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Stereoelectronic Characterization and Catalytic Potential of a 1,3-Bis(2,6-terphenyl)-Substituted N-Heterocyclic Carbene

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The preparation of a 1,3-bis(2,6-terphenyl)imidazol-2-ylidene, IDitop (Ditop = 2,6-bis(4-tolyl)phenyl-) is reported. Several late transition metal complexes as well as the selenium adduct of IDitop were prepared to study and compare the stereoelectronic properties of IDitop to other well-known N-heterocyclic carbenes (NHCs). A study of the steric character of IDitop taken from crystal structure data of the complexes and adducts reveals a high degree of flexibility. Preliminary application to challenging Suzuki coupling reactions was undertaken.

Introduction

During the last two decades, flexible, sterically demanding N-heterocyclic carbenes (NHC) have become widely utilized as ancillary ligands in challenging cross-coupling reactions.[1] When coordinated to *d*-block metals, the steric bulk and strong σ-donor capacity of these NHCs stabilize the active species in catalysis. Whilst, their flexible bulk, can rearrange to permit competing steric requirements at the metal *e.g.* substrate binding *vs.* reductive elimination.[2] Following Glorius' seminal works with bisoxazoline-derived NHCs (IBiox),[3] cyclic (alkyl)(amino)carbenes (CAACs) and 1,3-bis(aryl)imidazol-2-ylidenes such as IPent,[4] IPr*[5] and related systems,[6] which are bulkier analogues of the ubiquitous IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), have been widely deployed in cross-coupling reactions (see Figure 1).[2a,7]

Inspired by Goto's and Kawashima's report of a 1,3-bis(3,5-terphenyl)imidazol-2-ylidene[8] and the report of a series of 1,3-bis(naphthyl)imidazolin-2-ylidenes by Dorta,[9] one of us reported a silver complex of a super bulky 1,3-bis(2,6-terphenyl) imidazol-2-ylidene, AgCl(IDitop) (**2**; Ditop = 2,6-bis(4-tolyl) phenyl-, see Figure 1).[10] The molecular structure of **2** reveals the pendant p-tolyl groups are positioned above and below the silver atom giving rise to a confirmation that closely mimics that of the C_2-symmetric "Sandwich" NHCs recently reported by Zhou.[11] This complex displays considerable dynamic behavior in solution, as indicated by NMR spectroscopy, indicative of considerable conformational flexibility. As part of our ongoing research into the development of new catalysts containing bulky NHC ligands, we were interested in the isolation and characterization of free IDitop, as well as investigating its steric and electronic character.

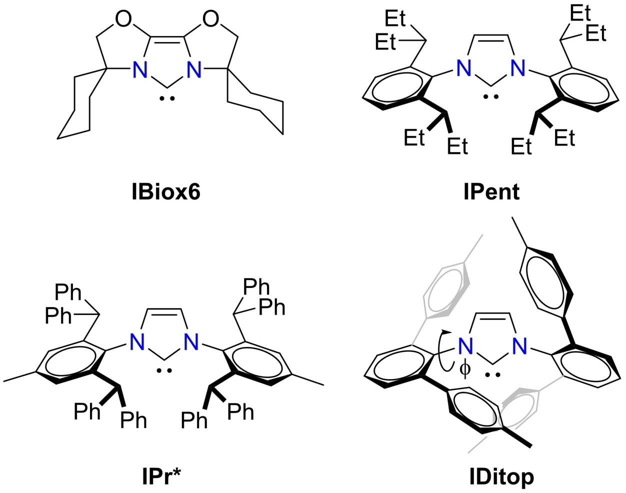

Figure 1. Prominent examples of flexible NHCs and IDitop.

The percentage buried volume (%V_{bur}) model,[12] has gained considerable popularity as a means to quantify the steric hindrance around a metal center by a ligand (Figure 2A).[13] Subsequent studies have cautioned about over extrapolating %V_{bur} values for a particular ligand to different metal coordination spheres.[14] In particular, rotation of *N*-aryl groups with respect to plane of the NHC (φ_1 and φ_2) may account for a large portion of the flexibly of the NHC (see Figure 1).[15] To address these deficiencies, the %V_{bur} methodology was utilized to generate topographic steric maps of ligands and catalytic pocket (Figure 2B), which have provided insight into the origins of the regiochemical selectivity.[15–16]

Several recent studies have noted a dependence on remote steric effects in reaction outcomes,[17] which were not captured by %V_{bur} calculations, but were captured using Tolman's steric parameter or 'cone angle' (θ),[18] or it's underutilized successor, the solid angle (Ω).[19] The solid angle is best visualized as the area of the shadow projected by the ligand atoms on a sphere surrounding the complex (Figure 2C). For simplicity, this can be expressed as a percentage of the total surface area of the

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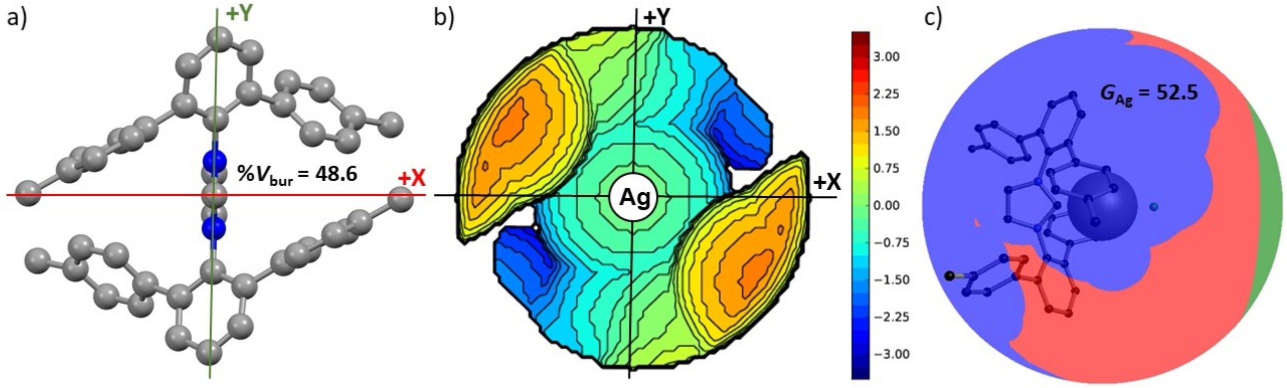


Figure 2. Representations of the steric character of IDitop in **2**: a) $\%V_{bur}$, b) steric map, c) solid angle (blue shading on a red sphere).

sphere (G-parameter, G_M) or as an equivalent cone angle.[20] To this end, we and others, have previously used solid angle measurements to quantify the steric bulk of NHCs and other ligands.[21] Thereby supporting that multiple steric descriptors be employed when investigating structure activity relationships.

In this work, we describe the synthesis of a series of complexes of IDitop, to study the electronic and steric properties of this ligand, and its potential as an auxiliary ligand in group 10 metal catalyzed cross coupling reactions.

Results and Discussion

Synthesis

The Free NHC, IDitop (**1**), was prepared in moderate yield by treating a THF slurry of IDitop·HCl with *n*-butyllithium at 0 °C (Scheme 1). Infrared spectroscopy of metal carbonyl complexes has been commonly employed to examine the electronics of NHCs. Given the inherent toxicity of $Ni(CO)_4$ we made no attempt to prepare $[Ni(CO)_3(IDitop)]$ (**3**). Instead, we prepared [IrCl(COD)(IDitop)] (**4**), by reacting $[Ir(\mu\text{-}Cl)(COD)]_2$ with **1**. Subsequent, treatment with CO afforded $[IrCl(CO)_2(IDitop)]$ (**5**).[22] To further probe the electronics of **1** by NMR spectroscopy, the bis(carbene) palladium complex, $[PdBr_2({}^iPr\text{-}Bzim)(IDitop)]$ (**6**; ^{i}Pr-Bzim = 1,3-diisopropylbenzimidazolin-2-ylidene), and the selenium adduct of **1**, IDitop·Se (**7**), were prepared using the methodology of Huynh[23] and Ganter[24] respectively (Scheme 1). Group 10 cross coupling precatalysts featuring **2**, $[PdCl(\eta^3\text{-cin})(IDitop)]$ (**8**; cin = cinnamyl), $[PdCl_2(3\text{-Cl-pyridinyl})(IDitop)]$ (**9**), [NiCl(Cp)(IDitop)] (**10**) and $[NiCp_2(IDitop)]$ (**11**) were prepared by adaptions of literature procedures (Scheme 1).[25]

The ^{1}H NMR spectra of **1**, **5**–**7**, **9**–**11** display time averaged C_{2v} symmetry at 298 K, consistent with facile rotation about the N–C and C–C bonds on the NMR timescale. By contrast, the room temperature ^{1}H NMR spectra of **4** and **8** each feature two tolyl methyl resonances that are indicative of spatial locking of the NHC.

