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Mesoionic triazolylidene nickel complexes: synthesis, ligand lability, and catalytic C–C bond formation activity

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Abstract. A set of triazolylidene (trz) nickel(II) complexes $[\text{NiCpX}(\text{trz})]$ was synthesized by a direct metallation of the corresponding triazolium salt with nickelocene, NiCp_2 . While at short reaction times and in the presence of a coordinating anion X, the monocarbene complex is preferably formed, long reaction times induce the gradual transformation of $[\text{NiCpX}(\text{trz})]$ to the biscarbene complexes $[\text{Ni}(\text{Cp})(\text{trz})_2]^+$. Kinetic analyses lend strong support to a consecutive pathway involving triazolylidene dissociation from $[\text{NiCpX}(\text{trz})]$ en route to the biscarbene complex. Similar carbene transfer is observed in a solid state reaction upon heating complex $[\text{NiCpX}(\text{trz})]$ in vacuo, which induces disproportionation to $[\text{NiI}_2(\text{trz})_2]$ and NiCp_2 , confirming that the Ni–C(trz) is kinetically labile. Both complexes $[\text{Ni}(\text{Cp})(\text{trz})_2]^+$ and $[\text{NiCpX}(\text{trz})]$ were efficient catalyst precursors for Suzuki-Miyaura cross coupling of arylbromides and phenylboronic acid with turnover frequencies exceeding 228 h^{-1} . Complex degradation after short reaction times, identified in separate experiments, prohibits high turnover numbers, and for high conversions, repetitive additions of triazolylidene nickel complex and phenylboronic acid is necessary.

Introduction

The development of new transition metal-based catalytic systems has been stimulated considerably by the discovery of N-heterocyclic carbenes (NHCs) as ligands that impart unique properties.¹ Progress is particularly well documented for the platinum group metals and gold,² yet remarkably less so for first row transition metals. However, procedures relying on 3d metal centers are highly attractive from an environmental and economic perspective, since most of the 3d metals are Earth-abundant and hence provide access to sustainable and inexpensive processes.³ Moreover, the mechanistically distinct behavior of 3d metals may offer potential to overcome some of the drawbacks associated with their noble metal congeners,⁴ and to induce new reactivity patterns.⁵ For example, nickel phosphine complexes were successfully utilized as catalyst precursors for cross-coupling reactions.⁶

The coordination of NHCs to nickel has been achieved by various methods, including the in-situ preparation of free NHCs and subsequent coordination to $\text{NiCl}_2(\text{L}_2)$,⁷ the reaction of nickelocene, NiCp_2 , with imidazolium salts,⁸ the reaction of imidazolium salts with Ag_2O and metallic nickel powder,⁹ and oxidative addition of neutral, C2-halide-functionalized benzimidazoles.¹⁰ The synthetic accessibility of NHC nickel complexes also stimulated the investigation of their catalytic activity. They have been successfully applied as catalysts in [2+2+2] cycloadditions of diynes and carbonyl compounds such as aldehydes or CO_2 ,¹¹ for the hydrosilylation of ketones¹² and alkynes,¹³ for hydrogen transfer reactions,¹⁴ olefin polymerization,¹⁵ as well as the activation of small molecules.¹⁶ In an effort to substitute more precious palladium catalysts, carbene nickel species were also utilized in catalytic cross-coupling reactions including Suzuki-, Kumada-, and Heck-type C–C bond formation,¹⁷ though success has been moderate to date. While conversions reached completion with aryl chlorides and even aryl fluorides,^{17s} reaction times and catalyst loadings are typically much higher than in benchmark palladium-catalyzed processes.

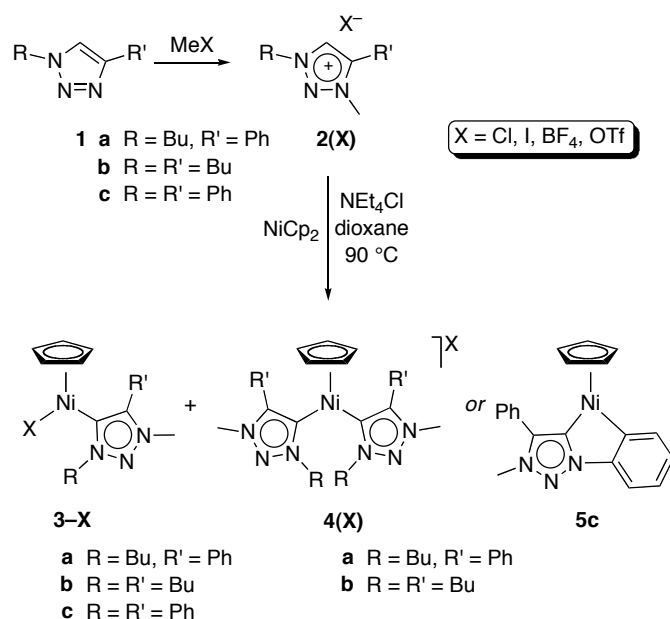
Inspired by these recent advances, we became interested in using triazolylidenes¹⁸ as a versatile subclass of NHCs as ligands in nickel complexes for catalytic applications. Specifically, triazolylidenes are stronger donating ligands than Arduengo-type NHCs and they provide access to catalytically highly active metal centers.¹⁹ Here we report on the synthesis

of mono- and biscarbene nickel Cp complexes (Cp = cyclopentadienyl, C₅H₅⁻), and first investigations into catalytic C_{Ar}-C_{Ar} bond formation in Suzuki-Miyaura cross-coupling reactions. In these initial studies, we focused on a set of triazolylidene ligands with phenyl and butyl substituents, as these wingtip groups impart different electronic and steric properties to the metal center.

Results and Discussion

Synthesis of triazolylidene nickel complexes. Triazolium salts **2a-c(X)** were available through standard copper-catalyzed [3+2] cycloaddition,²⁰ which afforded the triazoles **1a-c**, and subsequent methylation using either MeI, MeOTf, or Me₃OBF₄ (X = I, OTf, BF₄, respectively), or after ion exchange over a Dowex resin (X = Cl). These salts were metalated with nickelocene (Scheme 1) following a procedure previously described for imidazolium salt metalation,^{8,17q,21} thus affording either the monocarbene complex **3** or the biscarbene complex **4**, or a mixture of the two complexes (Scheme 1). Mixtures of **3** and **4** were readily separated by column chromatography purification over silica and elution with EtOAc/pentane or Et₂O/pentane. The first fraction yielded the neutral monocarbene complexes [NiCp(trz)X], **3-X**, as red solids, while the second fraction furnished the ionic biscarbene complexes [NiCp(trz)₂]X, **4a(X)** and **4b(X)**, as green compounds (trz = 1,2,3-triazol-5-ylidene). Yields after column chromatography were typically higher for **4** (30–50%) than for **3** (20–25%). The complexes are generally stable in solution and the solid state, except for **3b-Cl**, which decomposed in solution within less than one hour.

Scheme 1



Formation of mono- and biscarbene complexes was unambiguously demonstrated by the pertinent ratios of the integrals of the Cp protons and those of the triazolylidene substituents in the NMR spectrum, revealing a 1:1 and a 1:2 Cp/trz ratio respectively. When starting from the iodide salts **2a–c(I)**, a mixture of two monocarbene complexes **3–Cl** and **3–I** was obtained that contain either a Cl[–] or a I[–] ligand bound to the nickel center due to halide scrambling with NEt₄Cl, which was used as additive for the metallation. These two species were difficult to separate, yet they display slightly different NMR signatures, which helped for unambiguous assignment. For example, the signals of the Cp protons appeared around δ_{H} 4.8–5.0 ppm in the iodide complexes, while they are shifted upfield to δ_{H} 4.7–4.8 ppm in the chloride analogues. In the corresponding biscarbene complexes **4(X)**, the Cp signal is diagnostically downfield shifted and appears at δ_{H} 5.2–5.4 ppm. The carbene resonance was remarkably independent of the nature of the spectator ligand and appeared in all complexes **3–X** and **4(X)** in a narrow range, δ_{C} 148–150 ppm.

Complex **3b–I** featured two broad multiplet resonances for the NCH₂ protons around 5.1 and 4.7 ppm, indicating restricted rotation about the Ni–C_{trz} bond (CDCl₃ solution). Slight warming induced coalescence into a single resonance ($T_{\text{coal}} = 40$ °C), and similar behavior was observed for the signal assigned to the C-bound methylene group (Fig. S1a). From

temperature-dependent NMR spectroscopy, an energy barrier $\Delta G^\ddagger = 61.0 \pm 0.2 \text{ kJ mol}^{-1}$ was derived for this Ni–C rotation. Interestingly, the 2-imidazolylidene homologue of the nickel complex **3b–I**, viz. $[\text{Ni}(\text{Cp})\text{I}(\text{NHC})]$ (NHC = *N,N'*-dibutylimidazol-2-ylidene), which was prepared by salt metathesis from the bromo species,^{17q} features two well-resolved multiplets for the N–CH₂ groups at room temperature. No line broadening was observed upon heating to 60 °C (Fig. S1b), indicating slow exchange processes and a rotation barrier $> 64 \text{ kJ mol}^{-1}$. Due to the isosteric relationship of this complex and **3b–I**, we attribute the lower rotation barrier of **3b–I** to weaker bonding of the triazolylidene ligand to the nickel center as compared to imidazol-2-ylidenes.

