMR data of the macrocycle, see Table 1. NMR data of the 4-tolylsulfonyl substituents: δ (H) 2.37 (s, isochronous Me), 7.29, 7.59, 7.69 (phenyl); δ (C) 21.5 (isochronous Me), 127.4, 127.8, 130.0, 130.1, 133.8, 135.7, 143.9, 144.2 (phenyl). Anal. Calcd (%) for C₃₃H₃₉N₃NiO₆S₃·C₄H₈O (800.7): C, 55.50; H, 5.92; N, 5.25; Ni, 7.33. Found: C, 55.61; H, 6.01; N, 5.07; Ni, 6.70.

(E,E)-1,6,11-Tris(4-tolylsulfonyl)-1,6,11-triazacyclopentadeca-3,8-dien-13-yne-nickel(0) (4). A solution of 2 (300 mg, 0.45 mmol) in THF (40 mL) was combined with a solution of $Ni(cod)_2$ (110 mg, 0.40 mmol) in THF (10 mL) at room temperature. After initial mixing the solution was left without agitation for 1-3 days. The yellow color faded slowly, and somewhat spontaneously large, almost colorless crystals separated. The crystals were isolated by filtration, washed with diethyl ether, and dried under vacuum at 20 °C (1 h): yield 255 mg (80%). Mp: 228-230 °C (dec). The complex readily released solute THF under vacuum. For the X-ray structure determination, crystals were directly taken from the mother liquor, dipped in perfluoropolyether oil, and mounted on the diffractometer. IR (ATR): ν 2839, 1344, 1163 cm⁻¹. For NMR data of the macrocycle, see Table 2. NMR data of the 4-tolylsulfonyl substituents: δ (H) 2.35 (s, 6H), 2.36 (s, 3H), Me; 7.26 (4H), 7.28 (2H), 7.58 (2H), 7.62 (4H), phenyl; δ(C) 21.6 (isochronous Me), 127.7, 127.8, 130.0, 130.1, 133.9, 134.4, 144.2, 144.3. ESIpos-MS (CD₂Cl₂): m/e 725 [M - THF]⁺. Anal. Calcd (%) for C₃₃H₃₇N₃NiO₆S₃·C₄H₈O (798.7): C, 55.64; H, 5.68; N, 5.26; O, 14.02; Ni, 7.35; S, 12.04. Found: N, 5.19; Ni. 7.62

(*E,E*)-1,6,11-Tris(4-tolylsulfonyl)-1,6,11-triazacyclopentadeca-3,8-dien-13-yne-dinickel(0)-1,5-cyclooctadiene (5). A solution of complex 4 (240 mg, 0.30 mmol) in THF (40 mL) was combined with a solution of Ni(cod)₂ (85 mg, 0.31 mmol) in THF (10 mL) at room temperature. After initial mixing the solution was left undisturbed, and in the course of 3 days complex 5 separated in the form of small intergrown, dark orange crystals. The mother liquor was removed, and the product was washed with diethyl ether and dried under vacuum: yield 245 mg (91%). Mp: 225–227 °C (dec). Interestingly, the crystals grew preferentially on the surface of a Teflon-coated stirring bar and on scratched glass. IR (ATR): ν 2870, 1342, 1163 cm⁻¹. Anal. Calcd (%) for C₄₁H₄₉N₃Ni₂O₆S₃ (893.4): C, 55.12; H, 5.53; N, 4.70; Ni, 13.14. Found: C, 55.87; H, 5.59; N, 4.61; Ni, 11.19. Recordings of ¹H and ¹³C NMR and ESIpos mass spectra were prevented by insolubility of the compound.

Reaction of Complexes 3, 4, and 5 with CO. A solution (or suspension) of complexes **3, 4, and 5** (about 30 mg) in 5 mL of THF was stirred under an atmosphere of carbon monoxide. The initial yellow color of the solution disappeared within about 3 min. The volatile components were evaporated under vacuum. The colorless condensate was oxidized with H_2O_2 and positively tested for Ni(II), suggesting that Ni(CO)₄ had been formed. The free macrocycle, forming a white solid, remained in the reaction flask.