Structural Analysis

The structure of the free carbene, **1**, was determined by X-ray diffraction (Figure 3). Two full molecules are contained in the asymmetric unit, however, the metrical parameters of both molecules are similar, thus only one will be discussed here. The N–C–N angle of 101.44(13)° is comparable to that in IMes (101.4(2)°).[26] The most significant difference found between these two NHCs was the distance between the nitrogens and the *ipso* carbons of the principle aryl rings. In **1**, the mean bond length of 1.434 Å, is considerably longer than that in IMes (1.380 Å).[26] Presumably this results of the increased steric bulk, for instance, similarly elongated $N\text{–}C_{ipso}$ bond lengths were reported for IPr* (1.440 Å). Contrasting the molecular structure of IPr* ($\varphi_1 = 81°$ and $\varphi_2 = -88°$), the planes of the principal aryl groups deviate significantly from being perpendicular to the plane of the NHC ($\varphi_1 = 62°$ and $\varphi_2 = -67°$). This affords a staggered conformation, which is likely due to intramolecular buttressing of the terphenyl units.[27]

Single crystals of the metal complexes **4**, **6**, **8**–**11** and the selenium adduct **7** could be grown suitable for their structures

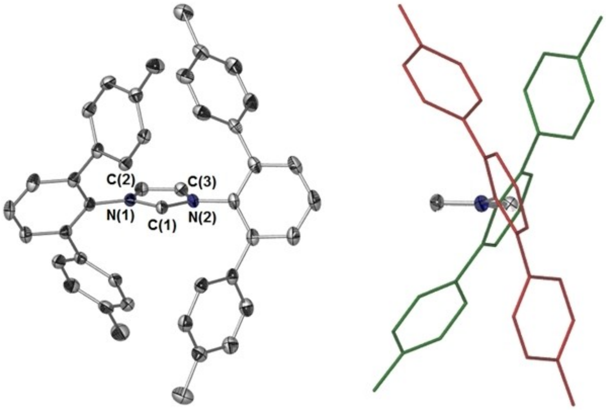
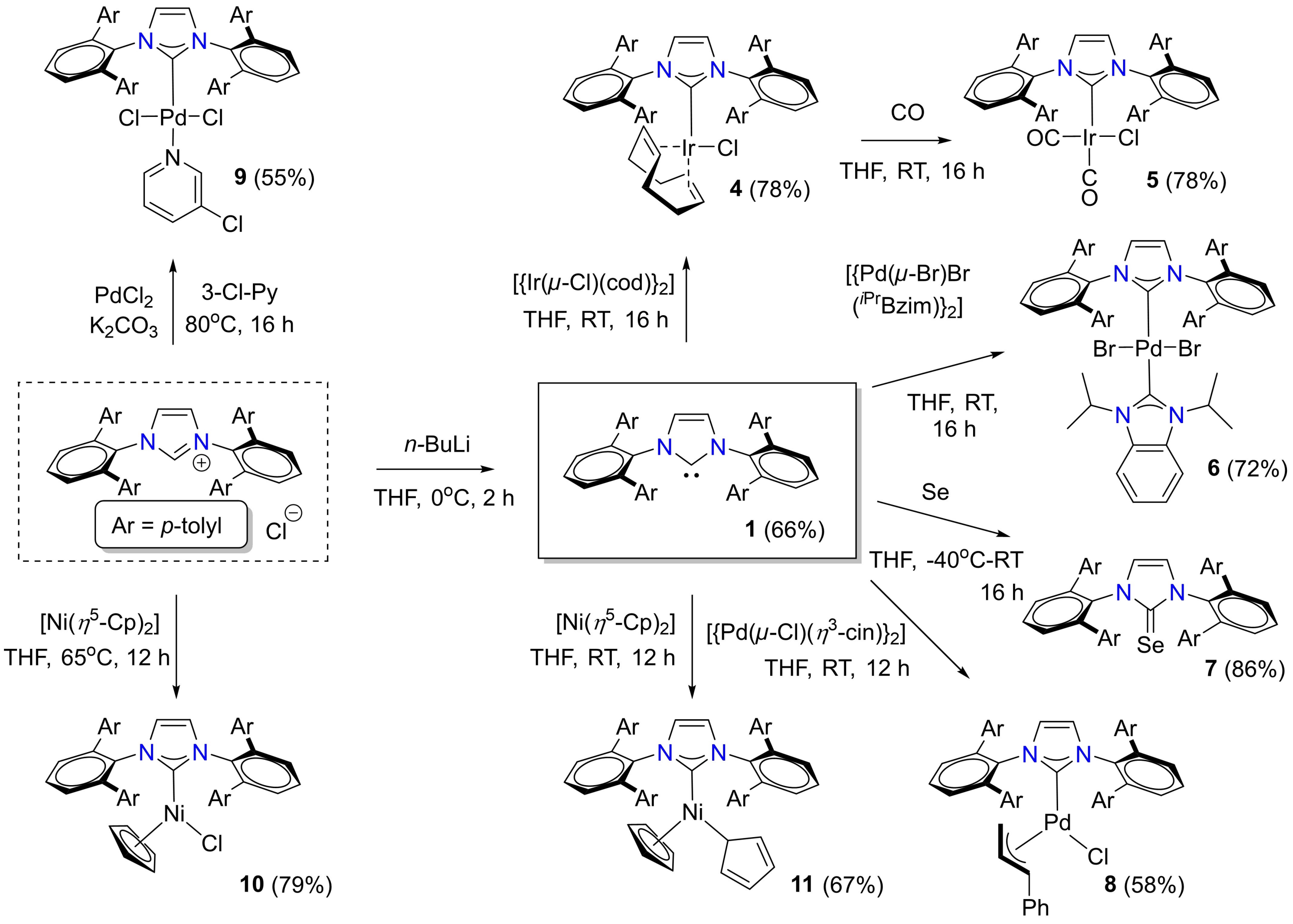


Figure 3. Molecular structure of **2** (50 % displacement ellipsoids, left; wireframes, right). Two perspectives displayed. All hydrogen atoms omitted for clarity.



