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Nickel(II) complexes of highly σ-donating cyclic (alkyl)(amino)- and malonate-carbenes: syntheses and catalytic studies

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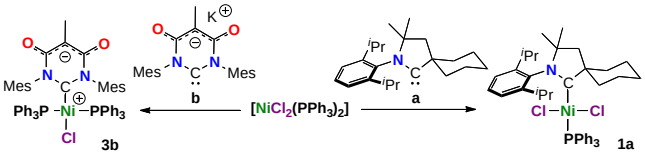
Supporting Information Placeholder

ABSTRACT: $[NiCl_2(PPh_3)_2]$ reacted with the cyclic (alkyl)(amino)carbene, IPr-CAAC^{Me2}-Cy (**a**), and with the anionic malonate-carbene, Mes-*malo*NHC^{Me}-Mes (**b**), to give the neutral and zwitterionic complexes, $[NiCl_2$(IPr-CAAC^{Me2}-Cy)$(PPh_3)]$ (**1a**) and [NiCl(Mes-*malo*NHC^{Me}-Mes)$(PPh_3)_2]$ (**3b**), resulting from the respective substitution of one neutral triphenylphosphine (L-type) and one anionic chloride (X-type) ligand. Complex **1a** decomposed in the presence of traces of protons to give the nickelate salt, [(IPr-CAAC^{Me2}-Cy)·H]$[NiCl_3(PPh_3)]$ (**2a**). Complex **3b** was insoluble in most organic solvents and thus difficult to purify and characterize, but the propensity of **b** to substitute X-type ligands was further illustrated by the substitution of iodide from the N-heterocyclic carbene complex, [NiICp(IMe)], to give the zwitterionic heteroleptic bis-carbene complex, [NiCp(IMe)(Mes-*malo*NHC^{Me}-Mes)] (**4b**), which was characterized by X-ray crystallography. The latter was post-functionalized by the addition of methyl triflate on the malonate moiety to give the corresponding cationic species, [NiCp(IMe)(Mes-*malo*NHC$^{Me}{}_{Me}$-Mes)](OTf) (**5c**), in which the ligand electron-donicity is greatly reduced. Complexes **3b**, **4b** and **5c** are the first Ni(*malo*NHC) species, and **1a** joins a very restricted list of Ni(CAAC) complexes. The catalytic activity of **1a**, **4b** and **5c** were studied in a cross-coupling reaction, a reduction reaction of a C–heteroatom double bond, and in a C–H bond functionalization reaction.



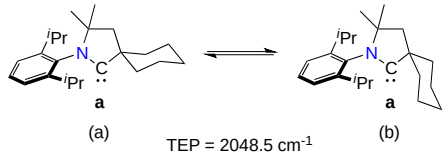
INTRODUCTION

Nickel *N*-heterocyclic carbene complexes are an important class of pre-catalysts that are applied in a large array of organic transformations.[1] The low cost and high abundance of nickel – which is the 23rd most abundant metallic element, present at a concentration of 84 g/ton in Earth's crust *vs.* 0.015 g/ton of Pd for instance[2] – as well as its intrinsic fascinating reactivity[3] prompt chemists to pay more and more attention to this class of complexes. However, even if the array of possible reactions is vast, most of the Ni(NHC)-catalyzed reactions deserve to be optimized for potential industrialization of these processes. In this regard, the main challenges include: (i) the reduction of catalyst loadings, (ii) the use of less demanding reaction conditions, and (iii) the development of user-friendly pre-catalysts. Achieving these goals goes through the development of novel efficient well-defined Ni(II) pre-catalysts instead of the very air sensitive and highly flammable $Ni(COD)_2$/NHC systems used in the vast majority of the applications developed up to now.[1] To enhance the activity of well-defined Ni(II)−NHC pre-catalysts, one option is to fine tune the steric and electronic properties of the NHC and/or of the other ligands. In this context, efforts from our group have for several years now been directed towards the diversification of well-defined $[NiCpL(NHC)]^{(+)}$ complexes by playing on the nature of the three ligands that constitute the coordination sphere of the nickel center.[4] Up to now, our modifications of the NHC ligands have been limited to variations of the *N*-substituents of classical imidazol-2-ylidenes:[4d,f,g] an interesting strategy would be to use other types of carbenes that have been shown to have a positive effect in some metal-catalyzed processes.[5]

Among the variety of less classical carbenes, cyclic (alkyl)(amino)carbenes (CAACs),[6] whose coordination chemistry with nickel is virtually unknown,[7] captured our attention. Indeed, the replacement of one of the electronegative and π-donating nitrogen atoms of diaminocarbenes by a σ-donating and non π-donating carbon atom renders CAACs both more σ-donating and π-accepting than diaminocarbenes. Thus, the Tolman's electronic parameter (TEP) of the common IPr-CAAC^{Me2}-Cy (**a**) of 2048.5 cm^{-1} shows that it is an *overall* (slightly) better donor than classical NHCs;[8,9] the TEP provides a convenient way to evaluate

the *overall* donor properties of a ligand but does not give any information about the relative weight of their σ donation and π back donation.[7c,10] However, the ^{31}P NMR chemical shift of its phosphinidene adduct shows that it is also much more π-accepting than diaminocarbenes,[10] thereby demonstrating that it is in fact a much stronger σ-donor than NHCs. Moreover, the different and more encumbered steric environment generated by the presence of a quaternary carbon center in α-p□□□□□□□□ to the carbene carbon may also be of interest when compared to classical NHCs.[6a] It is increasingly recognized that both the steric bulk and ligand flexibility are important factors that control the catalytic activity.[11] Thus, the possibility for IPr-CAAC^{Me2}-Cy (**a**) to adopt a conformation (a) that generates a small steric bulk in order to allow the approach of sterically hindered substrates (Scheme 1a), and another conformation (b) with a more significant steric footprint that would facilitate the reductive elimination step (Scheme 1b),[6a,11] suggested that highly active Ni(CAAC) catalysts may be accessible. This is illustrated by the [PdCl(η^3-C_3H_5)(IPr-CAAC^{Me2}-Cy)]-catalyzed α-arylation of propiophenone with aryl chlorides, which gave the best results observed so far for this reaction.[6a,12] We herein describe the synthesis and catalytic studies of the first nickel complex bearing this CAAC ligand.[7]

Scheme 1. Flexible steric bulk of IPr-CAAC^{Me2}-Cy (a)



Another promising class of carbenes is that of anionic pyrimidin-2-ylidenes that possess a malonate backbone and give rise to zwitterionic complexes upon complexation to a metal center.[13] The use of such species – better known as *malo*NHCs – can indeed be beneficial in catalysis, as the anionic moiety of the backbone of the *malo*NHC is pointing toward the outer coordination sphere, and does thus not interfere with the metal's cavity shape.[13a] Moreover, they are among the most *overall* electron donating cyclic diaminocarbenes, as shown by the TEP value of Mes-*malo*NHC^{Me}-Mes (**b**) of 2042.5 cm^{-1},[8,9,13d] and they exhibit important π-accepting properties, as highlighted by complete reactivity and computational studies on the free anionic **b**,[14] which thus makes them very strong σ-donors, similarly to CAACs.[7c] Finally, their electronic properties can be easily tuned by trapping the anionic moiety with an electrophile without modifying the ligand's steric bulk (Fig. 1).[13b] Consequently, we decided to also study the yet unknown coordination chemistry of **b** with nickel,[15] and the activity of the resulting complexes in various organic transformations. Our findings are reported herein.