Further confirmation of the structural assignments of these complexes was obtained from X-ray diffraction analysis of single crystals of representative complexes. Figure 1 shows the molecular structures of **3c–I**, **4a(BF₄)**, and **4b(Cl)**.²² As deduced from the ¹H NMR spectra, the nickel center in these structures is bound to one and two triazolylidene ligands, respectively. The nickel center adopts a distorted pseudo-trigonal coordination geometry and the sum of the angles with Ni as vertex are 360.0° in all three complexes. All Ni – C_{trz} bond lengths are 1.88 Å, similar to analogous imidazol-2-ylidene complexes.^{17q} The C_{trz}–Ni–C_{trz} angle in **4a(BF₄)** is significantly more acute than the C_{trz}–Ni–I angle in **3c–I** (87.83(7)° vs 98.04(7)°), while this angle is wide in **4b(Cl)**, 96.31(5)°, thus suggesting considerable flexibility in the ligand arrangement and only minor effects associated to steric trz/I[–] vs trz/trz repulsion in the nickel coordination sphere. This flexibility is also demonstrated by the variation of the C1–Ni–Cp_{centroid} angles between 127.47(9)° and 137.22(6)°. The carbene is coordinated in a symmetrical mode in all complexes with all yaw distortions²³ smaller than 2.5°.

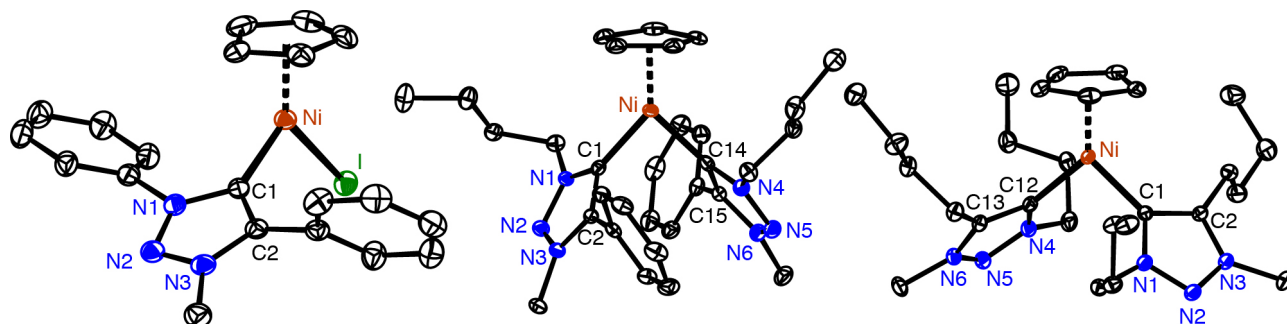


Fig. 1 ORTEP representation of complex **3c–I**, **4a(BF₄)**, and **4b(Cl)** (50% probability, hydrogen atoms and non-coordinating anions omitted for clarity).

Table 1. Selected bond lengths (Å) and angles (°) for complexes **3c–I**, **4a(BF₄)**, and **4b(Cl)**

	3c (X=I)	4a(BF₄) (X=C14)	4b(Cl) (X=C12)
Ni–C1	1.879(3)	1.882(2)	1.893(1)
Ni–X	2.5133(5)	1.886(2)	1.890(1)
Ni–C _p centroid	1.7562(13)	1.7536(8)	1.7723(5)
N1–C1	1.374(3)	1.372(2)	1.375(1)
C2–C1	1.388(4)	1.396(2)	1.401(2)
C1–Ni–X	98.04(7)	87.83(7)	96.31(5)
C1–Ni–C _p centroid	127.47(9)	137.22(6)	132.18(4)
X–Ni–C _p centroid	134.34(5)	134.95(6)	131.51(4)

Of note, complex **4c** has not been detected even in traces. The formation of this complex is presumably suppressed by steric congestion induced by the arrangement of four phenyl substituents in a putative biscarbene complex. Instead, traces (<5%) of complex **5c** featuring a cyclometallated triazolylidene ligand were isolated as red crystals. While the carbene carbon was observed by NMR spectroscopy at a diagnostic resonance frequency (δ_{C} 149.7 ppm), a second low-field signal at δ_{C} 150.6 ppm indicates another nickel-bound carbon. Moreover, one of the N-bound phenyl groups features only four proton resonances that are all desymmetrized. These data are in agreement with other cyclometalated triazolylidene complexes.²⁴ Further evidence for cyclometalation was obtained from a single crystal X-ray diffraction of complex **5c** (Fig. 2). As in the mono- and biscarbene complexes above, the nickel center in **5c** adopts a trigonal planar coordination geometry (sum of angles is 359.98(6)°, Table 1). The Ni–C_{trz} bond measures 1.870(1) Å and is thus slightly shorter than the Ni–C_{ph} bond (1.898(1) Å). While the bite-angle of the C,C-bidentate triazolylidene ligand is rather acute, C1–Ni–C10 84.64(5)°, it is worth noting that this angle is very similar to the C_{trz}–Ni–C_{trz} angle in the biscarbene complex **4a(BF₄)**. Another common feature of the two complexes is the fact that the nickel center is exclusively bound to carbon atoms. As a result of the chelation, however, the carbene bonding is not symmetric as demonstrated by a large yaw angle of 16.0°.

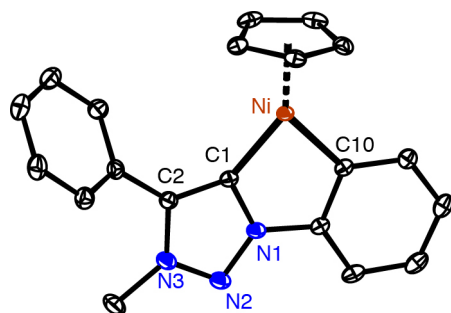


Fig. 2 ORTEP representation of complex **5c**, (50% probability, hydrogen atoms and second independent molecule of the asymmetric unit omitted for clarity). Selected bond lengths and angles: Ni–C1, 1.870(1) Å, Ni–C10, 1.898(1) Å, Ni–Cp_{centroid}, 1.7501(5) Å; C1–Ni–C10, 84.64(5)°, C1–Ni–Cp_{centroid}, 140.38(4)°, C10–Ni–Cp_{centroid}, 134.96(4)°.

Selectivity of complex formation. To better understand the factors that govern complex formation and product selectivity (mono- vs biscarbene complexes), the reaction conditions for complex synthesis were modulated. Variables included the anion of the triazolium salt, the presence of an external source of halide (NEt₄X), and the reaction time. Analysis of the crude reaction mixtures before chromatographic separation was greatly facilitated by the diagnostic chemical shifts of the Cp protons and the N–CH₃ group of the triazole system, which allowed complexes **3**, **4** (and **5c**) to be unambiguously distinguished. All reactions gave a maximum of four different species in variable ratios, specifically: (i) the monocarbene complex **3–X**, (ii) the biscarbene complex **4(X)** or the cyclometalated complex **5c**, (iii) the starting material triazolium salt **2**, and (iv) the triazole **1** as a result of CH₃⁺ loss. Similar demethylation of triazolium salts was previously noted by Bertrand and coworkers in the presence of strong bases such as KO^tBu or free triazolylidene.^{18b} Outcomes from variation of the triazolium halide and the addition of external halide salts are compiled in Table 2.

Table 2. Modification of reaction conditions ^a

Entry	2(X)	NEt ₄ Cl/ eq.	Time /h	3–X /%	4(X) /%	1 /%	2(X) /%
1	2a(Cl)	0	20	43	43	14	0
2	2a(I)	0	20	2	0	84	14
3	2a(OTf)	0	20	0	0	100	0
4	2a(BF₄)	0	20	0	0	100	0

5	2a(I)	1	20	14 ^b	36	50	0
6	2a(OTf)	1	20	3	70	22	5
7	2a(BF₄)	1	20	0	36	35	29
8	2a(Cl)	0	2	67	33	0	0
9	2a(I)	1	2	69 ^b	10	3	18
10	2a(I)	1 ^c	0.16	0	100	0	0
11	2a(I)	0.1 ^c	0.16	0	13	0	87
12	2a(I)	0.1 ^c	2	23 ^b	35	0	42

13	2b(I)	1	20	27 ^b	21	52	0
14	2b(OTf)	1	20	1	22	9	68
15	2b(BF₄)	1	20	1	4	34	60
16	2b(I)	1	4	79 ^b	13	0	8

17	2c(Cl)	0	4	81	0	19	0
18	2c(I)	0	4	39	0	61	0
19	2c(I)	1	4	67 ^b	0	33	0

^a all reactions at 90 °C, % yield determined by ¹H NMR spectroscopy; ^b Mixture of two compounds (X= Cl, I) ; ^c NEt₄F used instead of NEt₄Cl.