Scheme 1. Preparation of IDitop (**1**), IDitop metal complexes and adducts. Percentage yields are shown in brackets.

to be determined by X-ray diffraction. Poor X-ray data was repeatedly obtained for **5**, however, the data was sufficient to unambiguously establish molecular connectivity. These structures allow the steric profile of the IDitop to be evaluated across a diverse range of different metal center geometries. The geometries and metrics about the metal centers are largely unremarkable. Despite this, a wide range of φ_1 and φ_2 are observed. For instance, in **6**, $\varphi_1=59^\circ$ and $\varphi_2=-88^\circ$, whilst in **9**, $\varphi_1=60^\circ$ and $\varphi_2=-52^\circ$, are measured (Figure 4a and b). These data indicate that IDitop is indeed quite flexible as more eclipsed conformations are accessible. One striking feature of the square planar complexes, **4**–**6** and **9**, the carbene plane is significantly twisted with respect to the metal coordination plane (Figure 4c and d). For example, in **9**, this interplanar angle is 52.6°, rather than the idealized 90°.[28] By way of comparison, the interplanar angles in IPr,[25b] IPent[4a] and IPr*[29] analogues are 79.3°, 72.5° and 65.8° respectively. Indeed the palladium's coordination plane in **9** appears to be coplanar to both proximal pendent *p*-tolyl groups (Figure 4c), indicating the deviation is likely due to steric constraints about the metal center imposed by the ligand.[27b]

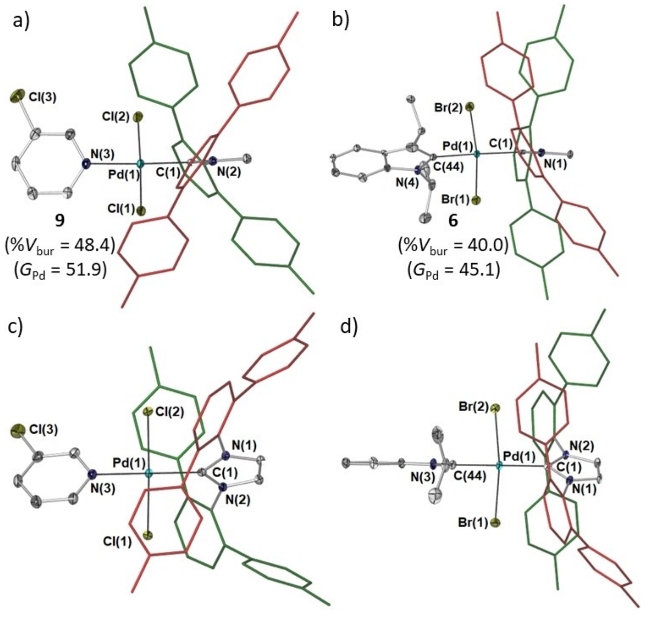


Figure 4. Molecular structures of **9** (a and c) and **6** (b and d). Two perspectives each shown; view perpendicular to the NHC plane (a and b) and view perpendicular to the palladium coordination plane (c and d). Structures shown with 50% displacement ellipsoids. All hydrogen atoms omitted and terphenyls depicted as wireframes for clarity.

Steric Parameters and Flexibility

A large range of %V_{bur} and G-parameter values were calculated for IDitop over the series of complexes (Table 1). For the aforementioned square planar palladium complexes, **6** and **9**, the difference in the %V_{bur} values are vast (8.4). The standard deviation of the %V_{bur} values measured for IDitop across compounds **2**–**10**, normalized for M–NHC distance, is 4.0. By comparison, the standard deviations of %V_{bur} values, for the available structures in the analogous series of IMes, IPr, IPent and IPr* compounds are 1.0, 3.9, 4.7 and 5.4 respectively.[30] This data indicates the degree of flexibility of IDitop is akin to that of IPr. A similar trend is shown by the standard deviations of the normalized solid angle measurements ($G_{2.0}$); IMes (1.3), IPr (2.0), IDitop (2.8), IPent (2.8) and IPr* (3.9),[30] though in this instance IDitop is akin to IPent. To this end, the M–C normalized %V_{bur} and G values both provide valuable insights into the steric character of IDitop (Table 1). For instance, **8** and **11** have near identical $G_{2.0}$ values, yet their %V_{bur} value are 44.2 and 37.3 respectively. As solid angle measurements are thought to better account for bulk more distant from the metal compared to %V_{bur} value measurements, these data indicate the bulk of IDitop lies on the frontier of the metal's coordination sphere.[17a]

Table 1. Steric metrics[a] for IDitop calculated from the X-ray structures.

Compound	%V_{bur}[b]	%V_{bur} [2.0 Å][c]	G_M[b]	$G_{2.0}$[c]
1	–	54.9[d]	–	54.5[d]
2[10]	48.6	49.7	52.5	53.1
4	40.5	40.7	46.1	46.3
5	45.4	46.3	50.4	50.8
6	40.0	39.1	45.1	45.9
7	44.3	41.3	49.0	47.2
8	43.1[d]	44.2[d]	47.8[d]	48.2[d]
9	48.4	48.1	51.9	51.7
10	41.8	40.3	47.7	46.6
11	39.5	37.3	49.1	48.0

[a] %V_{bur} values were calculated with Samb*V*ca 2.1[16b] using the default parameters: sphere radius, 3.50 Å; mesh spacing, 0.10; bond radii, 1.17; H atoms are excluded. Solid angle measurements (G-values) were calculated using Solid-G.[20] [b] Calculated using the M–C or Se–C distances from the crystal structures. [c] Calculated utilizing a normalized M–C or Se–C distances of 2.00 Å. [d] Mean of the individual structures in the asymmetric unit.

Donor Character

To gain further insight into the electronic structure of **1** we conducted DFT calculations at the B3LYP–D3/def2-TZVP level of theory. These suggest the σ-donation and π-acceptor properties of **1** should mirror those of IMes and IPr,[30] Though, the computed gas-phase proton affinity (PA) for **1** (278.9 kcal/mol) was found to be greater than the other aforementioned NHCs (272.5 and 271.4 kcal/mol respectively). Whilst the lone-pair σ-orbital of carbene (E_σ) was found to be slightly higher in energy in **1**, the vacant p-orbital of the carbene (E_π) was considerably higher in energy relative to those calculated for IMes and IPr (Table 2). These data predict **1** to have comparable σ-donor character to IMes and IPr, but inferior π-acceptor character.

The Tolman electronic parameter (TEP) is a well-known experimental measure for the overall donor properties of ligands, which is typically obtained by measuring the infrared stretching frequency of the CO bonds in tetrahedral $(L)Ni(CO)_3$ complexes (L is a ligand of interest).[31] More recent studies have employed a linear regression model to obtain TEP values from the mean CO stretching frequencies of $[RhCl(CO)_2(L)]$ or $[IrCl(CO)_2(L)]$ compounds.[22,32] The IR spectrum of **5** (CH_2Cl_2 solution) shows two intense CO stretching bands at 2055 and 1973 cm^{-1}, which are notably red-shifted relative to those reported in related complexes containing bis(aryl) imidazol-2-ylidenes (Table 2). Using Nolan's linear regression equation,[22] the TEP value was calculated to be 2041.9 cm^{-1}, indicating that IDitop has unexpectedly excellent donor ability, comparable to ring expanded NHCs (*cf.* 2042–2051 cm^{-1}),[33] mesoionic carbenes (cf. 2037–2041 cm^{-1})[34] and cyclic (alkyl)(amino)carbenes (cf. CAAC^{Men}, 2041.0 cm^{-1}).[35]

It is well established that whilst this model provides a means to measuring the overall electronics of the NHC by examining the degree of backdonation to the carbonyl ligands, it does not allow the deconvolution of σ and π contributions.[36] Hence, we next turned to Huynh's electronic parameter (HEP), a ^{13}C NMR spectroscopy-based methodology, which primarily

Table 2. Experimental and DFT calculated properties for compounds: NHC, $[IrCl(CO)_2(NHC)]$ and $[Ni(CO)_3(NHC)]$.