RESULTS AND DISCUSSION

Synthesis of Ni(IPr-CAAC^{Me2}-Cy) complexes. Initial studies focused on reacting freshly generated IPr-CAAC^{Me2}-Cy (**a**) with various nickel sources such as

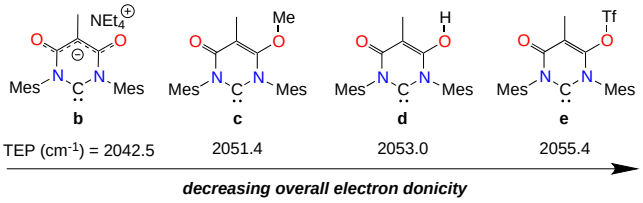
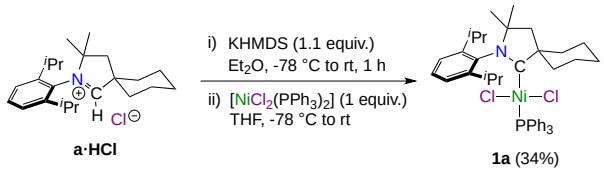


Figure 1. Electron-donicity of Mes-*malo*NHC^{Me}-Mes (**b**), and of its electrophile-trapped derivatives. TEP values calculated from ν(CO)^{av} values measured for [RhCl(CO)$_2$(NHC)] complexes.[13d]

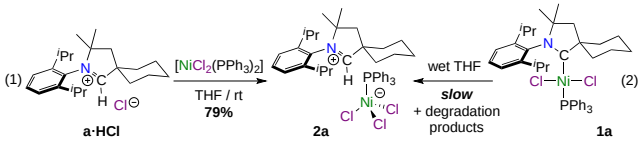
$NiCl_2$·(DME), Ni(acac)$_2$, [NiClCp(PPh$_3$)] or $NiCp_2$ in THF (Cp = η^5-C_5H_5). All reactions led to intractable mixtures. In contrast, when a solution of **a** in THF was added to a suspension of [$NiCl_2(PPh_3)_2$] in THF at –78 °C and the temperature was raised to room temperature, a color change from dark green to reddish took place within minutes, and a violet solid, identified as [$NiCl_2$(IPr-CAAC^{Me2}-Cy)(PPh$_3$)] (**1a**), was isolated in 34% yield after work-up (Scheme 2). The ^{1}H NMR spectrum of **1a** indeed shows the presence of PPh$_3$ and IPr-CAAC^{Me2}-Cy ligands in a 1:1 integrated ratio, showing that **a** has substituted one PPh$_3$ ligand rather than a chloride, and thus behaves as a L-type ligand, similar what is observed with classical NHCs. The complexation of **a** to the nickel center in **1a** was clearly identified by the absence of the pyrrolidinylium proton of (IPr-CAAC^{Me2}-Cy)·HCl (**a·HCl**) and of the corresponding carbon in its ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively (Figures S1 and S2 in the Supporting Information). Unfortunately, we have been unable to observe the signal of the corresponding carbene carbon, possibly because of the coupling to the ^{31}P nucleus of the PPh$_3$ ligand in *trans* position, which may render it difficult to observe.[16]

Scheme 2. Synthesis of [$NiCl_2$(IPr-CAAC^{Me2}-Cy)(PPh$_3$)] (1a)



In the former reaction however, it is noteworthy that if the deprotonation of **a·HCl** was not complete, non negligible amounts (depending on the amount of CAAC salt left) of a blue compound **2a** were formed after the addition of the reaction mixture onto [$NiCl_2(PPh_3)_2$] under otherwise unchanged reaction conditions. A control experiment run independently confirmed that **2a** is formed in high yield by the reaction at room temperature of **a·HCl** with [$NiCl_2(PPh_3)_2$)] in the absence of a base (Scheme 3, eqn. (1)). This blue species exhibits broad signals ranging from 0 to 14 ppm in its ^{1}H NMR spectrum in $CDCl_3$ or CD_2Cl_2, thus suggesting it contains a paramagnetic nucleus. In the more polar and dissociative CD_3CN, **2a** exhibits resonances that correspond in number and integrated intensities to **a·H**$^+$,[6a,17] as well as three large peaks in a 6:6:3 relative integrative ratio at 17.99, 4.52 and –2.33 ppm, respectively (Figure S4), thus suggesting it is composed of the CAAC salt and of a paramagnetic species bearing a PPh$_3$ ligand.

Scheme 3. Unexpected synthesis of the nickelate salt, [(IPr-CAAC^{Me2}-Cy)·H][NiCl$_3$(PPh$_3$)] (2a)



X-ray quality crystals were obtained by diffusion in *n*-pentane of a concentrated solution of **2a** in dichloromethane, and its molecular structure was determined by a single-crystal X-ray diffraction study. Crystallographic data and data collection parameters are listed in Table S1 (see the Supporting Information). Selected bond lengths and bond angles are collected in Table S2 and the structure is shown in Figure 2.

The molecular structure of **2a** reveals that it is a nickelate salt with one [(IPr-CAAC^{Me2}-Cy)·H]$^+$ cation and one [NiCl$_3$(PPh$_3$)]$^-$ anion present in the crystallographic unit, thus confirming our assumption from the ^{1}H NMR spectrum in CD$_3$CN. The structure of the cation is similar to that of the closely related [(IPr-CAAC^{Bn}-Cy)·H]$^+$ cation (with a chloride as the counter anion);[18] the aryl ring is oriented perpendicular to the pyrrolidinylium ring and the cyclohexyl ring is in a chair conformation in an "outspread wing" position. In the [NiCl$_3$(PPh$_3$)]$^-$ anion, the nickel atom is coordinated by three chlorine atoms and one phosphorus atom in a distorted tetrahedral geometry, with bond lengths and bond angles lying within the ranges found for other complexes containing [NiX$_3$(PR$_3$)]$^-$ anions (Table S2).[19,20]

Formation of the nickelate salt **2a** – together with other unidentified degradation products – was also observed when attempting to crystallize complex **1a** in THF that contained traces of water (Scheme 3, eqn. (2)). Although similar sensitivity of the nickel–carbene bond towards hydrolysis has recently been observed for [NiX$_2$(NHC)$_2$]-type complexes (where NHC is a 1,2,4-triazol-, a benzimidazol- or an imidazol-ylidene),[21] this fragility contrasts with the usual robustness of Metal–CAAC bonds.[6,7b,c,12] In addition, mass spectrometry of **1a** did not show the molecular ion

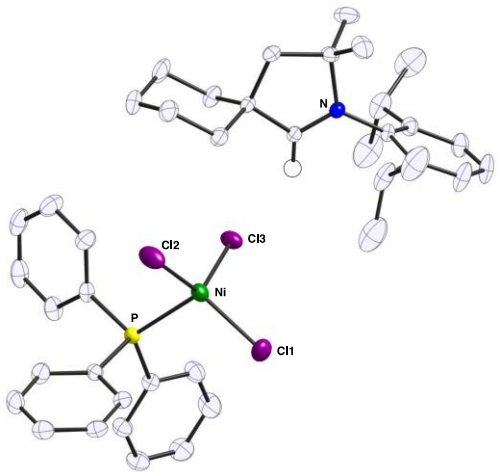


Figure 2. Structures of the cation and anion of **2a**. Only the pyrrolidinylium H is shown (as a white isotropic sphere). Ellipsoids are shown at the 50% probability level. Key atoms are labeled.