When using the triazolium salt **2a(X)** as a representative ligand precursor, a strong dependence on the triazolium anion was observed (Table 2, entries 1–8). The chloride salt **2a(Cl)** was fully converted after 20 h of reaction and yielded a 1:1 mixture of **3a–Cl** and **4a(Cl)** with some 14% of demethylated triazole **1a**. In contrast, the iodide analogue **2a(I)** was significantly less reactive (14% unconverted triazolium salt) and afforded only traces of **3a–I** along with significant quantities of demethylated triazole **1a**. The triazolium salts **2a(OTf)** and **2a(BF₄)** with less coordinating anions gave full conversion, however the product was exclusively the demethylated triazole **1a** and no formation of a triazolylidene nickel complex **3a–X** or **4a(X)** was detected. This demethylation pathway was considerably suppressed upon addition of NEt₄Cl (1 equiv) as an external Cl[–] source. Under these conditions, demethylation was less than 50%, though conversions were slower (5–30% starting material still observed after 20 h when OTf or BF₄ salts were used). The major product was the dicarbene complex

4a(X), after 20 h, though a strong preference towards the formation of the monocarbene complex **3a-Cl** was observed at initial reaction times when coordinating halides are present (entries 8,9). Notably, the stoichiometry of nickelocene in this reaction (0.5 or 1 molequiv.) had essentially no impact on product selectivity and the mono- vs biscarbene ratio was identical (Table S1). The selectivity towards the biscarbene complex in the presence of an external halide was even more pronounced when NEt₄F was used as an additive instead of NEt₄Cl (entries 10–12). In the presence of fluoride ions, total selectivity towards the biscarbene product **4a(X)** was noted and the reaction times were significantly shorter (10 min rather than several hours) for reaching full conversion. However, fluoride had no catalytic effect and with substoichiometric quantities of NEt₄F, **4a(X)** was formed only in quantities, corresponding to the fluoride concentration, and longer reaction times provided slowly **3a-X/4a(X)** ratios similar to those observe with NEt₄Cl as additive.

Similar trends were observed when starting from the ligand precursor **2b(X)** containing two butyl substituents on the heterocycle (entries 13–16; see also Table S2). Exclusive formation of the demethylated product took place in the absence of a halide source for triazolium salts with X = OTf, BF₄. In the presence of NEt₄Cl, monocarbene complex formation was favored at early stages of the reaction, and after 20 h, the biscarbene complex **4b(X)** was prevailing. The reactivity of the triazolium salt **2c(X)** was slightly deviating because of the inaccessibility of the biscarbene complex (see **5c** above; entries 17–19). The iodide salt **2c(I)** produced significant amounts of demethylated triazole **1c** in the absence of NEt₄Cl, while addition of chloride ions gave almost 70% of **3c-Cl/I**. Short reaction times (4 h) were required whereas after 20 h, most of the complex decomposed to the triazole **1c** (Table S3).

The enhanced reactivity of the chloride salts **2(Cl)** and the higher selectivity towards nickel coordination vs demethylation may be due to halide-assisted C_{trz}-H bond activation and C-H...X hydrogen bonding,²⁵ which is more effective with hard halides such as Cl⁻ and F⁻. In addition, small halides presumably facilitate Cp activation from nickelocene through initial halide coordination to form a transient nickelate complex [NiCp₂X]⁻ en route to C_{trz}-H bond activation and formation of complexes **3a-c**.

As noted above, stopping the reaction at early stages of complex formation changed the **3** vs **4**

selectivity substantially in favor of the monocarbene complex **3**. For example, a 2:1 ratio of **3a-Cl** and **4a(Cl)** was identified when reacting the triazolium salt with NiCp₂ for 2 h. Despite having reached full conversion of the triazolium salt at this stage, the **3/4** ratio changed during subsequent 18 h of reaction to a 1:1 mixture. This reactivity suggests that complex **3** is a precursor of the biscarbene complex **4** even in the absence of triazolium salt, thus pointing towards a triazolylidene ligand redistribution process.²⁶

Further support for such a carbene dissociation and re-binding process was obtained from time-dependent NMR spectroscopic monitoring of the reaction mixture starting from **2a(I)** and NiCp₂ in the presence of NEt₄Cl (Fig. 3). Accordingly, the monocarbene nickel complex **3a-X** was formed initially as the major product, reaching a maximum concentration after about 60 min. A rapid subsequent decay is observed with concomitant formation of **4a(X)**. The measured relative concentrations are in reasonable agreement with a kinetic profile of consecutive reactions (solid lines in Fig. 3) and thus lend support to the monocarbene complex **3a-X** as an intermediate in the formation of the biscarbene complex **4a(X)**. Already at early stages, significant quantities of demethylated triazole started to appear, and this product becomes predominant after very long reaction times (>24 h, Fig. S2). This reactivity trends imply that complex **4a(X)** is not stable at elevated temperatures. The constant ratio of complex **4a(X)** between 2 and 14 h is therefore probably a consequence of similar rates for decomposition of **4a(X)** and for formation of this species from the corresponding monocarbene complex **3a-X**. Hence, if the monocarbene complexes **3-X** are the desired products, short reaction times are essential, while biscarbene complexes **4-X** are selectively formed at medium reaction times (5–10 h) or in the presence of fluoride ions. Apparently, the presence of halides bound to the nickel center facilitate the dissociation of the triazolylidene in the monocarbene complexes **3-X**, which is in agreement with the enhanced formation of the biscarbene complex **4(X)** in the presence of smaller halides in the series F⁻ > Cl⁻ > I⁻ (see above).

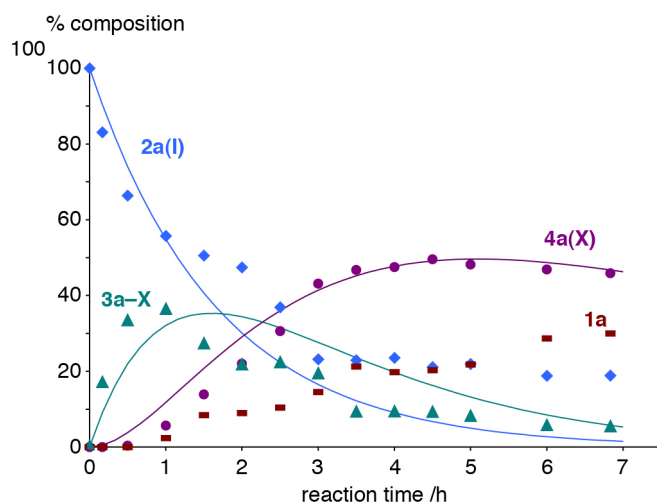


Fig. 3 Time-dependent monitoring of the metalation of triazolium salt **2a(I)** with Ni(Cp)₂; relative concentrations of **2a(X)** (diamonds), **3a-X** (triangles), **4a(X)** (circles), and **1a** (bars) and the corresponding modeled concentrations for a consecutive reaction **2a(X)**→**3a-X**→**4a(X)** with relative observed rate constants $k_1 = 0.6$ and $k_2 = 0.65$, and a superimposed first-order decay of **4a(X)** (relative observed rate k_3 for **4a(X)**→**1a** is 0.1).

Carbene transfer from complexes 3-X. Upon drying complex **3a-I** under vacuum and slight warming, sublimation of NiCp₂ was visually detected and unambiguously identified by IR spectroscopy.²⁷ The process was significantly accelerated when a solid sample was heated in vacuo to 100 °C, cleanly yielding **6a** as a new biscarbene complex in addition to nickelocene (Scheme 2).^{28,29} In the ¹³C NMR spectrum, complex **6a** is characterized by a diagnostic lowfield chemical shift of the carbene, δ_C 160.23 ppm. This resonance is at significantly lower field than in the Cp-containing complexes **3a-I** and **4a(I)** (δ_C 148–150 ppm). Likewise, the proton resonances of the triazolylidene ligand move upfield when compared to the Cp-precursor complex ($\Delta\delta_H$ about 0.2 ppm for NCH₂ and NCH₃ groups), and the Cp signals are absent in the spectra of **6a**. Two isomers with almost identical NMR patterns are observed in a 3:1 ratio, and these were assigned to the *syn* and *anti* orientation of the wingtip substituents in **6a**.^{24c} Similarly, complex **3b** disproportionated in vacuo and yielded the corresponding Cp-free biscarbene complex **6b**.