Compound	IDitop	IMes	IPr	IPr*
NHC δ $^{13}C_{carbene}$ (ppm)[a]	223.4	219.69[g][26]	220.6[37]	220.02[38]
proton affinity (kcal mol^{-1})[b]	278.9	272.5	271.4	–
E_σ (eV)	−5.77838	−5.86709	−6.00875	–
E_π (eV)	0.926555	0.611989	0.551017	–
$[IrCl(CO)_2(NHC)]$ ν_{CO}(exp) (cm^{-1})[c]	2055, 1973	2066, 1980[22,32b]	2067, 1981[22,32b]	2067.6, 1983.6[39]
$[IrCl(CO)_2(NHC)]$ ν_{CO}(DFT) (cm^{-1})[d]	2036, 1963	2048, 1971	2049, 1971	–
$[Ni(CO)_3(NHC)]$ ν_{CO}(exp) (cm^{-1})[c]	–	2051, 1970[12]	2052, 1970[12]	2052.7, 1997.5, 1973.7[40]
$[Ni(CO)_3(NHC)]$ ν_{CO}(DFT) (cm^{-1})[d]	2024, 1967, 1965	2027, 1973, 1967	2028, 1974, 1964	–
TEP[e]	2041.9	2049.6[22]	2050.2[22]	2051.7[39]
HEP	176.7[h]	177.2[23]	177.5[23]	–
NHC·Se δ ^{77}Se (ppm)[f] {$^1J_{CSe}$ (Hz)}	121.3 {235}	27[41] {231}[42]	90[39] {234}[41]	105.8 {–}[39]

[a] Acquired in C_6D_6 at 298 K. [b] See supporting information. [c] Acquired in CH_2Cl_2. [d] Unscaled values. [e] Calculated by linear regression, from ref 22. [f] Acquired in $CDCl_3$ at 298 K. [g] Acquired in THF-d_8 at 298 K. [h] Confirmed by HMBC, chemical shift internally referenced to the solvent residual signal at 77.7 ppm.[23]

detects the σ-donating ability of a ligand.[23] The ^{13}C resonance for the carbenic carbon of the benzimidazol-2-ylidene in **6** indicated IDitop to be slightly weaker σ-donor than IPr and IMes (Table 2), on Huynh's scale.[23] It is however noteworthy that Huynh has reported that HEP values obtained for very bulky ligands likely underestimate the donor character.[36,43]

Subsequently, Ganter reported that the σ-donor character of NHCs could be probed by measuring the $^{1}J_{\mathrm{CSe}}$ coupling constants of their corresponding selenium adducts.[42] The $^{1}J_{\mathrm{CSe}}$ measured for **7** (235 Hz) is comparable to those reported for the selenium adducts of IMes (231 Hz) and IPr (234 Hz).[41] Ganter has also shown that $\delta(^{77}\mathrm{Se})$ for these adducts can provide insight into the π-acceptor strengths of the NHCs within the adducts.[44] The ^{77}Se NMR resonance for **7** (δ 121.3) indicates that IDitop lies toward the poorly π-accepting region of the spectrum, but is a comparable π-acid to common bis(aryl) imidazol-2-ylidenes (Table 2).

These conflicting metrics prompted further computational analysis of **5**. It is noteworthy that the red-shifting of the CO stretching bands for **5** relative to other bis(aryl)imidazol-2-ylidenes was reproduced by DFT calculations at the BP86-D3/def2-TZVP[45] level of theory (Table 2), though this was observed to a much lesser degree for the hypothetical Ni carbonyl complex, **3** (Table 2). In contrast to the recently reported [RhCl(CO)$_2$(ITr)] (ITr = [(HCNCPh$_3$)$_2$C:]), for which a similarly low TEP was reported,[46] notably (>1 kcal mol^{-1}) arene-Ir donor-acceptor interactions were not observed by second-order perturbation analysis. Examination of the molecular orbitals of **5**, show the HOMO primarily localized on the d_{z^2} orbital, with minor contribution from the pendant p-tolyl groups (Figure 5).[30] The frontier orbitals of **5** are notably destabilized relative to its IMes congener.

The myriad of conflicting data suggests a limitation of the available models, in particular TEP, to quantify the electronic character of the bis(2,6-terphenyl) substituted NHC, **1**.

Preliminary Catalytic Studies

Having established the flexibility of IDitop, our attention turned to the execution of sterically challenging Suzuki coupling reactions. Given the impressive performance of precatalysts such as [PdCl(η^3-cin)(IPr*)],[47] we restricted our study to use of the IDitop substituted analogue (**8**). The Suzuki coupling of 1-bromonapthalene and 2,4,6-trimethylphenylboronic acid was undertaken to optimize the reaction conditions.[30] Interestingly, those modelled upon Organ's Pd-PEPPSI-IPent conditions were found to perform best.[4a]

We then proceeded in evaluating a variety of hindered Suzuki-Miyaura couplings with aryl bromides (Table 3). Whilst satisfactory reaction outcomes were obtained for the synthesis

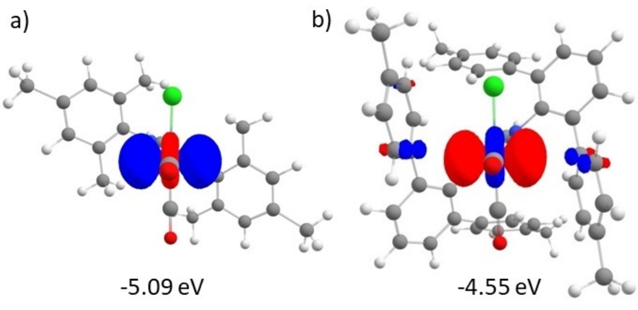
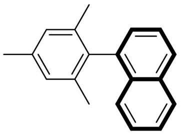
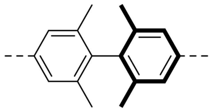
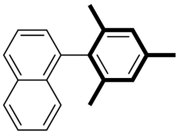
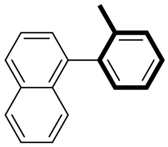
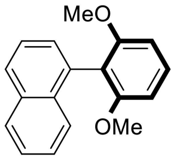
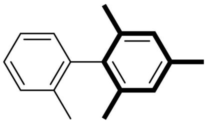
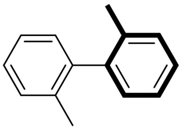
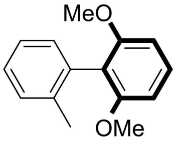


Figure 5. HOMO a) [IrCl(CO)$_2$(IMes)] and b) [IrCl(CO)$_2$(IDitop)].

Table 3. Suzuki-Miyaura cross-coupling of aryl bromides (ArBr) with arylboronic acid (**Ar′**B(OH)$_2$).[a]

Entry	Ar–**Ar′**	Precatalyst	Conv.[b]
1		**8**	94
2[25a]		PdCl(cin)(IPr)	89[c,d]
3[21a]		PdCl(cin)(IMes)	32[e]
4		**8**	0
5[4a]		Pd-PEPPSI-IPent	88[f]
6[47]		PdCl(cin)(IPr*)	99[g]
7		**8**	99
8		**8**	99
9		**8**	22
10		**8**	80[c]
11		**8**	99
12		**8**	76

[a] Reagents and conditions: ArBr (0.5 mmol), Ar′B(OH)$_2$ (1.0 mmol), KO^{t}Bu (1.2 mmol), precatalyst (1 mol%), ^{t}BuOH (2.0 mL), 65 °C, 20 h. [b] Conversions determined by ^{1}H NMR spectroscopy, as the average of duplicate experiments. [c] Isolated yield. [d] Reagents and conditions: ArBr (1.0 mmol), Ar′B(OH)$_2$ (1.05 mmol), KO^{t}Bu (1.1 mmol), precatalyst (0.05 mol%), ^{i}PrOH (1.0 mL), 25 °C, 3.5 h. [e] Reagents and conditions: ArBr (0.98 mmol), Ar′B(OH)$_2$ (1.2 mmol), KO^{t}Bu (1.0 mmol), precatalyst (1 mol%), ^{i}PrOH (4.0 mL), 25 °C, 2 h. [f] Reagents and conditions: ArBr (1.0 mmol), Ar′B(OH)$_2$ (0.5 mmol) KO^{t}Bu (0.75 mmol), precatalyst (2 mol%), ^{t}BuOH (1 mL), 4 Å M.S. [g] Reagents and conditions: ArX (0.5 mmol), Ar′B(OH)$_2$ (1.0 mmol), KOH (1.5 mmol), precatalyst (1 mol %), DME (1.0 mL), 25 °C, 18 h.

of di- and tri-ortho-substituted biaryls (entries 1,7-12), no tetra-ortho-substituted biaryls were detected (entry 4).