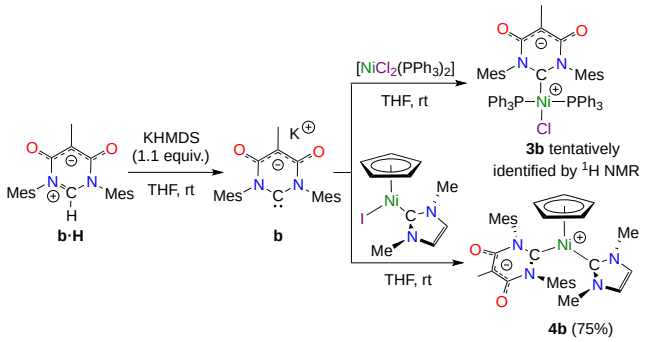
and only exhibited fragments such as [(IPr-CAAC^{Me2}-Cy)·H]$^+$ in the positive ion mode (Figure S3 in the Supporting Information).

Synthesis of Ni(Mes-*malo*NHC^{Me}-Mes) complexes. By analogy with the known syntheses of half-sandwich nickel complexes bearing a classical imidazol-[4d,f,g,22] or imidazolin-2-ylidene[23] ligand, we first investigated the reaction between the pyrimidinium betaine, **[(**Mes-*malo*MHC^{Me}-Mes)·H] (**b·H**), and nickelocene in refluxing THF. However, no reaction occurred, and unreacted starting materials were recovered. We then investigated the complexation of the anionic free carbene **b** – *in situ* generated by deprotonation of **b·H** with potassium bis(trimethylsilyl)amide (KHMDS) at room temperature – with different sources of nickel. The reactions of **b** with NiCl$_2$·(DME), Ni(acac)$_2$, NiCp$_2$, and [NiClCp(PPh$_3$)] all led to intractable mixtures. In contrast, the reaction of **b** with [NiCl$_2$(PPh$_3$)$_2$] led to the formation of a light violet solid, which precipitated out of the solution and was tentatively identified as the zwitterionic species [NiCl(Mes-*malo*NHC^{Me}-Mes)(PPh$_3$)$_2$] (**3b**) (Scheme 4) according to its ^{1}H NMR spectrum in DMSO-d_6 (Figure S6). The presence of **b** was confirmed by its characteristic signals, integrating in a 1:2 relative ratio to the PPh$_3$ signals. However, its very low solubility in organic solvents precluded its recrystallization and thus its isolation as an analytically pure solid.

The preferential substitution of Cl$^-$ rather than that of PPh$_3$ by **b** in [NiCl$_2$(PPh$_3$)$_2$], in contrast to what had been observed with **a** (*vide supra*), tended to corroborate the previously observed tendency that *malo*NHCs behave like X-type ligands[13a,d] in contrast to NHCs and CAACs. We thus decided to react **b** with the half-sandwich complex, [NiICp(IMe)], with the idea of substituting the iodide ligand, and indeed clean formation of the zwitterionic heteroleptic bis-carbene complex, [NiCp(IMe)(Mes-*malo*NHC^{Me}-Mes)] (**4b**), occurred at room temperature (Scheme 4). One may note however here that this synthetic strategy differs from that employed for the preparation of the related zwitterionic heteroleptic bis-carbene copper(I) complex, [Cu(IMe)(Mes-*malo*NHC^{Me}-Mes)], which was synthesized through bromide abstraction from the anionic [CuBr(Mes-*malo*NHC^{Me}-Mes)]$^-$ with KHMDS, before addition of IMe.[13c]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **4b** are straightforward (Figures S7 and S8 in the Supporting Information).

Scheme 4. Syntheses of the Ni(Mes-*malo*NHC^{Me}-Mes) complexes 3b and 4b



They show the presence of one η^5-Cp group, one IMe ligand and one Mes-*malo*NHC^{Me}-Mes ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the carbene carbons are observed at 162.7 and 189.9 ppm, respectively, thus highlighting the differences in electronic donor properties of the two carbenes, in agreement to what had been observed for the related heteroleptic bis-carbene complex, [Cu(IMe)(Mes-*malo*NHC^{Me}-Mes)].[13d] In addition, the spectra reveal that a molecular mirror plane that bisects the molecule is present on the NMR time scale. This effective mirror plane contains the nickel atom, the IMe and *malo*NHC^{Me} carbene carbons, and the Cp centroid. The protons of the IMe ring and the NMe groups thus resonate as two singlets in a 1:3 relative integrated ratio in the ^{1}H NMR spectrum. The protons of the methyl group of the *malo*NHC^{Me} ring, the *ortho*-methyl groups, the *meta*-protons, and the *para*-methyl groups of the mesityl groups appear as four singlets in a 3:12:4:6 relative integrated ratio. Nevertheless, the signals of the two *ortho*-methyls and the two *meta*-hydrogens are somewhat broad at room temperature. A variable-temperature ^{1}H NMR experiment was thus performed on a CD_2Cl_2 solution of **4b** between 296 and 243 K (Figure S9). As the temperature was decreased, the *ortho*-methyl resonances became even broader, and eventually split into two signals at a temperature (T_C) of *ca.* 283 K. Similar signal splitting was observed for the aromatic *meta*-hydrogen signals at *ca.* 273 K. The free energy of activation ($\Delta G^{\neq}$) for this fluxional process (based on the coalescence temperature of the *ortho*-methyl groups and, independently, of the *meta*-aromatic protons) is of 56.5 ± 1.5 kJ.mol^{-1}.[24] This result likely indicates impossible full rotation about the N–mesityl bonds, and restricted rotation about the Ni–C$_{malo\mathrm{NHC}}$ at low temperature, similarly to what was previously observed in the sterically congested Cp* mono-carbene complex [NiClCp*(IMes)] (Cp* = η^5-C_5Me_5).[4a] This contrasts, however, with the apparent absence of rotational barrier on the NMR time scale at room temperature for the closely related *bis*-carbene complex, [NiCp(IMe)(IMes)]$^+$,[4e] thus suggesting more important steric crowding in **4b**, as expected with a 6-membered NHC.[25]

