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Synthesis of neutral nickel–methyl complexes with monodentate imines and their sequential insertion of carbon monoxide and imine

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Dedicated to Professor Robert Bergman, and his many contributions to chemistry.

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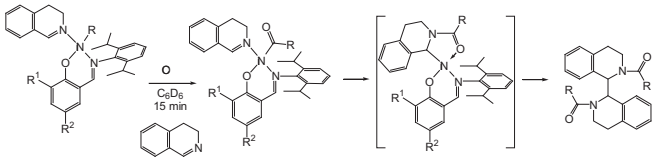
ABSTRACT

Neutral nickel–imine complexes of the form (N^O)Ni(R)(R^1N=C(H)R^2) (N^O = salicylaldiminato; R = CH_3, Ph; R^1 = alkyl; R^2 = aryl) can be prepared by the reaction of (tmeda)Ni(CH_3)$_2$, imine and the corresponding salicylaldiminato ligand. The addition of carbon monoxide to these complexes lead to the *in situ* generation of the corresponding nickel–acyl complexes. With *N*-methyl or *N*-benzyl substituted imines, these complexes reductively eliminate the phenolic and acyl ligands to generate esters. However, the less sterically encumbered 3,4-dihydroisoquinoline can couple with the nickel–acyl ligand to form 1,2-diamides in high yield. *In situ* ^{1}H NMR analysis suggests this reaction occurs via insertion of imine into the nickel-acyl bond to form a nickel-bound amide complex.



1. Introduction

The migratory insertion reaction of multiply bonded substrates into transition metal–carbon bonds has significant utility in synthetic chemistry. This reaction has been perhaps most thoroughly exploited with olefins, as illustrated in metal catalyzed poly(olefin) syntheses [1]. Additionally, the migratory insertion of alkenes is a critical step in many organic synthetic transformations (e.g. Heck reaction [2], alkene–alkyne coupling reactions [3], reductions [4], and many others [5]). In contrast to olefins, the use of imine C=N double bonds in migratory insertion into late transition metal–carbon bonds is more limited [6,7]. This difference may result from a number of factors. The insertion of imines into metal–carbon bonds often involves cleavage of a strong C=N π-bond, and its replacement with a C–N single bond, which has less of a driving force than alkene insertion [8]. In addition, stable aldimines typically have substituents at both nitrogen and carbon, rendering these compounds more hindered than α-olefins, and often coordinate to transition metals in a σ-fashion through the nitrogen lone pair instead of via π-coordination, the postulated requirement for insertion [9]. Despite these features, examples of both catalytic and stoichiometric processes involving imine insertion into late transition metal–carbon bonds have been reported [6]. These typically involve insertion to form metal-nitrogen bonded intermediates or products.

As an alternative to these approaches, both Sen and co-workers [10] and ourselves [8] and have demonstrated that cationic Pd(II) complexes mediate the sequential insertion of carbon monoxide (CO) and imines to generate metal–amide chelates (Scheme 1). A similar reaction can also occur with cationic nickel and manganese–carbonyl complexes [11]. Notably, imine insertion proceeds with a regiochemistry to form a new metal–carbon bond,

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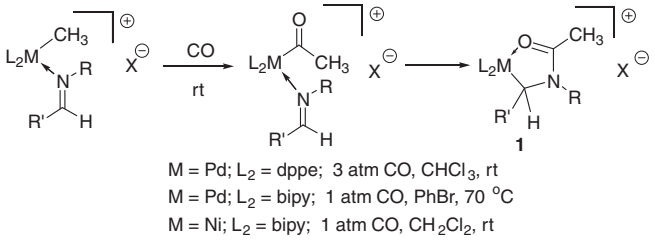
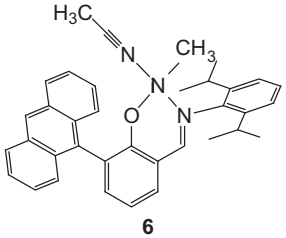


Scheme 1. The sequential insertion of CO and imines with cationic complexes.

and thus represent the fundamental steps in a potential CO/imine co-polymerization. While the strong coordination of the acyl-oxygen to the cationic metal center in **1** inhibits the creation of an empty coordination site for further insertion steps, Sun and coworkers have recently reported that neutral cobalt–carbonyl complexes are not inhibited by chelation, and can mediate the sequential insertion polymerization of carbon monoxide and imines to build up polyamides [12]. We have observed that the less Lewis acidic neutral Pd(II) complexes **2** (Scheme 2), generated via oxidative addition of *N*-acyl iminium salts to Pd(0), can also undergo further insertion of carbon monoxide to afford a transient six-membered palladacycle **3**. This intermediate lacks any stabilizing ligand, and undergoes rapid β-hydride elimination to generate an α-amide substituted ketene **4**, which is in equilibrium with its closed heterocyclic form (1,3-oxazolium-5-oxide or Münchnone, **5**) [13].