Conclusion

In summary, we report the preparation a number of transition metal complexes and adducts of a 1,3-bis(2,6-terphenyl) substituted NHC. Spectroscopy as well as the solid-state structures of these compounds enabled insights into the donicity and flexibility of IDitop relative to other NHCs. Suzuki coupling reactions undertaken employing IDitop as an auxiliary ligand on the precatalyst afforded excellent outcomes for the synthesis of di- and tri-ortho-substituted biaryls, but not for the more challenging tetra-ortho substituted biaryls.

Experimental Section

General Experimental: All experiments were carried out in dry glassware under Ar using standard Schlenk techniques and freshly dried and degassed solvents (all solvents were dried with a column except for THF, diethyl ether and dimethoxyethane, which were dried with Na and distilled from sodium benzophenone ketyl). Starting materials and research chemicals were obtained from commercial suppliers where appropriate and used without further purification. IDitop·HCl,[10] [{Ir(μ-Cl)(cod)}$_2$],[48] [{Pd(μ-Br)Br(^{i}Pr-bzim)}$_2$],[49] [{Pd(μ-Cl)(η^3-cin)}$_2$][25a,50] were synthesized following literature known procedures. NMR spectra were measured on Bruker Avance III 300 MHz, 400 MHz and 600 MHz spectrometers at 298 K. Chemical shifts (δ) are given in ppm (parts per million) values, coupling constants (J) in Hz (Hertz). Multiplicities are denoted as singlet (s), doublet (d), treiplet (t), septet (sept) or multiplet (m) and prefixed broad (br) where applicable. Spectra were referenced due to solvent residual signal, excepting ^{77}Se spectra which were referenced externally to a saturated solution of diphenyl diselenide in CDCl$_3$ at 25 °C (δ_{Se} 463 ppm).[51] Compounds for infrared spectroscopy (4000 to 400 cm^{-1}) were prepared as Nujol mulls or dichloromethane solutions and the spectra recorded on a Nicolet Avatar 320 FTIR spectrophotometer (NaCl windows). Spectra are reported in wavenumbers (cm^{-1}) and the intensity of the absorbances is denoted as strong (s), medium (m) or weak (w) and prefixed broad (br) or sharp (sh) where applicable. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were conducted at the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand or at the Microanalytical unit of the Australian National University, Canberra, Australia. All crystal structures have been measured on a Bruker APEX-II diffractometer with a Mo microfocus source and CCD detector, at 150(2) K. See the Supporting Information.

Synthesis of IDitop (1): IDitop·HCl (696 mg, 1.12 mmol) was suspended in THF (20 mL) and treated with ^{n}BuLi (0.70 mL, 1.12 mmol) dropwise at 0 °C. The reaction mixture was gradually warmed to room temperature over 2 hours before the volatiles were removed *in vacuo* and the crude material extracted into diethyl ether and filtered. The filtrate was concentrated to the point of incipient crystallization and allowed to stand overnight at room temperature. The resulting colorless crystals were isolated by decanting the supernatant and, dried under vacuum to give IDitop (432 mg, 0.74 mmol, 66 %). m.p. 194 °C. Satisfactory elemental analysis was not obtained presumably due to air sensitivity. For example, elemental analysis calculated for $C_{43}H_{36}N_2$: C: 88.93; H: 6.25; N: 4.82; Found: C: 87.82; H: 6.31; N: 4.75. ^{1}H NMR (300.13 MHz, C$_6$D$_6$) δ 2.08 (s, 12H, CH_3), 5.88 (s, 2H, 4,5-H_2), 6.89 (d, $^3J_{HH}$ 7.8 Hz, 8H, 3,5-Ar′*H*), 7.07 (t, $^3J_{HH}$ 6.9 Hz, 2H, 4-Ar*H*), 7.24 (d, J_{HH} 7.8 Hz, 4H, 3,5-Ar*H*), 7.26 (d, 8H J_{HH} 7.8 Hz, 8H, 2,6-Ar′*H*). ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 21.2 (*C*H$_3$), 121.8 (N*C*H), 127.5, 128.7, 130.5, 131.1 (Ar*C*H), 136.4, 137.6, 138.4, 140.3 (Ar*C*), 223.4 (N*C*N).

Synthesis of [IrCl(COD)(IDitop)] (4): A suspension of IDitop·HCl (275 mg, 0.45 mmol) in THF (10 mL) was treated with ^{n}BuLi (0.28 mL, 0.45 mmol) dropwise at 0 °C. The reaction mixture warmed gradually to room temperature over a period of 2 hours before being transferred into a solution of [{Ir(μ-Cl)(COD)}$_2$] (157 mg, 0.22 mmol) in THF (15 mL) at ambient temperature. After stirring for 16 hours, the solvent was removed under reduced pressure. The crude material was extracted into toluene (ca. 15 mL) and filtered. The filtrate was concentrated (~5 mL) and, upon standing at room temperature overnight, deposited yellow crystals of the title compound (263 mg, 0.29 mmol, 64 %). m.p. 78 °C (dec). Satisfactory elemental analysis was not obtained. For example, elemental analysis calculated for $C_{51}H_{44}N_2ClIr$: C: 66.83; H: 5.28; N: 3.06; Found: C: 68.07; H: 5.60; N: 3.26. ^{1}H NMR (300.13 MHz, CDCl$_3$) δ 0.96 (*br* m, 2H, COD–CH_2), 1.36 (*br* m, 2H, COD–CH_2), 1.64 (*br* m, 2H, COD–CH_2), 1.91 (m, 2H, COD–C*H*), 2.05 (*br* m, 2H, COD–CH_2), 2.34 (s, 6H, CH_3), 2.40 (s, 6H, CH_3), 4.13 (m, 2H, COD–C*H*), 6.40 (s, 2H, 4,5-H_2), 6.99 (d, $^3J_{HH}$ 8.1 Hz, 4H, 3,5-Ar*H*), 7.13 (d, $^3J_{HH}$ 7.7 Hz, 8H, 3,5-Ar′*H*), 7.27–7.33 (m, 8H, 2,6-Ar′*H*), 7.44 (t, $^3J_{HH}$ 7.5 Hz, 2H, 4-Ar*H*). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 21.4, 21.5 (*C*H$_3$), 28.7, 33.8 (COD–*C*H$_2$), 51.6, 81.9 (COD–*C*H), 124.4 (N*C*H), 128.4, 128.7, 128.8, 129.2, 123.0, 131.1, 131.5 (Ar*C*H), 135.8, 136.4, 136.8, 137.2, 137.5, 138.9, 141.3 (Ar*C*), 179.9 (N*C*N).

Synthesis of [IrCl(CO)$_2$(IDitop)] (5): A suspension of IDitop·HCl (100 mg, 0.16 mmol) in THF (5 mL) was treated with ^{n}BuLi (0.10 mL, 0.16 mmol) dropwise at 0 °C. The reaction mixture warmed gradually to room temperature over a period of 2 hours before being transferred into a solution of [{Ir(μ-Cl)(COD)}$_2$] (157 mg, 0.22 mmol) in THF (5 mL) at ambient temperature. The argon atmosphere was replaced with carbon monoxide and the reaction stirred at room temperature for 16 hours. The volatiles were removed *in vacuo* and the crude solid extracted into the minimum volume of dichloromethane and filtered whereupon cooling to −20 °C overnight afforded yellow plates of [IrCl(CO)$_2$(IDitop)] (100 mg, 0.12 mmol, 72 %) m.p. 252 °C (dec.). Elemental analysis calculated for $C_{45}H_{36}N_2O_2ClIr$: C, 62.52; H: 4.20; N: 3.24; Found C: 62.67; H: 4.23; N: 3.28. ^{1}H NMR (300.13 MHz, CDCl$_3$) δ 2.34 (s, 12H, CH_3), 6.41 (s, 2H, 4,5-H_2), 7.06 (d, 8H, $^3J_{HH}$ 7.5 Hz, 3,5-Ar′*H*), 7.16 (d, 8H, $^3J_{HH}$ 6.9 Hz, 2,6-Ar′*H*), 7.31 (d, 4H, $^3J_{HH}$ 7.2 Hz, 3,5-Ar*H*), 7.45 (t, 2H, $^3J_{HH}$ 7.5 Hz, 4-Ar*H*). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 21.4 (*C*H$_3$), 124.1(N*C*H), 128.8, 128.9, 129.6, 129.9 (Ar*C*H), 131.2, 133.7, 134.6, 137.5 (Ar*C*), 166.4 (*C*O), 176.6 (N*C*N), 180.3 (*C*O). IR (dichloromethane) *v* 1973 (*sh, m*), 2055 (*sh, m*), (carbonyl stretches). IR (Nujol) ν 1963 (*s*), 2043 (*s*), (carbonyl stretches).