Scheme 2

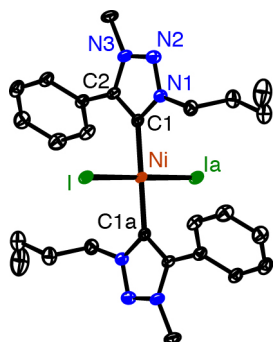
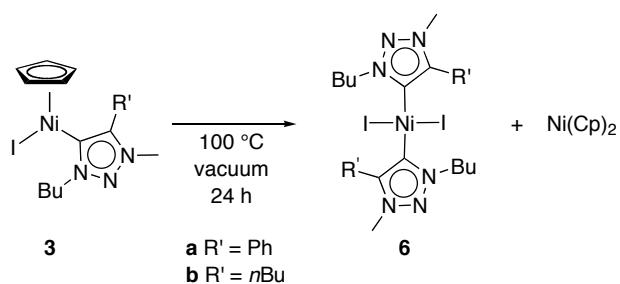


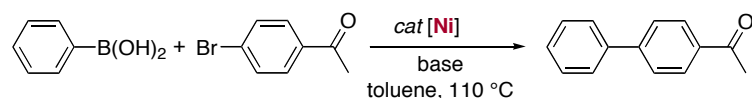
Fig. 4 ORTEP representation of Complex **6a** (50% probability, H atoms omitted). Selected bond lengths and angles: Ni1–C1 1.911(2) Å, Ni1–I1 2.5074(1) Å, C1–Ni1–I1 88.95(5)°, I1–N1–C1–C2 84.41(19)°, I1a–Ni1–C1–N1 87.98(15)°.

An X-ray diffraction analysis revealed a square-planar nickel center that coincides with a crystallographic inversion center (Fig. 4). The two Ni–C_{trz} bonds are thus identical by symmetry (Ni–C1 1.911 Å), and they are slightly longer than in the trigonal planar complexes, presumably as a consequence of the *trans* arrangement of the two carbene ligands. The triazolylidene heterocycles are bent out of the nickel coordination plane by essentially 90°, similar to the distortions observed in other square planar triazolylidene metal complexes.^{24c}

The disproportionation of complexes **3–X** to NiCp₂ and complexes **6a,b** suggests a remarkably labile Ni–C_{trz} bond in these complexes. This lability is in agreement with the observed formation of biscarbene complexes **4(X)** from the corresponding monocarbene precursors **3–X**, which requires a formal carbene transfer. Such a reactivity pattern also provides a rationale for the gradual decomposition of **4(X)** via base-induced demethylation of the triazolylidenes as observed during the synthesis of **4(X)** following pathways as stipulated by Bertrand and coworkers previously.^{18b} Related carbene transfer from nickel(II) has been noted recently by Morris and by Chen,³⁰ and our group has demonstrated that triazolylidenes and imidazolylidenes may migrate when bound to late transition metals.^{26,31}

Catalytic Suzuki-Miyaura cross coupling. Inspired by the catalytic activity of imidazolylidene nickel complexes in Suzuki-Miyaura cross-coupling of aryl halides with phenylboronic acid,³² the nickel complexes **3a–c** and **4a,b** were evaluated as catalyst precursors in this reaction (Table 3). The catalytic performance of the monocarbene complex **3a** was very similar to that of the biscarbene complex **4a**, though no conversion was noted in the blank reaction (entries 1–3). Hence, the carbene nickel complexes indeed act as catalyst precursors. The conversion after 4 h was identical to the conversion after 2 h, which implies catalyst deactivation at early stages.

Table 3. Suzuki–Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid catalyze by complexes **3a** and **4a**^a



entry	[Ni]	base	% yield (10 min)	% yield (2 h)	% yield (4 h)
1	---	K ₂ CO ₃	<3	<3	<3
2	3a–Cl	K ₂ CO ₃	14	28	27
3	4a(Cl)	K ₂ CO ₃	16	31	31
4	4a(Cl)	K ₃ PO ₄	12	40	47
5	4a(Cl)	NEt ₄ F	5	21	21
6	4a(Cl)	K ₂ CO ₃ ^b	9	44	42
7	4a(Cl)	K ₃ PO ₄ ^c	9	44	43

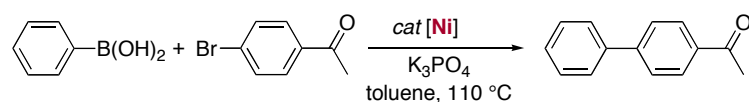
^a Reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.3 mmol), base (2.6 mmol), Ni complex (0.02 mmol, 2 mol%), toluene (3.0 mL), 110 °C; NMR spectroscopic yields. ^b H₂O (20 μL) added.

Optimization of catalytic conditions included variation of the base (Table 3, entries 3–5). K₃PO₄ gave better conversion after 4 h than NEt₄F or K₂CO₃ and it was also the only base which kept the catalytic system moderately active beyond 2 h. In contrast, NEt₄F and K₂CO₃ induced lower activity. When 20 μL of H₂O was added to the reaction in an attempt to increase the solubility of the inorganic base, conversions after 2 hours improved (entries 6,7). However, the absence of activity beyond that time indicates catalyst deactivation also under these conditions. The use of more polar solvents such as DMA or THF was detrimental to

catalytic activity, as no conversion was observed in these solvents at all. Likewise, lowering of the reaction temperature to 90 °C had a negative impact and led to much lower conversions after 2 h (22% vs 40% at 110 °C).

The mono- and biscarbene nickel complexes **3a,b** and **4a,b** with different anions X^- were subsequently tested under these optimized conditions (K_3PO_4 , toluene, 110 °C). Complex **3b-I** containing two butyl substituents on the triazolylidene produced 76% biaryl product after 10 min (TOF > 228 h^{-1}) and displayed the highest activity in the series. This activity also competes very favorably with the most active nickel-based cross-coupling catalysts known to date (TOFs around 300 h^{-1}).¹⁷ Complex **3a-I** with a butyl/phenyl substitution pattern showed lower catalytic activity under the same conditions, suggesting a direct influence of the ligand structure on the catalytic activity (Table 4, entries 1,2, Fig. S3). Similar trends were observed for **4a(I)** and **4b(I)**, though only after longer reaction times (entries 3,4). While mono- and biscarbene complexes show similar activity for butyl/phenyl substituted carbene nickel complexes (entries 1 vs 3, *cf* also entries 2,3 in Table 3), the monocarbene complex **3b-I** outperforms its dicarbene homologue **4b(I)** significantly.

Table 4. Arylation of bromoacetophenone with different carbene nickel complexes ^a



entry	[Ni]	% yield (10 min)	% yield (2 h)
1	3a-I	12	43
2	3b-I	76	80
3	4a(I)	12	30
4	4b(I)	15	66
5	4b(BF₄)	35	77
6	4b(BF₄)^b	50	88

^a General conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), catalyst (2 mol%), toluene (3.0 mL), 110 °C; NMR spectroscopic yields. ^b 5 mol% catalyst loading.

Exchange of the non-coordinating anion in the biscarbene nickel complex **4b(I)** for BF_4 more than doubled the initial rates as indicated by the 35% conversion after 10 min for **4b(BF₄)** as

compared to 15% when using **4b(I)**. However, this effect is tempered after prolonged reaction times and final spectroscopic yields are similar. In contrast, substitution of the iodide for a chloride had only marginal implications on the catalytic activity. In an attempt to reach full conversion to demonstrate the synthetic utility of these carbene nickel complexes, the catalyst loading was increased from 2 to 5 mol% **4b(BF₄)**. Remarkably, this reaction gave only slightly better conversions (50% better conversion after 10 min, 15% better conversion after 2 h), clearly less than expected for a 2.5-fold catalyst loading. Hence, yields are probably not limited by catalyst fatigue (and maximum turnovers), but by side reactions that induce catalyst or substrate decomposition.

We investigated this hypothesis in more detail with complex **3b-I**, which induced the highest catalytic activity in the initial catalyst screening experiments. Variation of the catalyst loading from 0.5 to 1 to 2 mol% gave the expected duplication of yield at early stages of the reaction (*cf* 21%, 43%, and 76% yield after 10 min, respectively, Table 5 entries 1–3; see Fig. S4 for time conversion profiles). This performance indicates that full activity is achieved under these conditions. Further increasing the catalyst loading to 5 mol% had no further effect and initial rates are almost identical (entry 4). Again, catalytic activity drops markedly after these initial conversions, and after about 30 min, production of biaryl products ceased.

Table 5. Optimization of supply of **3b-I** for high catalytic conversions ^a

Reaction scheme: Phenylboronic acid + 4-bromoacetophenone $\xrightarrow[\text{toluene, 110 } ^\circ\text{C}]{\text{cat } \mathbf{3b-I}, \text{K}_3\text{PO}_4}$ 4-phenylacetophenone

entry	3b-I /mol%	% yield			
		10 min	20 min	30 min	1 h
1	0.5	21	--	23	25
2	1	43	--	58	66
3	2	76	--	76	77
4	5	78	--	84	86
5 ^b	2	80	87 ^c	86	86
6 ^c	2	77	--	80	80

7 ^d	2	72	79	--	--
8 ^e	2	76	87	89	100

^a Reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.3 mmol), K₃PO₄ (2.6 mmol), complex **3b-I**, toluene (3.0 mL), 110 °C; NMR spectroscopic yields. ^b **3b-I** (2 mol%) added after 10 and 20 min.

^c initial PhB(OH)₂ quantity was 1.6 mmol. ^d PhB(OH)₂ (30 mol%) added after 10 min. ^e **3b-I** (2 mol%) and PhB(OH)₂ (30 mol%) added after 10 and 30 min.