ASSOCIATED CONTENT

S Supporting Information

NMR spectra of complexes **3** and **4** (Figures S1–S10), DSC curves for compounds **3–5** (Figures S11–S13), and additional information on the X-ray structure determinations of **4** and **5** (Figures S14, S15 and Tables S1–S4). Description of the Ni(0)-catalyzed Suzuki–Miyaura coupling reactions (Tables S5, S6) and spectroscopic characterization of the products. CIF files containing X-ray crystallographic data for **4** and **5**. This material is available free of charge via the Internet at http:// pubs.acs.org. Supplementary crystallographic data (**4**, CCDC

849420; 5, CCDC 849421) can also be obtained free of charge 2005, 1

via http://www.ccdc.cam.ac.uk/deposit.

AUTHOR INFORMATION

Corresponding Author

*E-mail: anna.roglans@udg.edu; poerschke@kofo.mpg.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The project was funded by the program Acciones Integradas Hispano-Alemanas between Germany (DAAD, BMBF) and Spain (MICINN, Spanish Ministry of Science and Innovation, Project AIB2010DE-00262). Financial support from the MICINN (Projects CTQ2008-05409, CTQ2011-23121) and the Generalitat de Catalunya (Project 2009SGR637) is also gratefully acknowledged. S.B. thanks the University of Girona for a predoctoral grant.

REFERENCES

(1) (a) Wilke, G. Angew. Chem. 1960, 72, 581. (b) Wilke, G. Angew. Chem. 1963, 75, 10; Angew. Chem., Int. Ed. Engl. 1963, 2, 105.
(c) Bogdanovic, B.; Kröner, M.; Wilke, G. Liebigs. Ann. Chem 1966, 699, 1.

(2) Fischer, K.; Jonas, K.; Wilke, G. Angew. Chem. 1973, 85, 620; Angew. Chem., Int. Ed. Engl. 1973, 12, 565.

(3) Wilke, G.; Bogdanović, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmermann, H. Angew. Chem. **1966**, 78, 157; Angew. Chem., Int. Ed. Engl. **1966**, 5, 151.

(4) (a) Bonrath, W.; Pörschke, K.-R.; Michaelis, S. Angew. Chem. 1990, 102, 295; Angew. Chem., Int. Ed. 1990, 29, 298. (b) Proft, B.; Pörschke, K.-R.; Lutz, F.; Krüger, C. Chem. Ber. 1991, 124, 2667. (c) Krause, J.; Bonrath, W.; Pörschke, K.-R. Organometallics 1992, 11, 1158. (d) Pörschke, K.-R.; Pluta, C.; Proft, B.; Lutz, F.; Krüger, C. Z. Naturfosch. B 1993, 48, 608. (e) Proft, B.; Pörschke, K.-R.; Lutz, F.; Krüger, C. Chem. Ber. 1994, 127, 653. (f) Krause, J.; Haack, K.-J.; Cestaric, G.; Goddard, R.; Pörschke, K.-R. J. Chem. Soc., Chem. Commun. 1998, 1291. (g) Krause, J.; Cestaric, G.; Haack, K.-J.; Seevogel, K.; Storm, W.; Pörschke, K.-R. J. Am. Chem. Soc. 1999, 121, 9807. (h) Blum, K.; Chernyshova, E. S.; Goddard, R.; Jonas, K.; Pörschke, K.-R. Organometallics 2007, 26, 5174.

(5) Hratchian, H. P.; Chowdhury, S. K.; Gutiérrez-García, V. M.; Amarasinghe, K. K. D.; Heeg, M. J.; Schlegel, H. B.; Montgomery, J. *Organometallics* **2004**, *23*, 4636.

(6) Chernyshova, E. S.; Goddard, R.; Pörschke, K.-R. Organometallics 2007, 26, 4872.

(7) For a review, see: Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1999**, *99*, 3153.