Synthesis of [PdBr$_2$(^{i}Pr-bzim)(IDitop)] (6): A solution of **1** (100 mg, 0.17 mmol) in THF (5 mL) was added dropwise to a solution of [{Pd(μ-Br)Br(^{i}Pr-bzim)}$_2$] (77 mg, 0.08 mmol) also in THF (5 mL) at ambient temperature. The mixture was and stirred for 14 hours before the solvent was removed under reduced pressure and the residue extracted into dichloromethane (ca. 10 mL). The extract was filtered through a short path of celite and the filter cake eluted with dichloromethane (2×10 mL). Subsequent removal of volatiles gave the title complex as a yellow solid (64 mg, 0.61 mmol, 72 %). m.p. 160 °C (dec.). Satisfactory elemental analysis was not obtained. For example, elemental analysis calculated for $C_{56}H_{54}N_4Br_2Pd$: C: 64.10; H: 5.19; N: 5.34; Found: C: 62.66; H: 5.55; N: 5.38. ^{1}H NMR (300.13 MHz, C$_6$D$_6$) δ 1.57 (d, $^3J_{HH}$ 7.2 Hz, 12H, ^{i}Pr–CH_3), 2.25 (s, 12H, CH_3), 6.19 (s, 2H, 4,5-H_2), 6.26 (sept, $^3J_{HH}$ 7.2 Hz, 2H, ^{i}Pr–C*H*), 6.87 (m, 2H, bzim-Ar*H*), 7.01 (d, $^3J_{HH}$ 7.8 Hz, 8H, 3,5-Ar′*H*), 7.20 (m, 2H, bzim-

Ar*H*), 7.22 (m, 2H, 4-Ar*H*), 7.34 (d, J_{HH} 7.8 Hz, 4H, 3,5-Ar*H*), 7.54 (d, J_{HH} 7.8 Hz, 8H, 2,6-Ar'*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.9, 21.4 (CH_3), 53.3 (*C*H(CH_3)), 112.6 (Ar*C*), 121.4 (Ar*C*H), 124.1 (N*C*H), 128.5, 128.8, 130.3, 130.7, 133.6 (Ar*C*H), 135.1, 136.3, 136.4, 141.5 (Ar*C*), 176.17 (bzim-N*C*N), 176.44 (IDitop-N*C*N).

Synthesis of IDitop·Se (7): A solution of **1** (100 mg, 0.17 mmol) was added to a stirred suspension of elemental selenium (200 mg, 2.53 mmol) in THF (5 mL) at −40 °C. The mixture was warmed gradually to room temperature over a period of 16 hours. Particulates were subsequently removed by filtration through a short path of celite which was eluted with EtOAc (2×10 mL). The combined filtrate was concentrated under reduced pressure (~ 2 mL). Addition of hexane induced a white precipitate which was collected on a frit and dried to give IDitop·Se as a white powder (91 mg, 0.14 mmol, 86%). m.p. 294 °C. ESI HRMS calculated for $[C_{43}H_{36}N_2Se+Na]^+$ *m/z* 683.1941; Found: *m/z* 683.1936. ^{1}H NMR (400.14 MHz, $CDCl_3$) δ 2.39 (s, 12H, CH_3), 6.37 (s, 2H, 4,5-H_2), 6.94 (d, $^3J_{HH}$ 8.0 Hz, 8H, 3,5-Ar'*H*), 7.03 (d, $^3J_{HH}$ 8.0 Hz, 8H, 2,6-Ar'*H*), 7.19 (d, $^3J_{HH}$ 7.7 Hz, 4H, 3,5-Ar*H*), 7.39 (t, $^3J_{HH}$ 7.7 Hz, 2H, 4-Ar*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 21.5 (CH_3), 121.0 (N*C*H), 128.9, 129.5, 131.8 (Ar*C*H), 133.3, 136.4, 136.8, 141.4 (Ar*C*), 162.1 (N*C*Se, $^1J_{CSe}$ 235.16 Hz). ^{77}Se NMR (76.33 MHz, $CDCl_3$) δ 129.2.

Synthesis of [PdCl(cin)(IDitop)] (8): A suspension of IDitop·HCl (275 mg, 0.48 mmol) in THF (10 mL) was treated with ^{n}BuLi (300 μL, 0.48 mmol) dropwise at 0 °C. After 2 hours, a solution of [{Pd(μ-Cl)(η^3-cin)}$_2$] (125 mg, 0.24 mmol) in THF (5 mL) was added and the mixture gradually warmed to room temperature over a period of 12 hours. The solvent was removed under reduced pressure and the crude solid extracted into dichloromethane (ca. 10 mL) and filtered through a short path of celite. The filter cake was eluted with dichloromethane (2×10 mL) and the filtrate concentrated under reduced pressure (ca. 5 mL). Addition of hexane induced a yellow precipitate which was collected on a frit and dried to give the title complex (233 mg, 0.28 mmol, 58%). m.p. 142 °C (dec.); Elemental analysis calculated for $C_{52}H_{43}N_2ClPd$: C: 74.28; H: 5.51; N: 3.33; Found: C: 74.19; H: 5.54; N: 3.46. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 0.75 (d, $^3J_{HH}$ 11.8 Hz, 1H, H_{trans}(CH_{cis})CHPh), 1.95 (d, $^3J_{HH}$ 7.5 Hz, 1H, H_{cis}(CH_{trans})CH), 2.30 (br s, 6H, CH_3), 2.36 (br s, 6H, CH_3), 4.37 (d, $^3J_{HH}$ 12.8 Hz, 1H, CHC*H*Ph), 4.97 (m, 1H, C*H*CHPh), 6.39 (br s, 2H, 4,5-H_2), 7.05–7.30 (m, 25H, IDitop-Ar*H* + Cin-3,4,5-Ar*H*), 7.65 (d, $^3J_{HH}$ 7.2 Hz, 2H, Cin-2,6-Ar*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4 (CH_3), 44.8 (CH_2), 86.9, 109.9 (*C*H), 126.4 (N*C*H), 127.5, 128.2, 128.6, 128.9, 129.4, 130.9, 131.6 (Ar*C*H), 135.9, 136.7, 137.2, 138.7 (Ar*C*), 183.6 (N*C*N).

Synthesis of [PdCl$_2$(3-Cl-pyridinyl)(IDitop)] (9) aka PEPPSI-IDitop: IDitop·HCl (617 mg, 1.00 mmol), $PdCl_2$ (177 mg, 1.00 mmol) and K_2CO_3 (691 mg, 5.00 mmol) were suspended in 3-chloropyridine (5 mL) and heated to 80 °C for 16 h. The reaction mixture was cooled to room temperature, diluted with dichloromethane (15 mL) and filtered through short path of celite. The filtrate was concentrated under vacuum and the crude material triturated with pentane to give pure PEPPSI-IDitop as a light yellow solid (479 mg, 0.55 mmol, 55%). m.p. 218 °C (dec.). Elemental analysis calculated for $C_{48}H_{40}Cl_3N_3Pd$: C: 66.14; H: 4.63; N: 4.82. Found C: 65.76; H: 4.97; N: 5.04. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 2.38 (s, 12H, CH_3), 6.29 (br s, 1H, 4,5-H_2), 7.17 (dd, $^3J_{HH}$ 5.3 Hz, $^3J_{HH}$ 8.0 Hz, 1H, Py-5-Ar*H*), 7.22–7.33 (m, 20H, IDitop-Ar*H*), 7.40 (br t, J_{HH} 7.6 Hz, 2H, 4-Ar*H*), 7.65 (ddd, J_{HH} 1.4 J_{HH} 2.3 Hz J_{HH} 8.2 Hz, 1H, Py-6-Ar*H*), 8.47 (dd, J_{HH} 1.4 J_{HH} 5.6 Hz, 1H, Py-4-Ar*H*), 8.63 (d, $^4J_{HH}$ 2.1 Hz, 1H, Py-2-Ar*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5 (CH_3), 124.0 (Py-Ar*C*H), 124.8 (N*C*H), 128.6, 129.1, 129.8, 131.1 (Ar*C*H), 131.5 (Py-Ar*C*Cl), 135.7 (Ar*C*), 137.1 (Py-Ar*C*H), 137.2, 137.7, 139.0 (Ar*C*), 149.7 (Py-Ar*C*H), 150.6 (N*C*N), 151.6 (Py-Ar*C*H).