The structure of **4b** was determined by an X-ray diffraction study. Crystallographic data and data collection parameters are listed in Table S1 (see the Supporting Information). Key bond lengths and bong angles are collected in Table 1, and the structure is shown in Figure 3. As expected, the molecular structure features a nickel atom bonded to a η^5-Cp group, a Mes-*malo*NHC^{Me}-Mes and a IMe moiety in a two-legged piano stool geometry. The resulting pseudo-trigonal coordination of nickel is globally similar to that of other half-sandwich complexes of general formula [NiCp†L(NHC)],[4,23,26] and is directly comparable to that of [NiCp(IMe)(IMes)]$^+$.[4e] Thus, similarly to what was observed with the latter,[4e] the planes defined by the two carbene rings of **4b** are almost orthogonal to each other and the two mesityl rings are close to perpendicular to the *malo*NHC^{Me} ring plane. However, the Ni–carbene and Ni−C$_{Cp}$ bond lengths as well as the C(1)−Ni−C(2) and N(1)–C(1)–N(2) angles are significantly larger in **4b** than in [NiCp(IMe)(IMes)]$^+$ (Table 1), which is in accord with

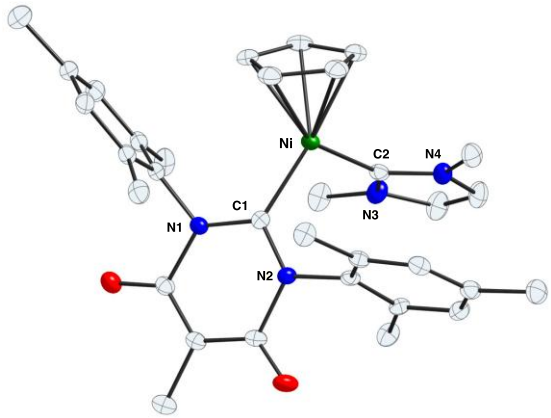


Figure 3. Structure of **4b**, showing all non-H atoms. Ellipsoids are shown at the 50% probability level. Key atoms are labeled.

Table 1. Selected bond lengths (Å) and angles (°) for 4b and [NiCp(IMe)(IMes)]$^+$ with Esd's in parentheses

	4b	[NiCp(IMe)(IMes)]$^{+4e}$
Ni−C(1)^a	1.946(2)	1.906(3)
Ni−C(2)^a	1.907(2)	1.899(3)
Ni−Cp$_{cent}$^{b}	1.792	1.772
Ni−C$_{Cp}$ av^c	2.157	2.136
C(1)−Ni−C(2)	98.78(9)	96.91(11)
C(1)−Ni−Cp$_{cent}$^{a}	137.92	135.99
C(2)−Ni−Cp$_{cent}$^{a}	122.92	126.89
N(1)–C(1)–N(2)^a	113.98(19)	103.1(2)
N(3)–C(2)–N(4)^a	103.5(2)	104.4(2)

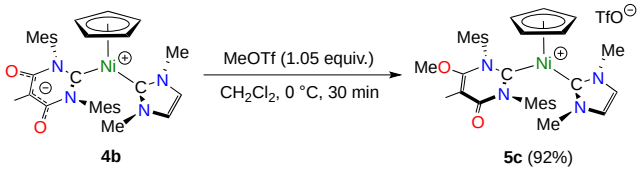
^{a}In [NiCp(IMe)(IMes)]$^+$, C(1) is the IMes carbene carbons and C(2) the IMe carbene carbon. ^{b}Cp$_{cent}$= centroid of the Cp group. ^{c}Average Ni–C distance to the Cp ring

the more important steric footprint of the 6-membered Mes-*malo*NHC^{Me}-Mes ring compared to that of the 5-membered IMes ring (*vide supra*).

Treatment of the zwitterionic complex **4b** with methyl triflate at 0 °C cleanly afforded the corresponding cationic complex, [Ni(IMe)(Mes-*malo*NHC^{Me}$_{Me}$-Mes)Cp](OTf) (**5c**), which was isolated as a brown solid in excellent yield (Scheme 5). The ^{1}H NMR spectrum of **5c** clearly indicates that methylation of the malonate backbone took place at one of the exocyclic oxygen atom (Figure S10 in the Sup-

porting Information). In addition, in contrast to what is observed in the ^{1}H NMR spectrum of **4b**, the *para*-methyl groups of the two mesityl *N*-substituents of **5c** appear as two different signals integrating in a 1:1 relative ratio, confirming the lowering of the effective symmetry of the *malo*NHC ligand from C_{2v} in **4b** to C_s in **5c**. Similarly, the *ortho*-methyl groups appear as two singlets integrating for 6 protons each. Furthermore these signals are broad at RT, which likely indicates restricted rotations about the Ni–$C_{malo\mathrm{NHC}}$ and N–Mesityl bonds as observed in **4b** (*vide supra*). Finally, it is noteworthy that the carbene carbon of ligand **c** is observed at 207.0 ppm in the ^{13}C{^{1}H} NMR spectrum (Figure S11), thus showing that the ^{13}C chemical shifts of **b** and **c** (in **4b** and **5c**) are negatively correlated with their electronic donor properties as was already observed with closely related [FeCp(CO)$_2$(*malo*NHC)] complexes.[13d] All other signals of **5c** are comparable to those of **4b**, and deserve no particular comment.

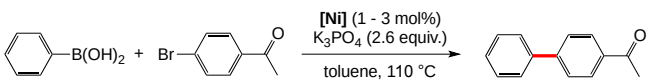
Scheme 5. Post-functionalization of the malonate backbone of 4b



Catalytic studies of the new nickel carbene complexes. The Ni(CAAC) complex **1a** and the Ni(*malo*NHC) complexes **4b** and **5c** have been evaluated as pre-catalysts for various reactions for which our previously reported half-sandwich Ni(NHC) complexes have shown interesting activities, *i.e.* in: (i) the Suzuki-Miyaura coupling of aryl bromides in the absence of a co-catalyst or reductant,[4c,e,f] (ii) the hydrosilylation of aldehydes,[27] and (iii) the α-arylation of acyclic ketones with aryl bromides.[28]

Thus, the activities of **1a**, **4b** and **5c** were first evaluated for the coupling of phenylboronic acid with 4-bromoacetophenone in the sole presence of K_3PO_4 in toluene at reflux (Table 2). Under these conditions, the CAAC complex **1a** proved to be a poor catalyst, with only 13% conversion to 4-phenylacetophenone after 1 h of reaction with a catalytic loading of 3 mol% (Table 2, entry 1). Similarly, the activities of the heteroleptic bis-carbene complexes **4b** and **5c** proved to be rather low with only 21 and 23% conversion to the desired coupling product (entries 2 and 3). This is markedly lower than what was observed with [NiCp*(NCMe)(IPr)](PF$_6$)[4c] or [NiICp(Mes-NHC-*n*Bu)][4f] (entries 4 and 5), but is in line with what was observed with the *bis*-NHC analogue of **4b** and **5c**, [NiCp(IMe)(IMes)](PF$_6$) (entry 6),[4e] and may be explained