We reasoned that the most likely pathways leading to catalysis breakdown involve decomposition of the carbene nickel complex. Therefore, a run with 2 mol% catalyst loading was repeated, though fresh nickel complex **3b-I** was supplied at regular intervals. After 10 and 20 min, 0.02 mmol (2 mol%) complex were added. While the first addition induced an increase of conversion from 80% to 86%, the second addition did not prompt further conversion and the reaction halted at a 87% spectroscopic yield (entry 5). Likewise, addition of a further portion of phenylboronic acid either from the beginning or after the initial 10 min of rapid conversion had only a marginal effect (entries 6,7). When both components are added simultaneously after 10 and 30 min (2 mol% **3b-I** and 30 mol% PhB(OH)₂, entry 8), spectroscopic yields rapidly reached 100% and after 40 min, full conversion of bromoacetophenone was observed. Hence, we conclude that the stability of the carbene nickel complexes indeed compromised the formation of the biaryl product in high yields, and this drawback can be mitigated by repetitive additions of small quantities of both nickel complex and boronic acid substrate. While this protocol provides a methodology for complete conversion and may thus become useful for Suzuki-Miyaura cross-coupling using earth-abundant nickel as opposed to much more expensive and rare palladium, stability and turnover numbers need further improvement. Moreover, the nickel complexes are susceptible to a variety of side reactions, leading to highly complex processes in these nickel-catalyzed transformations.

Reactivity of the nickel complexes under catalytically relevant conditions. Based on the catalyst deactivation due to the limited stability of the carbene nickel complexes, we investigated the stability of the monocarbene complex **3b-I** under catalytically relevant conditions in more detail. Thus, simple heating of the complex in toluene to the reaction

temperature (110 °C) indicates an appreciable thermal robustness of the complex in solution. After 10 min, no degradation was observed by ^1H NMR spectroscopy (hexamethylbenzene as internal standard; Table S4). After 30 min, about 10% of **3b-I** were converted, and concomitantly, signals due to the Cp-free biscarbene complex **6b** became visible in almost stoichiometric quantity (4%, corresponding to 8% triazolylidenes). The disproportionation continues slowly and reaches 6% **6b** and 80% **3b-I** after 1 h along with traces of triazole **1b**. This reactivity supports the kinetic lability of the carbene in these nickel complexes. In contrast, no reactivity has been observed under these conditions for the biscarbene complex **4b(I)**. When the same stability test was performed in the presence of K_3PO_4 as the base used for cross-coupling catalysis, gradual complex decomposition is deduced as the signals due to **3b-I** diminish to 75% (after 10 min) and further to 52% after 1 h, with only traces of **6b** formed (<5%) and some biscarbene complex **4b(X)**. This degradation is further accelerated in the presence of 4-bromoacetophenone (53% and 13% **3b-I** remaining after 10 min and 1 h, respectively). This degradation may be rationalized with an initial reaction of the substrate with the nickel complex, and may not necessary lead to unproductive species in a putative catalytic cycle. Moreover, the substantial concentration of **3b-I** after 30 min in the presence of K_3PO_4 with or without a base suggests sufficient availability of catalyst precursor for further conversion and is not consistent with the inactivity of the catalytic system after few minutes of reaction (see above).

In sharp contrast, complex **3b-I** almost instantaneously disappears when heated in the presence of K_3PO_4 and $\text{PhB}(\text{OH})_2$ and after 5 min, we were unable to detect any carbene nickel complex even in trace amounts. Likewise, no signals were observed that could be attributed to the triazolium salt precursor or the triazole. This rapid decomposition of **3b-I** is in good agreement with the catalytic results and also provides a rationale for the need to add both carbene nickel complex and phenylboronic acid to reach full conversion in catalytic cross-coupling reactions. Also it suggests an incompatibility of the triazolylidene nickel complexes with acidic substrates. Possibly, the use of boronic esters or trifluoroborate systems $\text{R}-\text{BF}_3^-$ as coupling agents³³ may be more suitable for application with this new class of nickel-based catalyst precursors. Also strengthening of the nickel carbene bonding, *e.g.*

through chelation,³⁴ may become a useful strategy for improving the catalytic performance of these triazolylidene nickel species.

Conclusion

A series of new triazolylidene nickel(II) complexes were prepared including monocarbene complexes coordinated to a Ni(Cp)X unit, biscarbene complexes coordinated to a Ni(Cp) unit, and biscarbene complexes bound to a NiI₂ scaffold. Detailed investigations allowed conditions to be tailored to selectively form only a specific type of complex. A recurring feature in these synthetic studies is the kinetic lability of the Ni–C(triazolylidene) bond, which enables remarkably facile carbene dissociation and coordination to a different nickel center both in solution and in the solid state as observed in the formation of biscarbene complexes from the pure monocarbene precursor. Hence, metal-carbene bonds may not be robust per se and hence, these ligands may fulfil roles other than strong donor ligands.

The catalytic activity of these new carbene nickel complexes in aryl-aryl cross-coupling reactions is appreciable and full conversions have been achieved in less than 1 h. However and in agreement with the carbene lability, rapid catalyst decomposition has been established, which seems to be exacerbated, in particular, by the presence of phenylboronic acid as coupling reagent. Different coupling reagents may reduce catalyst decomposition and may thus provide an avenue for using nickel as a replacement for palladium as the prevalent metal source for catalytic cross-coupling. Further work along those lines and aiming at stabilizing the nickel–triazolylidene bond are currently in progress in our laboratories.

Experiment Section

General. All solvents used for the reaction were purified using an alumina/catalyst column system (Thermovac Co.). Nickelocene,²⁷ the triazoles **1a–c**, and their triazolium salts **2a–c** were synthesized as described previously.^{24c,35} All other reagents are commercially available and were used as received. Microwave reactions were carried out using a Biotage Initiator 2.5, operating at 100 W irradiation power. Unless specified otherwise, NMR spectra were

recorded at 25 °C on Varian Innova spectrometers operating at 300, 400 500 or 600 MHz (^1H NMR) and 75, 100 or 125 MHz (^{13}C NMR), respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent resonances. Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland; residual solvents were also identified by ^1H NMR spectroscopy.

General procedure for the synthesis of the triazolylidene nickel(II) complexes 3 and 4.

To a solution of triazolium salts **2a–c** in 1,4-dioxane (10 mL) was added nickelocene (0.5 eq.). The mixture was stirred at 90 °C for 16 h. The solution slowly turned from dark green to dark brown. The solvent was then removed in vacuum, the residue was extracted with hot toluene (15 mL), and the extract was filtered through Celite, which was rinsed with toluene until the extracts were colorless. The combined extractions were concentrated under vacuum and passed through a neutral silica chromatography column and eluted with EtOAc/pentane or Et₂O/pentane. The red fraction (monocarbene complex **3**) and the green fraction (biscarbene complex **4**) were collected and evaporated to dryness.

Complex 3a–I. According to the general method from nickelocene (110 mg, 0.6 mmol) and triazolium salts **2a(I)** (343 mg, 1.0 mmol) in 4 h (Yield 148 mg, 31%). ^1H NMR (400 MHz, CD₂Cl₂): δ 8.07–7.93 (m, 2H, H_{Ph}), 7.70–7.51 (m, 3H, H_{Ph}), 5.20–5.01 (m, 2H, NCH₂), 4.93 (s, 5H, C₅H₅), 3.92 (s, 3H, NCH₃), 2.24–2.14 (m, 2H, NCH₂CH₂), 1.54 (sextet, $J_{\text{HH}} = 7.6$ Hz, 2H, CH₂CH₃), 1.08 (t, $J_{\text{HH}} = 7.6$ Hz, 3H, CH₂CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD₂Cl₂): δ 148.62 (C_{trz}–Ni), 145.28 (C_{trz}–Ph), 131.05, 130.16, 129.11, 129.00, 128.71, 126.61 (all C_{ph}), 91.90 (C₅H₅), 56.48 (NCH₂), 37.73 (NCH₃), 32.52 (NCH₂CH₂), 20.52 (CH₂CH₃), 14.13 (CH₂CH₃). Elem. Anal. calcd for C₁₈H₂₂IN₃Ni (465.99): C 46.39%, H 4.76%, N 9.02%; Found: C 46.21%, H 4.56%, N 9.11%.