Synthesis of [NiCl(Cp)(IDitop)] (10): IDitop·HCl (100 mg, 0.16 mmol) and [Ni(Cp)$_2$] (30 mg, 0.16 mmol) were combined in THF (10 mL) and heated at reflux for 16 hours. The mixture was cooled to room temperature and the volatiles were removed *in vacuo*. The crude solid was extracted into toluene (ca. 10 mL) and filtered. The filtrate was concentrated to half its volume and allowed to stand at room temperature overnight. The resulting dark purple crystals were isolated by decanting the supernatant (94 mg, 0.13 mmol, 79%). m.p. 203 °C (dec.). Elemental analysis calculated for $C_{48}H_{41}ClN_2Ni$: C: 77.91; H: 5.58; N: 3.79; Found: C: 78.40; H: 5.67; N: 3.47. ^{1}H NMR (300.13 MHz, THF-d_8) δ 2.35 (s, 12H, CH_3), 4.05 (s, 5H, Cp*H*), 6.89 (d, $^3J_{HH}$ 7.9 Hz, 8H, 3,5-Ar'*H*), 6.92 (s, 2H, 4,5-H_2), 7.28 (d, $^3J_{HH}$ 7.9 Hz, 4H, 3,5-Ar*H*), 7.35 (*br* s, 8H, 2,6-Ar'*H*), 7.44 (t, $^3J_{HH}$ 7.5 Hz, 2H, 4-Ar*H*). ^{13}C NMR (100.6 MHz, THF-d_8) δ 21.1 (CH_3), 93.2 (Cp*C*), 125.8 (N*C*H), 127.0, 129.1, 129.3, 130.5 (Ar*C*H), 132.1, 136.7, 137.1, 137.7 (Ar*C*). NCN resonance not observed.

Synthesis of [NiCp$_2$(IDitop)] (11): A suspension of IDitop·HCl (100 mg, 0.16 mmol) in THF (5 mL) was treated with ^{n}BuLi (0.10 mL, 0.16 mmol) dropwise at 0 °C. The mixture was gradually warmed to room temperature over 2 hours before being added to a stirred solution of [Ni(Cp)$_2$] (30 mg, 0.16 mmol) in THF (5 mL) at ambient temperature. The mixture was stirred for 16 hours before the solvent was removed *in vacuo* and the residue extracted into toluene (~15 mL). Particulates were removed by filtration and filtrate concentrated (ca. 5 mL). Upon standing at room temperature overnight, dark red crystals of [NiCp$_2$(IDitop)] were isolated by filtration (83 mg, 0.11 mmol, 67%). m.p. 161 °C (dec.). Elemental analysis calculated for $C_{53}H_{46}N_2Ni$: C: 82.93; H: 5.78; N: 3.65; Found: C: 82.98; H: 6.11; N: 3.48. ^{1}H NMR (300.13 MHz, THF-d_8) δ 2.38 (s, 12H, CH_3), 3.28 (s, 5H, η^5-Cp*H*), 4.97 (s, 5H, η^1-Cp*H*), 6.90 (*br* m, 8H, 3,5-Ar'*H*), 7.06 (*br* m, 8H, 2,6-Ar'*H*), 7.35 (*br* m, 4H, 3,5-Ar*H*), 7.48 (t, $^3J_{HH}$ 7.6 Hz, 2H, 4-Ar*H*), 7.53 (s, 2H, 4,5-H_2). ^{13}C NMR (75.5 MHz, THF-d_8) δ 21.3 (CH_3), 92.9 (η^5-Cp*C*), 108.4 (η^1-Cp*C*), 126.0 (N*C*H), 127.5, 128.9, 129.3, 129.4, 129.6, 130.4 (Ar*C*H), 132.8, 136.9, 137.2, 138.4 (Ar*C*), 181.1 (N*C*N).

General Procedure for Suzuki Coupling using precatalyst 8: A reaction vial was charged with boronic acid (1.00 mmol), KO^{t}Bu (135 mg, 1.20 mmol) and precatalyst **8** (8.41 mg, 1.00 mol%) inside a glovebox. Outside the glovebox, ^{t}BuOH (2 mL) was added and the vial placed in a preheated oil bath (65 °C) for 10 minutes. Arylbromide (0.50 mmol) was then injected and the mixture stirred for 20 hours. Removal of the solvent under reduced pressure afforded the crude product which was then analyzed by ^{1}H NMR spectroscopy ($CDCl_3$) to determine the extent of conversion.

Deposition Numbers 2002982 (for **1**), 2002983 (for **4**), 2002984 (for **5**), 2002985 (for **6**), 2002986 (for **7**), 2002987 (for **8**), 2002988 (for **9**), 2002989 (for **10**), and 2002990 (for **11**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbene ligands · Cross-coupling · Flexibility · Structure elucidation · Transition metals