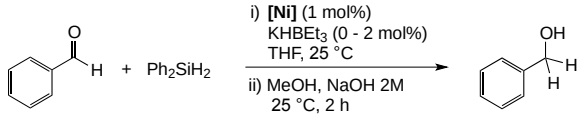
Table 2. Suzuki coupling of 4-bromoacetophenone with phenylboronic acid catalyzed by complexes 1a, 4b and 5c[a]



Entry	Catalyst (mol%)	Time (min)	Conversion (%)[b]
1	**1a** (3)	60	13
2	**4b** (3)	60	21
3	**5c** (3)	60	23
4	[NiCp*(NCMe)(IPr)](PF$_6$) (3)	10[c]	95[4c]
5	[NiICp(Mes-NHC-*n*Bu)] (1)	15	88[4f]
6	[NiCp(IMe)(IMes)](PF$_6$) (1)	60	20[4e]

[a]Reaction conditions: phenylboronic acid (1.3 mmol), 4-bromoacetophenone (1 mmol), K_3PO_4 (2.6 mmol), [Ni] (1 - 3 mol%) in toluene (3 mL) at 110 °C. [b]Conversions determined by ^{1}H NMR; average of two runs. [c]Reactions run at 90 °C.

Table 3. Hydrosilylation of benzaldehyde with diphenylsilane catalyzed by 1a, 4b and 5c[a]



Entry	Catalyst	Additive (mol%)	Time (h)	Conversion (%)[b]
1	**1a**	KHBEt$_3$ (2)	0.5	31
2	**4b**		1	12
3	**4b**	KHBEt$_3$ (2)	1	61
4	**5c**		1	5
5	**5c**	KHBEt$_3$ (2)	1	38
6[c]	[Ni(IMes)ClCp]		17	0[27a]
7	[Ni(IMes)ClCp]	NaHBEt$_3$ (2)	0.25	> 97[27a]

[a]Reaction conditions: activation of [Ni] with the additive in THF (4 mol) was followed by addition of benzaldehyde (1 mmol) and Ph_2SiH_2 (1 mmol), and the reaction mixture was stirred at 25 °C. [b]Conversions determined by ^{1}H NMR after methanolysis (MeOH, 2M NaOH) and extraction with Et_2O. [c]Reaction run with 5 mol% [Ni].

by the fact that **4b** and **5c** are coordinatively saturated and sterically congested. Thus apart from an eventual Cp ring slippage from the η^5- to an η^3- or η^1-coordination mode, there seems to be no other possibility for substrates to access the nickel center. Consequently, we studied the potential labilization of the Cp ring of **4b** and **5c** in an acidic medium, as previously described with NiCp(NHC) species bearing alkyl ligands.[29] However, when complex **4b** or **5c** was treated with HCl (1 equiv.) and KPF$_6$ (1 equiv.) in acetonitrile at room temperature, no reaction occurred. This is again similar to what had been observed with the related *bis*-NHC complexes[4e] and confirms their very low reactivity. Regarding the CAAC complex **1a**, the observed disappointing activity may result from its rather low stability.

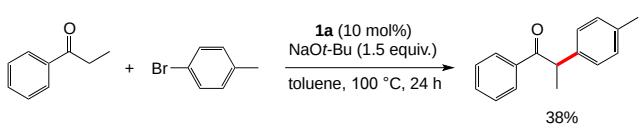
The activities of **1a**, **4b** and **5c** were also evaluated for the hydrosilylation of benzaldehyde with diphenylsilane as the hydrogen source (Table 3). Complexes **4b** and **5c** proved slightly active at room temperature in the absence of any additive (Table 3, entries 2 and 4). This is in marked contrast to [NiClCp(IMes)] – the most active half-sandwich Ni(NHC) pre-catalyst[27a] – which does not show any activity under similar reaction conditions, even after a prolonged

reaction time (entry 6), and was thus rather promising. However, in the presence of 2 mol% of a triethylborohydride salt, which allowed 1 mol% of [NiClCp(IMes)] to fully reduce benzaldehyde in 15 min (entry 7),[27a] **4b** and **5c** (1 mol%) only allowed 61 and 38% conversion after 1 h reaction (entries 3 and 5). Yet, one can note here that, in contrast to what was observed in the Suzuki coupling reaction, complex **4b** is twice as active as **5c**, thus showing that the decrease of electron donicity from **b** to **c** results in a reduction of catalytic activity in this case. A similar but more dramatic tendency had already been observed for the same reaction with the iron(II) complexes, [FeCp(CO)$_2$(Mes-*malo*NHC^{Me}-Mes)] and [FeCp(CO)$_2$(Mes-*malo*NHC$_{Me}$^{Me}-Mes)](OTf).[13d] The related zwitterionic heteroleptic bis-carbene copper(I) complex, [Cu(IMe)(Mes-*malo*NHC^{Me}-Mes)], showed very poor activity for the hydrosilylation of acetophenone.[13c]

The Ni(CAAC) complex **1a** was also briefly evaluated in this reaction. About 30% conversion was observed in 30 min in the presence of potassium triethylborohydride (Table 3, entry 1). This result also does not reach the efficiency of the [NiClCp(IMes)]/NaHBEt$_3$ (1:2) system.

Finally, we were particularly interested in evaluating **1a** as a pre-catalyst for the α-arylation of propiophenones with aryl halides to provide a point of comparison with [PdCl(η^3-C$_3$H$_5$)(IPr-CAAC^{Me2}-Cy)],[6a] as well as with [NiCl$_2$(IPr)(PPh$_3$)], which only differs from **1a** by the nature of the carbene ligand and is moderately active in this reaction,[30] and [NiClCp(IPr)], which is one of the most active nickel-based catalysts.[28] For that purpose, we reacted **1a** with propiophenone and 4-bromotoluene under the same conditions than those employed for [NiCl$_2$(IPr)(PPh$_3$)], *i.e.*: with 10 mol% of **1a** and 1.5 equiv. of sodium *tert*-butoxide in toluene at 100 °C for 24 h (Scheme 6). Only a 38% GC yield was observed, which is markedly lower than the 65 and 78% yields obtained with [NiCl$_2$(IPr)(PPh$_3$)][30] and [NiClCp(IPr)] (3 mol%),[28] respectively, and thus places **1a** far behind [PdCl(η^3-C$_3$H$_5$)(IPr-CAAC^{Me2}-Cy)].[6a] In addition, this result tends to show that replacement of IPr by the much more strongly σ-donating CAAC **a** in a [NiCl$_2$(carbene)(PPh$_3$)] complex has no beneficial impact for this reaction.

Scheme 6. α-Arylation of propiophenone with 4-bromotoluene catalyzed by 1a



CONCLUSIONS

In summary, new nickel(II) complexes of highly σ-donating CAAC and anionic *malo*NHCs were synthesized by reaction with [NiCl$_2$(PPh$_3$)$_2$]. The coordination chemistry of these ligands with nickel has clearly shown that CAACs behave as neutral L-type ligands, whereas *malo*NHCs behave as anionic X-type ligands towards this metal.