Complex 3a–Cl. According to the general method from nickelocene (188 mg, 1.0 mmol) and triazolium salt **2a(Cl)** (271 mg, 1.0 mmol) in 1 h (Yield 210 mg, 56%). ^1H NMR (300 MHz, CD₂Cl₂): δ 8.05 (d, $J_{\text{HH}} = 7.6$ Hz, 2H, H_{Ph}), 7.71–7.56 (m, 3H, H_{Ph}), 5.22 (t, $J_{\text{HH}} = 7.6$ Hz, 2H, NCH₂), 4.79 (s, 5H, C₅H₅), 3.93 (s, 3H, NCH₃), 2.29 (quintet, $J_{\text{HH}} = 7.6$ Hz, 2H, NCH₂CH₂),

1.58 (sextet, $J_{\text{HH}} = 7.6$ Hz, 4H, CH_2CH_3), 1.10 (t, $J_{\text{HH}} = 7.6$ Hz, 3H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 148.76 ($\text{C}_{\text{trz-Ni}}$), 144.79 ($\text{C}_{\text{trz-Ph}}$), 131.17 ($\text{C}_{\text{Ph ortho}}$), 130.25 ($\text{C}_{\text{Ph para}}$), 129.24 ($\text{C}_{\text{Ph meta}}$), 126.05 ($\text{C}_{\text{Ph ipso}}$), 91.78 (C_5H_5), 55.44 (NCH_2), 37.63 (NCH_3), 32.88 (NCH_2CH_2), 20.57 (CH_2CH_3), 14.14 (CH_2CH_3). Elem. Anal. calcd for $\text{C}_{18}\text{H}_{22}\text{ClN}_3\text{Ni}$ (374.53): C 57.22%, H 5.92%, N 11.22%; Found: C 57.82%, H 6.04%, N 10.60%. HR-MS: m/z calculated for $\text{C}_{18}\text{H}_{22}\text{N}_3\text{Ni}^+ [\text{M-Cl}]^+$: 338.11167; found 338.1160.

Complex 3b-I. According to the general method from nickelocene (188 mg, 1.0 mmol) and triazolium salt **2b(I)** (323 mg, 1.0 mmol) in 4 h (Yield 25 mg, 28%). ^1H NMR (600 MHz, CDCl_3 , 253 K): δ 5.28 (s, 5H, C_5H_5), 5.13–5.08, 4.76–4.67 (2 \times m, 1H, NCH_2), 3.89 (s, 3H, NCH_3), 3.25–3.15, 2.95 – 2.85 (2 \times m, 1H, $\text{C}_{\text{trzCH}_2}$), 2.14–2.06, 2.05–1.96 (2 \times m, 1H, NCH_2CH_2), 1.88–1.80, 1.68–1.58 (2 \times m, 1H, $\text{C}_{\text{trzCH}_2\text{CH}_2}$), 1.57–1.43 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$ and $\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2}$), 1.08–0.99 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 148.17 ($\text{C}_{\text{trz-Bu}}$), 143.99 ($\text{C}_{\text{trz-Ni}}$), 91.26 (C_5H_5), 55.40 (NCH_2), 36.04 (NCH_3), 32.10 (NCH_2CH_2), 31.14 ($\text{C}_{\text{trzCH}_2\text{CH}_2}$), 26.10 ($\text{C}_{\text{trzCH}_2}$), 23.03 ($\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2}$), 20.08 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 14.11, 14.01 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Elem. Anal. calcd for $\text{C}_{16}\text{H}_{26}\text{IN}_3\text{Ni}$ (446.00) \times 0.25 EtOAc: C 43.63%, H 6.03%, N 8.98%; Found: C 43.80%, H 5.58%, N 8.85%. HR-MS: m/z calculated for $\text{C}_{16}\text{H}_{26}\text{N}_3\text{Ni}^+ [\text{M-I}]^+$: 318.1480; found 318.1471.

Complex 3b-Cl. According to the general method from nickelocene (188 mg, 1.0 mmol) and triazolium salt **2b(Cl)** (232 mg, 1.0 mmol) in 4 h (Yield 263 mg, 74%). ^1H NMR (500 MHz, CD_2Cl_2): δ 5.12 (s, 5H, C_5H_5), 5.05 (t, $J_{\text{HH}} = 7.7$ Hz, 2H, NCH_2), 3.89 (s, 3H, NCH_3), 3.11 (t, $J_{\text{HH}} = 7.8$ Hz, 2H, $\text{C}_{\text{trzCH}_2}$), 2.19 (quint, $J_{\text{HH}} = 7.7$ Hz, 2H, NCH_2CH_2), 1.82 (quint, $J_{\text{HH}} = 7.8$ Hz, 2H, $\text{C}_{\text{trzCH}_2\text{CH}_2}$), 1.63–1.44 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$ and $\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2}$), 1.10–1.01 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). The complex appeared to be unstable in solution and longer measurements were not possible. The ^{13}C NMR data were therefore extracted from two-dimensional HSQC and HMBC experiments: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 138.2 ($\text{C}_{\text{trz-Ni}}$), 148.0 ($\text{C}_{\text{trz-Bu}}$), 91.0 (C_5H_5), 54.5 (NCH_2), 35.7 (NCH_3), 25.5 ($\text{C}_{\text{trzCH}_2}$), 32.1 (NCH_2CH_2), 31.2 ($\text{C}_{\text{trzCH}_2\text{CH}_2}$), 22.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 19.8 ($\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2}$), 13.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}_{\text{trzCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Recrystallization and

hence also microanalyses failed due to the instability. HR-MS: m/z calculated for $C_{16}H_{26}N_3Ni^+$ 318.1480; found 318.1477.

Complex 3c-I. According to the general method from nickelocene (188 mg, 1.0 mmol) and triazolium salt **2c(I)** (363 mg, 1.0 mmol) in 4 h (Yield 179 mg, 37%). 1H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, $J_{HH} = 7.7$ Hz, 2H, H_{Ph-N} *ortho*), 8.08 (d, $J_{HH} = 7.7$ Hz, 2H, H_{Ph-C} *ortho*), 7.69–7.56 (m, 6H, H_{Ph-N} and H_{Ph-C}), 4.82 (s, 5H, C_5H_5), 4.03 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 148.76 (C_{trz-Ph}) 148.65 (C_{trz-Ni}), 130.89, 130.20, 130.11, 130.02, 128.95, 128.87, 128.84, 125.63 ($8 \times C_{Ph}$), 92.02 (C_5H_5), 37.43 (NCH_3). Elem. Anal. calcd for $C_{20}H_{18}IN_3Ni$ (485.97): C 49.43%, H 3.73%, N 8.65%; Found: C 49.28%, H 3.58%, N 8.42%.

Complex 3c-Cl. According to the general method from nickelocene (188 mg, 1.0 mmol) and triazolium salt **2c(Cl)** (271 mg, 1.0 mmol) in 4 h (Yield 316 mg, 80%). 1H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, $J_{HH} = 7.5$ Hz, 2H, H_{Ph-N} *ortho*), 8.25 (d, $J_{HH} = 7.5$ Hz, 2H, H_{Ph-C} *ortho*), 7.73–7.60 (m, 6H, H_{Ph-N} and H_{Ph-C}), 4.64 (s, 5H, C_5H_5), 4.09 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 148.41(C_{trz-Ph}), 148.23 (C_{trz-Ni}), 130.89, 130.14, 130.09, 129.16, 129.06, 128.99, 128.82, 125.42 ($8 \times C_{Ph}$), 91.75 (C_5H_5), 37.61 (NCH_3). Elem. Anal. calcd for $C_{20}H_{18}ClN_3Ni$ (394.52): C 60.89%, H 4.60%, N 10.65%; Found: C 60.89%, H 4.55%, N 10.44%.

Complex 4a(I). According to the general method from nickelocene (97 mg, 0.51 mmol) triazolium salt **2a(I)** (343 mg, 1.0 mmol) and NEt_4Cl (166 mg, 1.0 mmol) in 16 h (Yield 95 mg, 28%). 1H NMR (400 MHz, CD_2Cl_2): δ 7.61–7.59 (m, 10 H, H_{Ph}), 5.27 (s, 5H, C_5H_5), 3.87 (s, 6H, NCH_3), 3.65 (t, $J_{HH} = 7.6$ Hz, 4H, NCH_2), 1.63–1.54 (m, 4H, NCH_2CH_2), 1.33–1.18 (m, 4H, CH_2CH_3), 0.93 (t, $J_{HH} = 7.4$ Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 148.40 (C_{trz-Ni}), 147.44 (C_{trz-Ph}), 131.69, 130.66, 129.55, 128.81 ($4 \times C_{Ph}$), 91.51 (C_5H_5), 54.54 (NCH_2), 38.33 (NCH_3), 32.46 (NCH_2CH_2), 20.50 (CH_2CH_3), 13.94 (CH_2CH_3). Elem. Anal. calcd for $C_{31}H_{39}IN_6Ni$ (681.28): C 54.65%, H 5.77%, N 12.34%; Found: C 54.80%, H 5.64%, N 12.00%.

Complex 4a(Cl). According to the general method from nickelocene (97 mg, 0.51 mmol) triazolium salt **2a(Cl)** (251 mg, 1.0 mmol) in 16 h (Yield 118 mg, 40%). 1H NMR (400 MHz, $CDCl_3$): δ 7.83–7.77 (m, 10H, H_{Ph}), 5.28 (s, 5H, C_5H_5), 4.00 (s, 6H, NCH_3), 3.52 (t, $J_{HH} = 7.4$

Hz, 4H, NCH₂), 1.54 (quintet, $J_{\text{HH}} = 7.4$ Hz, 4H, NCH₂CH₂), 1.26 (sextet, $J_{\text{HH}} = 7.4$ Hz, 4H, CH₂CH₃), 0.93 (t, $J_{\text{HH}} = 7.4$ Hz, 6H, CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 148.43 (C_{trz}-Ni), 147.47 (C_{trz}-Ph), 131.71, 130.59, 129.53, 128.80 (4 × C_{Ph}), 91.55 (C₅H₅), 54.52 (NCH₂), 38.31 (NCH₃), 32.42 (NCH₂CH₂), 20.45 (CH₂CH₃), 13.90 (CH₂CH₃). Elem. Anal. calcd for C₃₁H₃₉IN₆Ni (589.83): C 63.13%, H 6.66%, N 14.25%; Found: C 62.60%, H 6.47%, N 14.03%.