(8) (a) Cerezo, S.; Cortès, J.; López-Romero, J.-M.; Moreno-Mañas, M.; Parella, T.; Pleixats, R.; Roglans, A. *Tetrahedron* 1998, 54, 14885.
(b) Cortès, J.; Moreno-Mañas, M.; Pleixats, R. *Eur. J. Org. Chem.* 2000, 239.
(c) Cerezo, S.; Cortès, J.; Galvan, D.; Lago, E.; Marchi, C.; Molins, E.; Moreno-Mañas, M.; Pleixats, R.; Torrejón, J.; Vallribera, A. *Eur. J. Org. Chem.* 2001, 329.
(d) Cerezo, S.; Cortès, J.; Moreno-Mañas, M.; Parella, T.; Pleixats, R.; Torrejón, J.; Vallribera, A. *Eur. J. Inorg. Chem.* 2001, 1999.
(e) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Moreno-Mañas, M.; Vallribera, A. *Tetrahedron Lett.* 2002, 43, 5537.

(9) (a) Moreno-Mañas, M.; Pleixats, R.; Roglans, A.; Sebastián, R. M.; Vallribera, A. Arkivoc 2004, No. iv, 109. (b) Moreno-Mañas, M.; Pleixats, R.; Sebastián, R. M.; Vallribera, A.; Roglans, A. J. Organomet. Chem. 2004, 689, 3669. (c) Pla-Quintana, A.; Roglans, A.; Torrent, A.; Moreno-Mañas, M.; Benet-Buchholz, J. Organometallics 2004, 23, 2762. (d) Pla-Quintana, A.; Roglans, A.; Julián-Ortiz, J. V.; Moreno-Mañas, M.; Parella, T.; Benet-Buchholz, J.; Solans, X. Chem.—Eur. J.

2005, 11, 2689. (e) Pla-Quintana, A.; Torrent, A.; Dachs, A.; Roglans, A.; Pleixats, R.; Moreno-Mañas, M.; Parella, T.; Benet-Buchholz, J. *Organometallics* 2006, 25, 5612. (f) Dachs, A.; Masllorens, J.; Pla-Quintana, A.; Roglans, A.; Farjas, J.; Parella, T. *Organometallics* 2008, 27, 5768.

(10) (a) Masllorens, J.; Moreno-Mañas, M.; Pla-Quintana, A.; Roglans, A. Org. Lett. **2003**, *5*, 1559. (b) Masllorens, J.; González, I.; Roglans, A. Eur. J. Org. Chem. **2007**, 158.

(11) Jolly, P. W.; Mynott, R. Adv. Organomet. Chem. 1981, 19, 257.
(12) (a) Dierks, H.; Dietrich, H. Z. Kristallogr. 1965, 122, 1.
(b) Macchi, P.; Proserpio, D. M.; Sironi, A. J. Am. Chem. Soc. 1998, 120, 1447.

(13) (a) Pörschke, K.-R. Angew. Chem., Int. Ed. Engl. 1987, 26, 1288.
(b) Pörschke, K.-R. J. Am. Chem. Soc. 1989, 111, 5691. (c) Barrios-Francisco, R.; Benítez-Páez, T.; Flores-Alamo, M.; Arévalo, A.; García, J. J. Chem. Asian J. 2011, 6, 842.

(14) (a) Walther, D.; Schmidt, A.; Klettke, T.; Imhof, W.; Görls, H. Angew. Chem., Int. Ed. Engl. **1994**, 33, 1373. (b) Walther, D.; Klettke, T.; Imhof, W.; Görls, H. Z. Anorg. Allg. Chem. **1996**, 622, 1134.

(15) (a) Day, V. W.; Abdel-Meguid, S. S.; Dabestani, S.; Thomas, M. G.; Pretzer, W. R.; Muetterties, E. L. J. Am. Chem. Soc. **1976**, 98, 8289. (b) Maekawa, M.; Munakata, M.; Kuroda-Sowa, T.; Hachiya, K. Polyhedron **1995**, 14, 2879. (c) Kempter, A.; Gemel, C.; Cadenbach, T.; Fischer, R. A. Organometallics **2007**, 26, 4257. (d) Imhof, W.; Klettke, T.; Walther, D. Acta Crystallogr., Sect. E: Struct. Rep. Online **2007**, 63, m2567.