The CAAC complex, [NiCl$_2$(IPr-CAAC^{Me2}-Cy)(PPh$_3$)] (**1a**), resulting from the substitution of one PPh$_3$ ligand, proved to be proton sensitive and decomposed to the nickelate salt, [(IPr-CAAC^{Me2}-Cy)·H][NiCl$_3$(PPh$_3$)] (**2a**). The fragility of the Ni–CAAC bond in **1a** contrasts with the usual robustness of Metal–CAAC bonds, and may explain the poor catalytic activity of **1a** in the various reactions in which it was tested.

The zwitterionic *malo*NHC species, [NiCl(PPh$_3$)$_2$(Mes-*malo*NHC^{Me}-Mes)] (**3b**), resulting from the substitution of one chloride ligand, was insoluble in most organic solvents, which precluded its isolation as an analytically pure solid and its full characterization. Nevertheless, the propensity of *malo*NHCs to substitute anionic ligands was confirmed by the substitution of iodide from [NiICp(IMe)] to give the corresponding zwitterionic heteroleptic bis-carbene complex, [NiCp(IMe)(Mes-*malo*NHC^{Me}-Mes)] (**4b**). The latter was post-functionalized by addition of methyl triflate to give the cationic [NiCp(IMe)(Mes-*malo*NHC^{Me}$_{Me}$-Mes)](OTf) (**5c**), in which the malonate moiety of the ligand has been methylated, thus significantly reducing its electron-donicity without modifying its steric properties. As a consequence, **4b** proved twice as active as **5c** for the hydrosilylation of benzaldehyde with diphenylsilane. Yet the activity of **4b** remained moderate, perhaps because of its steric congestion, which renders the nickel center difficult to reach. No such difference was observed in the Suzuki coupling of 4-bromoacetophenone with phenylboronic acid, where both complexes showed rather poor activity, similarly to closely related bis-NHC species.

The study of the coordination chemistry of nickel with *malo*NHCs and CAACs is only in its infancy, and although these first Ni(IPr-CAAC^{Me2}-Cy) and Ni(Mes-*malo*NHC^{Me}-Mes) species have shown relatively disappointing activities in the catalytic reactions we have studied, we suspect that further work on the coordination chemistry of these strongly σ-donating carbenes and their families to nickel will give rise to interesting nickel-based catalysts in a near future.

EXPERIMENTAL SECTION

All reactions were carried out using standard Schlenk or glovebox techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon. Solution NMR spectra were recorded at 298 K on Bruker Ultra Shield 300, Bruker Spectrospin 400 or Bruker Avance III HD 500 spectrometers operating at 300.13, 400.14 or 500.14 MHz for ^{1}H and at 75.47, 100.61 or 125.77 MHz for ^{13}C{^{1}H}. The ^{1}H NMR variable-temperature experiments were recorded at 400 MHz in CD$_2$Cl$_2$ from 243 K to 296 K for complex **4b**. The chemical shifts are referenced to the residual deuterated or ^{13}C solvent peaks. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. IR spectra were recorded on a FT-IR Perkin Elmer Spectrum Two spectrometer equipped with a diamond ATR. Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, Université de Strasbourg. High resolution mass spectra were recorded on a Bruker micrOTOF-Q mass spectrometer by the Service the Spectrométrie de Masse, UMR CNRS 7177, Université de Strasbourg. GC analyses were performed with an Agilent 7820A GC system equipped with a 30-m capillary column (Agilent HP-5, cross-linked 5% phenyl silicone gum, 30 m × 0.32 mm × 0.25 μm). H$_2$/air was used as vector gas. The following GC conditions were used for the α-arylation experiments: initial temperature 80

°C, for 2 min, then rate 10 °C/min. until 220 °C and 220 °C for 15 min. For the hydrosilylation experiments, 1,3,5-trimethoxybenzene was used as the internal standard for the NMR yield determinations. Commercial compounds were used as received. $KHBEt_3$ solution (1M in THF) was purchased from Aldrich. The pyrrolidinylium salt (**a·HCl**),[18] the pyrimidinium betaïne (**b·H**),[13a,31] and [NiICp(IMe)][4a] were prepared according to the published methods.

Synthesis of [NiCl$_2$(IPr-CAAC^{Me2}-Cy)(PPh$_3$)] (1a) and of [(IPr-CAAC^{Me2}-Cy)·H][NiCl$_3$(PPh$_3$)] (2a). To a suspension of **a·HCl** (500 mg, 1.38 mmol) in Et_2O (10 mL) at −78 °C was added drop-wise a 0.5 M solution of KHMDS in toluene (3.04 mL, 1.52 mmol). The reaction mixture then was allowed to warm to room temperature, and stirred for 1 h before the volatiles were removed *in vacuo*. The free carbene **a** was extracted with THF (2 × 10 mL), and added to a suspension of [NiCl$_2$(PPh$_3$)$_2$] (903 mg, 1.38 mmol) in THF (20 mL) at −78 °C. The reaction medium was then allowed to warm to room temperature during which a color change from dark green to red was observed. The suspension was immediately filtered through Celite, and the filtrate was concentrated to *ca.* 10 mL before addition of *n*-pentane (30 mL). The precipitation of a white solid was observed. The suspension was again filtered through a Celite pad, and the filtrate concentrated to *ca.* 5 mL. Depending on the quantity of **a·HCl** still present in the reaction medium, a notable amount of deep blue crystals were formed, and subsequently filtered before washing with *n*-pentane (3 × 10 mL) and drying under vacuum to afford **2a** (X-ray quality crystals were obtained from a dichloromethane/pentane solution at RT). The reddish filtrate was placed at −28 °C overnight to yield **1a** (335 mg, 0.467 mmol, 34%) as a violet solid that was washed with *n*-pentane (3 × 20 mL) and dried under vacuum. **1a**: Anal. Calcd for $C_{41}H_{50}Cl_2NNiP$: C, 68.64; H, 7.03; N, 1.95. Found: C, 67.76; H, 7.13; N, 2.04. Elemental analyses on independent samples reproducibly gave similar low carbon values.[32] HR-MS (ESI): *m/z* [M+H]$^+$ calcd for $C_{23}H_{36}N$ [IPr-CAAC^{Me2}-Cy+H]$^+$ and $C_{18}H_{16}P$ [PPh$_3$+H]$^+$ 326.2848 and 263.0989, found 326.2855 and 263.0990. ^{1}H NMR (C_6D_6, 300.13 MHz): δ 7.85 (d, ^3J = 6.6 Hz, 6H, *o*-H$_{Ph}$), 7.42-7.37 (m, 3H, *p*- and *m*-H$_{Ar}$), 7.08-7.00 (m, 9H, *m*- and *p*-H$_{Ph}$), 3.78 (m, 2H, CH$_2$), 3.24 (sept., ^3J = 6.0, 2H, C*H*Me$_2$), 2.03 (br. d, 2H, CH$_2$), 1.80 (br. d, 2H, CH$_2$), 1.62 (br. d, 2H, CH$_2$), 1.58 (s, 2H, CMe$_2$C*H$_2$*), 1.47 (d, ^3J = 6.0, 6H, CH*Me$_2$*), 1.25 (m, 2H, CH$_2$), 1.19 (d, ^3J = 6.0, 6H, CH*Me$_2$*), 0.98 (s, 6H, C*Me$_2$*). ^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz): δ 148.5 (C$_{Ar}$), 136.4, 136.0, 132.9, 129.7, 129.5, 127.4, 126.2 (C$_{Ar}$ and C$_{Ph}$), 81.7, 64.4, 46.1, 39.4, 30.1, 29.2, 29.1, 26.1 23.3 (C$_{Aliph.}$). **2a**: Anal. Calcd for $C_{41}H_{51}Cl_3NNiP$ + ½ CH_2Cl_2: C, 62.59; H, 6.58; N, 1.76. Found: C, 62.72; H, 6.56; N, 1.75. ^{1}H NMR (CD_3CN, 400.14 MHz): δ 17.99 (v.br., 6H, *o*- or *m*-H$_{Ph}$), 8.69 (s, 1H, NCH), 7.64 (t, ^3J = 7.6 Hz, 1H, *p*-H$_{Ar}$), 7.49 (d, ^3J = 7.6 Hz, 1H, *m*-H$_{Ar}$), 4,52 (v.br., 6H, *o*- or *m*-H$_{Ph}$), 2.80 (br., 6H, C*H*Me$_2$ and CH$_2$), 2.26 (br. m,, 2H, CH$_2$), 2.08 (br. m, 2H, CH$_2$), 1.89 (br. m, 4H, CH$_2$), 1.64 (s, 6H, C*Me$_2$*).1.41 (d, ^3J = 6.4, 6H, CH*Me$_2$*), 1.17 (d, ^3J = 6.4, 6H, CH*Me$_2$*), –2.33 (v.br. 3H, *p*-H$_{Ph}$). ^{13}C{^{1}H} NMR (CD_3CN, 125.77 MHz): δ 194.6 (N*C*H), 145.1, 132.8, 132.2 (br.), 129.8, 126.3, 85.0, 53.7, 46.9, 35.6, 30.1, 29.4, 27.1, 25.8 22.5, 22.2.