Complex 4a(OTf). According to the general method from nickelocene (97 mg, 0.51 mmol) triazolium salt **2a(OTf)** (365 mg, 1.0 mmol) and NEt₄Cl (166 mg, 1.0 mmol) in 16 h (Yield 229 mg, 65%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.71–7.54 (m, 6H, H_{Ph}), 7.46–7.34 (m, 4H, H_{Ph}), 5.26 (s, 5H, C₅H₅), 3.79 (s, 6H, NCH₃), 3.68 (t, $J_{\text{HH}} = 7.4$ Hz, 4H, NCH₂), 1.60 (quintet, $J_{\text{HH}} = 7.4$ Hz, 4H, NCH₂CH₂), 1.26 (sextet, $J_{\text{HH}} = 7.4$ Hz, 4H, CH₂CH₃), 0.94 (t, $J_{\text{HH}} = 7.4$ Hz, 6H, CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 148.52 (C_{trz}-Ni), 148.49 (C_{trz}-Ph), 131.22, 130.76, 129.67, 128.81 (4 × C_{Ph}), 91.57 (C₅H₅), 54.54 (NCH₂), 37.64 (NCH₃), 32.41 (NCH₂CH₂), 20.49 (CH₂CH₃), 13.94 (CH₂CH₃). Elem. Anal. calcd for C₃₂H₃₉F₃N₆NiO₃S (703.44): C 54.64%, H 5.59%, N 11.95%; Found: C 54.46%, H 5.38%, N 11.75%.

Complex 4a(BF₄). According to the general method from nickelocene (97 mg, 0.51 mmol), triazolium salt **2a(BF₄)** (433 mg, 1.0 mmol) and NEt₄Cl (166 mg, 1.0 mmol) in 16 h (Yield 112 mg, 35%). ¹H NMR (400 MHz, CD₃OD): δ 7.65–7.60 (m, 6H, H_{Ph}), 7.42–7.38 (m, 4H, H_{Ph}), 5.28 (s, 5H, C₅H₅), 3.82 (t, $J_{\text{HH}} = 7.4$ Hz, 4H, NCH₂), 3.79 (s, 6H, NCH₃), 1.66 (quintet, $J_{\text{HH}} = 7.4$ Hz, 4H, NCH₂CH₂), 1.32 (sextet, $J_{\text{HH}} = 7.4$ Hz, 4H, CH₂CH₃), 0.97 (t, $J_{\text{HH}} = 7.4$ Hz, 6H, CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 150.08 (C_{trz}-Ni), 148.46 (C_{trz}-Ph), 131.89, 131.27, 130.22, 129.93 (4 × C_{Ph}), 92.24 (C₅H₅), 54.82 (NCH₂), 37.42 (NCH₃), 32.87 (NCH₂CH₂), 20.95 (CH₂CH₃), 13.97 (CH₂CH₃). Elem. Anal. calcd for C₃₁H₃₉BF₄N₆Ni (641.18): C 58.07%, H 6.13%, N 13.11%; Found: C 57.79%, H 6.02%, N 13.19%. HR-MS: m/z calculated for C₃₁H₃₉N₆Ni⁺ [M-BF₄]⁺: 553.2590; found 553.2568.

Complex 4b(I). According to the general method from nickelocene (97 mg, 0.51 mmol) triazolium salt **2b(I)** (323 mg, 1.0 mmol) and NEt₄Cl (166 mg, 1.0 mmol) in 16 h (Yield 61 mg, 19%). ¹H NMR (400 MHz, CDCl₃): δ 5.26 (s, 5H, C₅H₅), 4.52 (t, $J_{\text{HH}} = 7.6$ Hz, 4H, NCH₂), 4.06 (s, 6H, NCH₃), 2.97 (t, $J_{\text{HH}} = 7.4$ Hz, 4H, C_{trz}CH₂), 1.92 (quintet, $J_{\text{HH}} = 7.6$ Hz,

4H, NCH₂CH₂), 1.64–1.50 (m, 8H, C_{trz}CH₂CH₂ and NCH₂CH₂CH₂), 1.47–1.41 (m, 4H, C_{trz}CH₂CH₂CH₂), 1.04 (t, $J_{\text{HH}} = 7.6$ Hz, 6H, NCH₂CH₂CH₂CH₃), 1.01 (t, $J_{\text{HH}} = 7.4$ Hz, 6H, CH₃, C_{trz}CH₂CH₂CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 148.17 (C_{trz}-Bu), 145.41 (C_{trz}-Ni), 90.60 (C₅H₅), 54.71 (NCH₂), 37.90 (NCH₃), 32.15 (NCH₂CH₂), 31.07 (C_{trz}CH₂CH₂), 26.37 (C_{trz}CH₂), 23.11 (C_{trz}CH₂CH₂CH₂), 20.21 (NCH₂CH₂CH₂), 14.14 (C_{trz}CH₂CH₂CH₂CH₃), 13.93 (NCH₂CH₂CH₂CH₃). Elem. Anal. calcd for C₂₇H₄₇IN₆Ni (641.30): C 50.57%, H 7.39%, N 13.10%; Found: C 50.89%, H 7.62%, N 12.38%. HR-MS: m/z calculated for C₂₇H₄₇N₆Ni⁺ [M-I]⁺: 513.3216; found 513.3221.

Complex 4b(Cl): According to the general method from nickelocene (97 mg, 0.51 mmol) and triazolium salt **2b(Cl)** (232 mg, 1.0 mmol) in 16 h (Yield 49 mg, 18%). ¹H NMR (400 MHz, CDCl₃) δ 5.25 (s, 5H, C₅H₅), 4.50 (t, $J_{\text{HH}} = 7.7$ Hz, 4H, NCH₂), 4.09 (s, 6H, NCH₃), 2.97 (t, $J_{\text{HH}} = 7.6$ Hz, 4H, C_{trz}CH₂), 1.92 (quintet, $J_{\text{HH}} = 7.7$ Hz, 4H, NCH₂CH₂), 1.66–1.50 (m, 8H, C_{trz}CH₂CH₂ and NCH₂CH₂CH₂), 1.45 (sextet, $J_{\text{HH}} = 7.6$ Hz, 4H, C_{trz}CH₂CH₂CH₂), 1.09–1.01 (m, 12H, NCH₂CH₂CH₃ and C_{trz}CH₂CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.07 (C_{trz}-Bu), 146.16 (C_{trz}-Ni), 90.66 (C₅H₅), 54.61 (NCH₂), 37.39 (NCH₃), 32.16 (NCH₂CH₂), 31.44 (C_{trz}CH₂CH₂), 26.00 (C_{trz}CH₂), 23.10 (C_{trz}CH₂CH₂CH₂), 20.21 (NCH₂CH₂CH₂), 14.13 (C_{trz}CH₂CH₂CH₂CH₃), 13.92 (NCH₂CH₂CH₂CH₃). Elem. Anal. calcd for C₂₇H₄₇N₆NiCl (548.29) × 1.5 H₂O: C 56.22%, H 8.74%, N 14.57%; Found: C 56.49%, H 8.55%, N 14.51%.

Complexes 4b(OTf): According to the general method from nickelocene (97 mg, 0.51 mmol) triazolium salt **2b(OTf)** (345 mg, 1.0 mmol) and NEt₄Cl (166 mg, 1.0 mmol) in 16 h (Yield 72 mg, 22%). ¹H NMR (400 MHz, CDCl₃) δ 5.25 (s, 5H, C₅H₅), 4.50 (t, $J_{\text{HH}} = 7.6$ Hz, 4H, NCH₂), 3.97 (s, 6H, NCH₃), 2.90 (t, $J_{\text{HH}} = 7.4$ Hz, 4H, C_{trz}CH₂), 1.92 (quintet, $J_{\text{HH}} = 7.6$ Hz, 4H, NCH₂CH₂), 1.61–1.49 (m, 8H, C_{trz}CH₂CH₂ and NCH₂CH₂CH₂), 1.45 (sextet, $J_{\text{HH}} = 7.4$ Hz, 6H, C_{trz}CH₂CH₂CH₂), 1.08–1.01 (m, 12H, NCH₂CH₂CH₂CH₃ and C_{trz}CH₂CH₂CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 148.13 (C_{trz}-Bu), 145.01 (C_{trz}-Ni), 90.58 (C₅H₅), 54.50 (NCH₂), 36.86 (NCH₃), 32.13 (NCH₂CH₂), 31.39 (C_{trz}CH₂CH₂), 25.78 (C_{trz}CH₂), 23.08 (C_{trz}CH₂CH₂CH₂), 20.19 (NCH₂CH₂CH₂), 14.08 (C_{trz}CH₂CH₂CH₂CH₃), 13.91 (NCH₂CH₂CH₂CH₃). Elem. Anal. calcd for C₂₈H₄₇F₃N₆NiO₃S (662.27) : C 50.69%, H 7.14%, N 12.67%; Found: C 50.62%, H 7.00%, N 12.39%.