(16) (a) Walther, D.; Klettke, T.; Görls, H. Angew. Chem., Int. Ed. Engl. 1995, 34, 1860. (b) Klettke, T.; Walther, D.; Schmidt, A.; Görls, H.; Imhof, W.; Günther, W. Chem. Ber. 1996, 129, 1457.

(17) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. Synth. Commun. 1981, 11, 513. (b) Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457.
(c) Suzuki, A. J. Organomet. Chem. 1999, 576, 147. (d) Martin, R.; Buchwald, S. L. Acc. Chem. Res. 2008, 41, 1461.

(18) For monographies, see: (a) Handbook of Organopalladium Chemistry for Organic Synthesis; Negishi, E., Ed.; Wiley-Interscience, 2002; Vols. 1 and 2,. (b) Metal-Catalyzed Cross-Coupling Reactions; Meijere, A.; Diederich, F., Ed.; Wiley-VCH, 2004; Vols. 1 and 2, For selected reviews, see: (c) Kotha, S.; Lahiri, K.; Kashinath, D. Tetrahedron 2002, 58, 9633. (d) Tucker, C. E.; de Vries, J. G. Top. Catal. 2002, 19, 111. (e) Lipshutz, B. H. Adv. Synth. Catal. 2001, 343, 313.

(19) Percec, V.; Bae, J.-Y.; Hill, D. H. J. Org. Chem. 1995, 60, 1060. (20) For a recent review, see: (a) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A. M.; Garg, N. K.; Percec, V. Chem. Rev. 2011, 111, 1346. Selected references: (b) Saito, S.; Sakai, M.; Miyaura, N. Tetrahedron Lett. 1996, 37, 2993. (c) Saito, S.; Ohtani, S.; Miyaura, N. J. Org. Chem. 1997, 62, 8024. (d) Indolese, A. F. Tetrahedron Lett. 1997, 38, 3513. (e) Ueda, M.; Saitoh, A.; Oh-tani, S.; Miyaura, N. Tetrahedron 1998, 54, 13079. (f) Galland, J.-C.; Savignac, M.; Genêt, J.-P. Tetrahedron Lett. 1999, 40, 2323. (g) Leadbeater, N. E.; Resouly, S. M. Tetrahedron 1999, 55, 11889. (h) Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. Org. Lett. 2001, 3, 3049. (i) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. J. Org. Chem. 2004, 69, 3447. (j) Tang, Z. Y.; Hu, Q. S. J. Am. Chem. Soc. 2004, 126, 3058. (k) Tang, Z. Y.; Hu, Q. S. J. Org. Chem. 2006, 71, 2167. (l) Lee, C.-C.; Ke, W.-C.; Chan, K.-T.; Lai, C.-L.; Hu, C.-H.; Lee, H. M. Chem.-Eur. J. 2007, 13, 582. (m) Zhou, Y.; Xi, Z.; Chen, W.; Wang, D. Organometallics 2008, 27, 5911. (n) Kuroda, J.; Inamoto, K.; Hiroya, K.; Doi, T. Eur. J. Org. Chem. 2009, 2251. (o) Antoft-Finch, A.; Blackburn, T.; Snieckus, V. J. Am. Chem. Soc. 2009, 131, 17750. (p) Tu, T.; Mao, H.; Herbert, C.; Xu, M.; Dötz, K. H. Chem. Commun. 2010, 46, 7796. (q) Fan, X.-H.; Yang, L.-M. Eur. J. Org. Chem. 2010, 2457. (r) Molander, G. A.; Beaumard, F. Org. Lett. 2010, 12, 4022. (s) Zhao, Y.-L.; Li, Y.; Li, S.-M.; Zhou, Y.-G.; Sun, F.-Y.; Gao, L.-X.; Han, F.-S. Adv. Synth. Catal. 2011, 353, 1543. (t) Baghbanzadeh, M.; Pilger, C.; Kappe, C. O. J. Org. Chem. 2011, 76, 1507. (u) Tobisu, M.; Xu, T.; Shimasaki, T.; Chatani, N. J. Am. Chem. Soc. 2011, 133, 19505.