Synthesis of [(IPr-CAAC^{Me2}-Cy)·H][NiCl$_3$(PPh$_3$)] (2a). [NiCl$_2$(PPh$_3$)$_2$] (273 mg, 0.42 mmol) and **a·HCl** (151 mg, 0.42 mmol) were suspended in THF (4 mL) at room temperature. A color change from dark green to blue was observed within a few minutes. The resulting blue reaction medium was stirred for 15 min more, after the suspension was allowed to settle. The overlaying blue-green solution was then removed with a syringe, and the blue solid washed with THF (10 mL) and Et_2O (10 mL) before being dried under vacuum to yield **2a** (235 mg, 0.33 mmol, 79%). Anal. Calcd for $C_{41}H_{51}Cl_3NNiP$: C, 65.32; H, 6.82; N, 1.85. Found: C, 65.28; H, 6.99; N, 1.74. ^{1}H NMR (CD_3CN, 400.14 MHz): *vide supra*. ^{13}C{^{1}H} NMR (CD_3CN, 125.77 MHz): *vide supra*.

Synthesis of [NiCl(*malo*NHC$_{Me}$-Mes)(PPh$_3$)$_2$] (3b). A solution of **b·H** (100 mg, 0.276 mmol) in THF (3 mL) was treated at room temperature by drop-wise addition of a 0.5 M solution of KHMDS in toluene (610 µL, 0,304 mmol). The resulting yellow solution was stirred for 30 min before addition to a suspension of [NiCl$_2$(PPh$_3$)$_2$] (181 mg, 0276 mmol) in THF (5 mL) at 0 °C. The resulting red-brown suspension was stirred 5 min at this temperature before the temperature was raised to room temperature to give a reddish suspension after 15 min. The reaction media was filtered to give **3b** as a light violet solid that was washed with diethylether (3 × 10 mL) before drying under vacuum. ^{1}H NMR (DMSO-d_6, 400.14 MHz): δ 7.38 (br., 18H, *m*- and *p*-H$_{Ph}$), 7.22 (br., 12H, *o*-H$_{Ph}$), 7.03 (s, 4H, *m*-H$_{Ar}$), 2.27 (s, 6H, *p*-Me), 2.05 (s, 12H, *o*-Me), 1.80 (s, 3H, apical-C*H$_3$*).

Synthesis of [NiCp(IMe)(Mes-*malo*NHC^{Me}-Mes)] (4b). A solution of **b·H** (210 mg, 0.579 mmol) in THF (3 mL) was treated at room temperature by drop-wise addition of a 0.5 M solution of KHMDS in toluene (1.27 mL, 0.636 mmol). The reaction mixture was stirred for 30 min before addition of [NiICp(IMe)] (200 mg, 0.579 mmol) to the solution containing the free carbene **b**. The resulting red-brown solution quickly gave a brown suspension. After 30 min at room temperature, the reaction medium was evaporated to dryness before extraction of the brownish residue with CH_2Cl_2 (3 × 10 mL), and filtration over Celite. The filtrate was then concentrated to *ca.* 5 mL before addition of Et_2O (20 mL) to afford **4b** as a dark green solid that was subsequently washed with Et_2O until the washings were colorless, and dried under (252 mg, 0.433 mmol, 75%). Anal. Calcd for $C_{33}H_{38}N_4NiO_2$: C, 68.18; H, 6.59; N, 9.63. Found: C, 66.82; H, 6.41; N, 9.68. Elemental analyses on independent samples reproducibly gave similar low carbon values.[32] HR-MS (ESI): *m/z* [M+H]$^+$ calcd for $C_{33}H_{39}N_4NiO_2$ 581.2421, found 581.2439. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 6.96 (br. s, 4H, *m*-H), 6.84 (s, 2H, NC*H*), 4.72 (s, 5H, η^5-C$_5$*H$_5$*), 3.32 (s, 6H, NC*H$_3$*), 2.36 (s, 6H, *p*-Me), 2.00 (br., 12H, *o*-Me), 1.86 (s, 3H, *apical*-C*H$_3$*). ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 6.99 (br. s, 4H, *m*-H), 6.86 (s, 2H, NC*H*), 4.72 (s, 5H, η^5-C$_5$*H$_5$*), 3.28 (s, 6H, NC*H$_3$*), 2.39 (s, 6H, *p*-Me), 1.97 (br., 12H, *o*-Me), 1.72 (s, 3H, *apical*-C*H$_3$*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ 189.8 (N$_2$*C$_{malo}$*$_{NHC}$), 162.7 (N$_2$C$_{IMe}$), 162.0 (*C*O), 141.7 and 137.9 (*ipso*-/*p*-C$_{Ar}$), 137.4 (*o*-C$_{Ar}$), 129.4 (*m*-C$_{Ar}$), 124.2 (N*C*H), 93.3 (η^5-*C*$_5$H$_5$), 90.6 (*apical*-*C*CH$_3$), 39.2 (N*C*H$_3$), 21.2 (*p*-Me), 18.8 (*o*-Me), 9.0 (*apical*-*C*H$_3$). IR [ATR]: ν(C=O) 1665 (w), 1606 (s).