Complex 4b(BF₄). According to the general method from nickelocene (97 mg, 0.51 mmol) triazolium salt **2b(BF₄)** (310 mg, 1.0 mmol) and NEt₄Cl (166 mg, 1.0 mmol) in 16 h (Yield 6 mg, 4%). ¹H NMR (400 MHz, CD₃OD) δ 5.34 (s, 5H, C₅H₅), 4.51 (t, *J*_{HH} = 7.6 Hz, 4H, NCH₂), 4.00 (s, 6H, NCH₃), 2.99 (t, *J*_{HH} = 7.4 Hz, 4H, C_{trz}CH₂), 1.96–1.84 (m, 4H, NCH₂CH₂), 1.63–1.52 (m, 8H, C_{trz}CH₂CH₂ and NCH₂CH₂CH₂), 1.40 (sextet, *J*_{HH} = 7.4 Hz, 4H, C_{trz}CH₂CH₂CH₂), 1.08 (t, *J*_{HH} = 7.6 Hz, 6H, NCH₂CH₂CH₂CH₃), 1.01 (t, *J*_{HH} = 7.4 Hz, 6H, C_{trz}CH₂CH₂CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CD₃OD): δ 149.47 (C_{trz}-Bu), 147.65 (C_{trz}-Ni), 91.81 (C₅H₅), 55.42 (NCH₂), 36.93 (NCH₃), 33.07 (NCH₂CH₂), 31.94 (C_{trz}CH₂CH₂), 26.80 (C_{trz}CH₂), 24.01 (C_{trz}CH₂CH₂CH₂), 20.87 (NCH₂CH₂CH₂), 14.15 (C_{trz}CH₂CH₂CH₂CH₃), 14.06 (NCH₂CH₂CH₂CH₃). Elem. Anal. calcd for C₂₇H₄₇BF₄N₆Ni (601.20): C 53.94%, H 7.88%, N 13.98%; Found: C 53.73%, H 7.66%, N 13.50%. HR-MS: *m/z* calculated for C₂₇H₄₇N₆Ni⁺ [M-BF₄]⁺: 513.3216; found 513.3229.

Complex 5c. According to the general method from nickelocene (94 mg, 0.5 mmol) and triazolium salt **2c(Cl)** (271 mg, 1.0 mmol) in 26 h. ¹H NMR (500 MHz, CDCl₃): δ 7.66–7.46 (m, 7H, 5 H_{Ph-C} and 2 H_{Ph-N}), 7.04, 6.92 (2 × t, *J*_{HH} = 7.6 Hz, 2H, H_{Ph-N}), 5.24 (s, 5H, C₅H₅), 3.98 (s, 3H, NCH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 150.64 (C_{Ph-N}), 149.69 (C_{trz-Ni}), 148.44 (C_{trz-Ph}) 144.42 (C_{Ph-N}) 143.24 (C_{Ph-Ni}), 130.35, 129.90, 128.95, 125.36, 122.81, 114.03 (6 × C_{Ph}), 89.90 (C₅H₅), 36.64 (NCH₃). HR-MS: *m/z* [M]⁺ calculated for C₂₇H₄₇N₆Ni 513.3216, found 513.3229. This compound was only obtained in trace amounts, which were not sufficient for microanalysis.

Complex 6a. Complex **3a-I** was heated under vacuum to 100 °C for 24h. The red oil slowly turned to a pink solid. The solid was dissolve in CH₂Cl₂, and the mixture filtered through Celite. The filter was rinsed with copious amounts of CH₂Cl₂ until the extractions were colorless. The combined filtrates were concentrated to 1 mL and precipitated with pentane. The residue was collected and dried in vacuo. *Major isomer:* ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J*_{HH} = 7.6 Hz, 4H, H_{Ph ortho}), 7.62 (t, *J*_{HH} = 7.6 Hz, 4H, H_{Ph meta}), 7.55 (t, *J*_{HH} = 7.6 Hz, 2H, H_{Ph para}), 4.88 (t, *J*_{HH} = 7.6 Hz, 4H, NCH₂), 3.78 (s, 6H, NCH₃), 2.16 (quintet, *J*_{HH} = 7.6 Hz, 4H, NCH₂CH₂), 1.38 (sextet, *J*_{HH} = 7.6 Hz, 4H, CH₂CH₃), 0.96 (t, *J*_{HH} = 7.6 Hz, 6H, CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 160.23 (C_{trz-Ni}), 144.41 (C_{trz-Ph}), 130.81,

130.39, 129.35, 128.79 ($4 \times C_{Ph}$), 55.00 (NCH₂), 36.6 (NCH₃), 30.94 (NCH₂CH₂), 20.15 (CH₂CH₃), 13.89 (CH₂CH₃). *Minor isomer*: ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, $J_{HH} = 7.5$ Hz, 4H, H_{Ph ortho}), 7.47 (t, $J_{HH} = 7.5$ Hz, 2H, H_{Ph para}), 7.36 (t, $J_{HH} = 7.5$ Hz, 4H, H_{Ph meta}), 5.22 (t, $J_{HH} = 7.5$ Hz, 4H, NCH₂), 3.75 (s, 6H, NCH₃), 2.45 (quintet, $J_{HH} = 7.5$ Hz, 4H, NCH₂CH₂), 1.63 (sextet, $J_{HH} = 7.5$ Hz, 4H, CH₂CH₃), 1.11 (t, $J_{HH} = 7.5$ Hz, 6H, CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 160.23 (C_{trz-Ni}), 144.41 (C_{trz-Ph}), 130.39, 128.88, 128.79, 128.64 ($4 \times C_{Ph}$), 55.51 (NCH₂), 36.6 (NCH₃), 31.17 (NCH₂CH₂), 20.44 (CH₂CH₃), 13.95 (CH₂CH₃). Elem. Anal. calcd for C₂₆H₃₄I₂N₆Ni (743.09) \times 0.33 C₅H₁₂: C 43.32%, H 4.99%, N 10.95%; Found: C 43.54%, H 4.59%, N 10.34%. HR-MS: m/z calculated for C₂₆H₃₄IN₆Ni⁺ [M-I]⁺: 615.1243; found 615.1242.

Complex 6b. The procedure was analogous to that for **6a**, starting from complex **3b-I**, which afforded **6b** as a pink solid. ¹H NMR (500 MHz, CDCl₃): δ 5.03 (dt, $J_{HH} = 7.4$ Hz, 4H, NCH₂), 3.80 (s, 6H, NCH₃), 3.20 (dt, $J_{HH} = 7.4$ Hz, 4H, C_{trz}CH₂), 2.44 (quintet, $J_{HH} = 7.4$ Hz, 4H, NCH₂CH₂), 2.26 (quintet, $J_{HH} = 7.4$ Hz, 4H, C_{trz}CH₂CH₂), 1.62–1.44 (m, 8H, C_{trz}CH₂CH₂CH₂ and NCH₂CH₂CH₂), 1.12–1.01 (m, 12H, C_{trz}CH₂CH₂CH₂CH₃ and NCH₂CH₂CH₂CH₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 157.64 (C_{trz-Ni}), 144.41 (C_{trz-Bu}), 54.92 (NCH₂), 35.50 (NCH₃), 31.25 (NCH₂CH₂), 30.63 (C_{trz}CH₂CH₂), 26.05 (C_{trz}CH₂), 23.15 (C_{trz}CH₂CH₂CH₂), 20.28 (NCH₂CH₂CH₂), 14.07 (C_{trz}CH₂CH₂CH₂CH₃), 13.88 (NCH₂CH₂CH₂CH₃). Anal. calcd for C₂₂H₄₂I₂N₆Ni (743.09): C 37.58%, H 6.02%, N 11.95%; Found: C 37.59%, H 5.80%, N 10.88%. HR-MS: m/z calculated for C₂₂H₄₂IN₆Ni⁺ [M-I]⁺: 575.1869; found 575.1868.

Crystallographic details. Crystal data were collected using an Agilent (former Oxford Diffraction) SuperNova A diffractometer fitted with an Atlas detector. **4a(BF₄)**, **4b(Cl)**, **4b(BF₄)**, **5c**, and **6b** were measured with Mo-K α (0.71073 Å), **3c-I** and **4a(I)** with Cu-K α (1.54184 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed.³⁶ The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F² for all data using SHELXL-97.³⁷ Hydrogen atoms were added

at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Anisotropic thermal displacement parameters were used for all non-disordered non-hydrogen atoms. Crystallographic details are summarized in Tables S5–S11. CCDC numbers 1006473-1006479 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Material available: Synthetic procedures for the ligand precursors, spectroscopic data for **4b(Cl)** and **4b(OTf)**, details on the complex synthesis and catalytic runs, as well as X-ray crystal data in CIF format for all structures reported in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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