[1] S. Würtz, F. Glorius, *Acc. Chem. Res.* **2008**, *41*, 1523–1533.
[2] a) S. M. P. Vanden Broeck, F. Nahra, C. S. J. Cazin, *Inorganics* **2019**, *7*, 78; b) F. Nahra, D. J. Nelson, S. P. Nolan, *Trends Chem.* **2020**, *2*, 1096–1113.
[3] a) G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *Angew. Chem. Int. Ed.* **2003**, *42*, 3690–3693; *Angew. Chem.* **2003**, *115*, 3818–3821; b) G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *J. Am. Chem. Soc.* **2004**, *126*, 15195–15201.
[4] a) M. G. Organ, S. Çalimsiz, M. Sayah, K. H. Hoi, A. J. Lough, *Angew. Chem. Int. Ed.* **2009**, *48*, 2383–2387; *Angew. Chem.* **2009**, *121*, 2419–2423; b) A. Collado, J. Balogh, S. Meiries, A. M. Z. Slawin, L. Falivene, L. Cavallo, S. P. Nolan, *Organometallics* **2013**, *32*, 3249–3252.
[5] G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Marko, *Dalton Trans.* **2010**, *39*, 1444–1446.
[6] a) S. Dierick, D. F. Dewez, I. E. Markó, *Organometallics* **2014**, *33*, 677–683; b) S. G. Weber, C. Loos, F. Rominger, B. F. Straub, *Arkivoc* **2012**, *3*, 226–242; c) A. R. Martin, A. Chartoire, A. M. Z. Slawin, S. P. Nolan, *Beilstein J. Org. Chem.* **2012**, *8*, 1637–1643; d) X.-B. Lan, Y. Li, Y.-F. Li, D.-S. Shen, Z. Ke, F.-S. Liu, *J. Org. Chem.* **2017**, *82*, 2914–2925; e) P. Shaw, A. R. Kennedy, D. J. Nelson, *Dalton Trans.* **2016**, *45*, 11772–11780; f) D.-D. Lu, X.-X. He, F.-S. Liu, *J. Org. Chem.* **2017**, *82*, 10898–10911; g) R. Savka, S. Foro, H. Plenio, *Dalton Trans.* **2016**, *45*, 11015–11024; h) R. Savka, H. Plenio, *Eur. J. Inorg. Chem.* **2014**, 6246–6253.
[7] F. Izquierdo, S. Manzini, S. P. Nolan, *Chem. Commun.* **2014**, *50*, 14926–14937.
[8] M. Yamashita, K. Goto, T. Kawashima, *J. Am. Chem. Soc.* **2005**, *127*, 7294–7295.
[9] X. Luan, R. Mariz, M. Gatti, C. Costabile, A. Poater, L. Cavallo, A. Linden, R. Dorta, *J. Am. Chem. Soc.* **2008**, *130*, 6848–6858.
[10] S. G. Alexander, M. L. Cole, J. C. Morris, *New J. Chem.* **2009**, *33*, 720–724.
[11] C. Liu, H.-Q. Shen, M.-W. Chen, Y.-G. Zhou, *Organometallics* **2018**, *37*, 3756–3769.
[12] R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.
[13] A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759–1766.
[14] S. Felten, S. F. Marshall, A. J. Groom, R. T. Vanderlinden, R. M. Stolley, J. Louie, *Organometallics* **2018**, *37*, 3687–3697.
[15] F. Ragone, A. Poater, L. Cavallo, *J. Am. Chem. Soc.* **2010**, *132*, 4249–4258.
[16] a) L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, *35*, 2286–2293; b) L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano, L. Cavallo, *Nat. Chem.* **2019**, *11*, 872–879; c) P. Liu, J. Montgomery, K. N. Houk, *J. Am. Chem. Soc.* **2011**, *133*, 6956–6959.
[17] a) B. R. Dible, R. E. Cowley, P. L. Holland, *Organometallics* **2011**, *30*, 5123–5132; b) K. Wu, A. G. Doyle, *Nat. Chem.* **2017**, *9*, 779–784.
[18] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[19] a) D. White, B. C. Taverner, P. G. L. Leach, N. J. Coville, *J. Comb. Chem.* **1993**, *14*, 1042–1049; b) D. White, N. J. Coville, in *Advances in Organometallic Chemistry, Vol. 36* (Eds.: F. G. A. Stone, R. West), Academic Press, **1994**, pp. 95–158.
[20] I. A. Guzei, M. Wendt, *Dalton Trans.* **2006**, 3991–3999.
[21] a) S. K. Furfari, M. R. Gyton, D. Twycross, M. L. Cole, *Chem. Commun.* **2015**, *51*, 74–76; b) A. R. Leverett, A. I. McKay, M. L. Cole, *Dalton Trans.* **2015**, *44*, 498–500; c) A. R. Leverett, M. L. Cole, A. I. McKay, *Dalton Trans.* **2019**, *48*, 1591–1594; d) M. L. Cole, A. I. McKay, N. S. Ping, *Polyhedron* **2019**, *170*, 424–430; e) M. R. Gyton, M. Bhadbhade, M. L. Cole, *Z. Anorg. Allg. Chem.* **2019**, *645*, 768–776; f) M. R. Gyton, A. R. Leverett, M. L. Cole, A. I. McKay, *Dalton Trans.* **2020**, *49*, 5653–5661; g) K. N. Buys, M. L. Cole, A. I. McKay, *J. Organomet. Chem.* **2020**, *916*, 121204; h) M. O. Talbot, T. N. Pham, M. A. Guino-o, I. A. Guzei, A. I. Vinokur, V. G. Young, *Polyhedron* **2016**, *114*, 415–421; i) R. E. Cowley, P. L. Holland, *Inorg. Chem.* **2012**, *51*, 8352–8361; j) A. Hinz, *Chem. Eur. J.* **2019**, *25*, 3267–3271; k) K. L. Barnett, M. Vasiliu, T. H. Stein, M. V. Delahay, F. Qu, D. L. Gerlach, D. A. Dixon, K. H. Shaughnessy, *Inorg. Chem.* **2020**, *59*, 5579–5592.
[22] R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202–210.
[23] H. V. Huynh, Y. Han, R. Jothibasu, J. A. Yang, *Organometallics* **2009**, *28*, 5395–5404.
[24] A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269–5272.
[25] a) N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111; b) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem. Eur. J.* **2006**, *12*, 4743–4748; c) A. R. Martin, Y. Makida, S. Meiries, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2013**, *32*, 6265–6270; d) C. D. Abernethy, J. A. C. Clyburne, A. H. Cowley, R. A. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 2329–2330.
[26] A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
[27] a) A. I. McKay, M. L. Cole, *Dalton Trans.* **2019**, *48*, 2948–2952; b) A. R. Leverett, V. Diachenko, M. L. Cole, A. I. McKay, *Dalton Trans.* **2019**, *48*, 13197–13204.
[28] J.-N. Luy, S. A. Hauser, A. B. Chaplin, R. Tonner, *Organometallics* **2015**, *34*, 5099–5112.
[29] A. Chartoire, X. Frogneux, A. Boreux, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 6947–6951.
[30] See Supporting Information.
[31] C. A. Tolman, *J. Am. Chem. Soc.* **1970**, *92*, 2953–2956.
[32] a) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663–1667; b) S. Leuthäußer, D. Schwarz, H. Plenio, *Chem. Eur. J.* **2007**, *13*, 7195–7203.
[33] a) J. J. Dunsford, D. S. Tromp, K. J. Cavell, C. J. Elsevier, B. M. Kariuki, *Dalton Trans.* **2013**, *42*, 7318–7329; b) G. A. Blake, J. P. Moerdyk, C. W. Bielawski, *Organometallics* **2012**, *31*, 3373–3378; c) D. Martin, N. Lassauque, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2012**, *51*, 6172–6175; *Angew. Chem.* **2012**, *124*, 6276–6279.
[34] a) G. Ung, G. Bertrand, *Chem. Eur. J.* **2011**, *17*, 8269–8272; b) A. Merschel, D. Rottschäfer, B. Neumann, H.-G. Stammler, R. S. Ghadwal, *Organometallics* **2020**, *39*, 1719–1729.
[35] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855.
[36] H. V. Huynh, *Chem. Rev.* **2018**, *118*, 9457–9492.
[37] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.
[38] A. Gómez-Suárez, R. S. Ramón, O. Songis, A. M. Z. Slawin, C. S. J. Cazin, S. P. Nolan, *Organometallics* **2011**, *30*, 5463–5470.
[39] D. J. Nelson, A. Collado, S. Manzini, S. Meiries, A. M. Z. Slawin, D. B. Cordes, S. P. Nolan, *Organometallics* **2014**, *33*, 2048–2058.
[40] J. Balogh, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 3259–3263.
[41] Y. Koto, F. Shibahara, T. Murai, *Org. Biomol. Chem.* **2017**, *15*, 1810–1820.
[42] K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* **2015**, 2416–2425.
[43] A. Kumar, D. Yuan, H. V. Huynh, *Inorg. Chem.* **2019**, *58*, 7545–7553.
[44] S. V. C. Vummaleti, D. J. Nelson, A. Poater, A. Gómez-Suárez, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan, L. Cavallo, *Chem. Sci.* **2015**, *6*, 1895–1904.
[45] For the Ir atom, the SDD basis set and associated ECP was used.
[46] M. M. D. Roy, P. A. Lummis, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Eur. J.* **2017**, *23*, 11249–11252.
[47] A. Chartoire, M. Lesieur, L. Falivene, A. M. Z. Slawin, L. Cavallo, C. S. J. Cazin, S. P. Nolan, *Chem. Eur. J.* **2012**, *18*, 4517–4521.
[48] J. Choudhury, S. Podder, S. Roy, *J. Am. Chem. Soc.* **2005**, *127*, 6162–6163.
[49] H. V. Huynh, Y. Han, J. H. H. Ho, G. K. Tan, *Organometallics* **2006**, *25*, 3267–3274.
[50] P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.
[51] A. Sørensen, B. Rasmussen, M. Pittelkow, *J. Org. Chem.* **2015**, *80*, 3852–3857.

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