Synthesis of [NiCp(IMe)(Mes-*malo*NHC$^{Me}_{Me}$-Mes)](OTf) (5c). A solution of **4b** (200 mg, 0.344 mmol) in CH_2Cl_2 (10 mL) was placed at 0 °C before dropwise addition of MeOTf (40 µL, 0.361 mmol). The reaction mixture was then stirred for 30 min at 0 °C before the volatiles were removed *in vacuo* to afford **5c** (235 mg, 0.315 mmol, 92%) as a brown solid that washed with Et_2O (4 × 10 mL), and dried under vacuum. Anal. Calcd for $C_{35}H_{41}F_3N_4NiO_5S$: C, 56.39; H, 5.54; N, 7.52. Found: C, 54.99; H, 5.48; N, 7.22. Elemental analyses on independent samples reproducibly gave similar low carbon values.[32] HR-MS (ESI): *m/z* [M]$^+$ calcd for $C_{34}H_{41}N_4NiO_2$ 595.2578, found 595.2567. HR-MS (ESI): *m/z* [M]$^-$ calcd for CF_3SO_3 148.9515, found 148.9514. ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ 7.14 (s, 2H, *m*-H), 7.13 (s, 2H, *m*-H), 7.07 (s, 2H, NC*H*), 4.77 (s, 5H, η^5-C$_5$*H$_5$*), 3.50 (s, 3H, OC*H$_3$*), 3.28 (s, 6H, NC*H$_3$*), 2.45 (s, 3H, *p*-Me), 2.42 (s, 3H, *p*-Me), 2.01 (br. s, 9H, *o*-Me and *apical*-C*H$_3$*), 1.93 (br. s, 6H, *o*-Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz): δ 207.0 (N$_2$*C$_{malo}$*$_{NHC}$), 161.1, 159.1 and 155.8 (N$_2$*C$_{IMe}$*/*CO*/*C*-OMe), 141.2, 140.2, 139.1 and 138.0 (*p*-/ *ipso*-C$_{Ar}$), 136.6 and 136.1 (*o*-C$_{Ar}$), 130.4 and 130.3 (*m*-C$_{Ar}$), 125.9 (N*C*H), 106.2 (*apical*-*C*CH$_3$), 94.4 (η^5-*C*$_5$H$_5$), 62.5 (O*C*H$_3$), 39.3 (N*C*H$_3$), 21.3 and 21.3 (*p*-Me), 18.7 and 18.5 (*o*-Me), 9.7 (*apical*-*C*H$_3$). IR [ATR]: ν(C=O) 1684 (m), 1651 (m); ν(S=O) 1261 (s), 1147 (s).

General procedure for the Suzuki coupling of 4'-bromoacetophenone with phenylboronic acid. An oven dried Schlenk tube equipped with a stirring bar was charged with 4'-bromoacetophenone (199 mg, 1.00 mmol), phenylboronic acid (159 mg, 1.30 mmol), K_3PO_4 (552 mg, 2.60 mmol) and **1a**, **4b** or **5c** (0.03 mmol) before being put under an atmosphere of argon. Toluene (3 mL) was injected and the mixture immediately heated with vigorous stirring by putting the Schlenk tube in a preheated oil bath at 110 °C. After 60 min, the reaction was stopped by cooling the reaction to room temperature and allowing air to enter in the Schlenk tube. The conversions to 4-phenylacetophenone were determined by ^{1}H NMR spectroscopy after removing a sample with a syringe, drying it under high vacuum, extracting the residue with $CDCl_3$ and filtering the

solution in the NMR tube. All yields are the average value of at least two runs.

General procedure for the hydrosilylation of benzaldehyde with diphenylsilane. A 10 mL oven dried Schlenk tube containing a stirring bar was loaded with **1a**, **4b** or **5c** (0.01 mmol) and 4 mL of THF. The resulting solution was stirred for 5 min. A solution of $KHBEt_3$ in THF (20 µL, 1 M in THF, 0.02 mmol) was added dropwise, and the solution was stirred for 5 more min. Benzaldehyde (101 µL, 1.00 mmol) and Ph_2SiH_2 (186 µL, 1.00 mmol) were then added, in this order, and the reaction mixture was stirred in a preheated oil bath at 25 °C for 0.5 to 1 h (See Table 2). The reaction mixture was then quenched by the addition of methanol (2 mL) and 2 M NaOH (2 mL) and stirred for 2 h. After the addition of water (5 mL), the product was extracted with diethylether (3 x 10 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The conversions to benzyl alcohol were determined by ^{1}H NMR spectroscopy. All yields are the average value of at least two runs.

Procedure for the α-arylation of propiophenone with 4-bromotoluene. A 10 mL oven dried Schlenk tube containing a stirring bar was loaded with **1a** (72 mg, 0.10 mmol), NaO*t*-Bu (144 mg, 1.50 mmol), 4-bromotoluene (171 mg, 1.00 mmol), propiophenone (161 mg, 1.20 mmol) and toluene (3 mL). The resulting suspension was stirred in a preheated oil bath at 110 °C for 24 h. The reaction mixture was then quenched by the addition of a solution of saturated aqueous NH_4Cl (10 mL), and the product extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The yield of 1-phenyl-2-(*p*-tolyl)-propan-1-one was determined by GC. The obtained value is the average value of two runs.

X-ray Diffraction Study. Structure Determinations and Refinement. Single crystals of **2a** and **4b** suitable for X-ray diffraction studies were selected from batches of crystals obtained at RT from a dichloromethane/pentane solution for **2a** and at -35 °C from a dichloromethane solution for **4b**. Diffraction data were collected at 173(2) K on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). A summary of crystal data, data collection parameters and structure refinements is given in Table S1. The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)[33] from reflections taken from three sets of six frames, each at ten seconds exposure. The structure was solved by direct methods using SHELXS-2013.[34] The refinement and all further calculations were carried out using SHELXL-2013.[35] The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX2;33 transmission factors: T_{min}/T_{max} = 0.6337/0.7460 for **2a** and 0.6620/0.7456 for **4b**. For **2a**, the SQUEEZE instruction in PLATON[36] was applied. The residual electron density was assigned to half a molecule of dichloromethane.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.xxxxx.

NMR spectra of **1a**, **4b**, and **5c**, HR-MS spectrum of **1a,** variable temperature ^{1}H NMR analysis of **4b**, crystallographic data and selected bond lengths and angles of **2a** and **4b** (PDF)

Crystallographic data: CCDC numbers 1517958 (**2a**) and 1517959 (**4b**) (CIF)

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Notes

The authors declare no competing financial interest.

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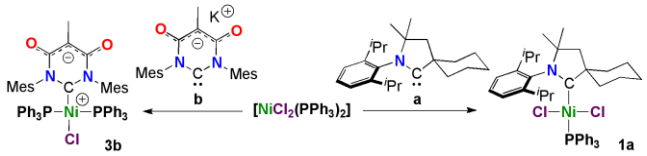
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