The ability of neutral cobalt and palladium complexes to mediate sequential insertion, relative to the stable cationic chelated-amide complexes **1**, is similar to the behavior of late metal catalysts with polar alkene monomers. In these systems, it is established that neutral nickel and palladium catalysts are less inhibited by functional group chelation than their cationic analogs, and can mediate further insertion reactions to build up polymers with functionalized alkenes [14]. For example, neutral κ^2-*N,O*-salicylaldiminato nickel complexes (e.g. **6**) are known to catalyze the co-polymerization of polar alkenes with substituted norbornenes, carbon monoxide, and α-ω functional olefins [15]. These features suggest that neutral late metal complexes might also be viable systems to mediate the sequential insertion of carbon monoxide and imines. However, the lower Lewis acidity in these complexes will presumably create a less electrophilic nickel–acyl ligand, which we have previously postulated is important for imine insertion into a metal–acyl bond [11b]. To probe the ability of these neutral complexes to mediate imine insertion, we describe below the synthesis and reactivity of the imine-coordinated nickel complexes (N^O)Ni(R)(R^1N=C(H)R^2) (N^O = salicylaldiminato; R = CH_3, Ph; R^1 = alkyl; R^2 = aryl). These complexes have been found to undergo rapid insertion of carbon monoxide, followed by coupling of the nickel–acyl ligand with sterically unencumbered *cis*-tethered imines, leading to the formation of 1,2-diamides.



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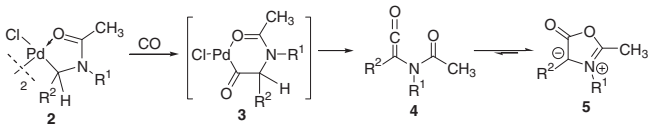


Scheme 2. CO insertion with neutral palladium-chelated amides.

2. Results and discussion

2.1. Synthesis of nickel–imine complexes

Neutral imine-coordinated complexes of the form (N^O)Ni(R)(R^1N=C(H)R^2) (N^O = salicylaldiminato; R = CH_3; R^1 = alkyl; R^2 = aryl) can be synthesised via the reaction of (tmeda)$NiMe_2$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) and the free phenolic ligand in the presence of imine, in analogy to the synthesis of related (salicylaldiminato)nickel complexes (Table 1) [16,17]. Removal of solvents and washing with pentane yielded complexes **8a–l** as orange powders. The ^{1}H and ^{13}C NMR spectra for **8a–l** display a downfield shift in the monodentate imine resonances upon coordination, consistent with η^1-binding of the imine through the nitrogen [e.g. **8g**: ^{1}H NMR: δ 8.43 (s, C*H*=N), ^{13}C NMR: δ 166.1 (*C*H=N), versus free *p*-Tol(H)C=NBn: ^{1}H NMR: δ 8.26 ppm (s, C*H*=N), ^{13}C NMR: δ 159.3 (*C*H=N)] [10]. ^{1}H-NOE NMR studies on **8g** show that the nickel–methyl ligand (δ −0.73) in close proximity to both the aldimine hydrogen (δ 8.43), and the isopropyl units in the chelated salicylaldiminato ligand [δ 4.16 (sept., 2H), δ 1.51 (d, 6H), 1.04 (d, 6H)]. All other spectroscopic data are consistent with the structure shown. While nickel complexes **8a–l** can be isolated in good yields, *N*-pentafluorophenyl- **8m** and *N*-phenyl **8n** substituted imines, were not isolable, despite being observed *in situ* by ^{1}H NMR spectroscopy.[1] The lower stability of these complexes is likely the result of a weaker nickel–imine bond between these poorly basic imines and the neutral nickel complex.

The phenyl-substituted nickel complex **9** can also be prepared via reaction of (N^O)Ni(Ph)(PPh_3) [18] (N^O = salicylaldiminato) and 3,4-dihydroisoquinoline, with CuCl as a phosphine scavenger (Scheme 3). Precipitation of the complex with pentane afforded a yellow powder. The spectroscopic data observed for **9** are analogous to those for the nickel–methyl complexes.

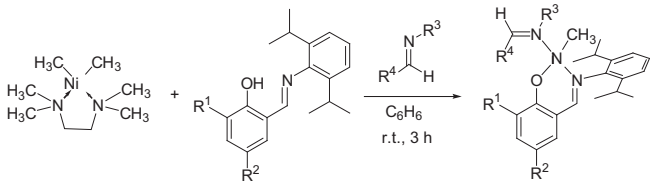
As previously noted for the analogous nickel–acetonitrile complex **6** [16], imine complexes **8** decompose in benzene at ambient temperature to generate uncoordinated imine and *bis*-(salicylaldiminato)nickel (II) complexes **10** (Table 2) [19]. This decomposition is accelerated by steric bulk (entries 1 and 2), and electron withdrawing groups (entries 4, 5) on the salicylaldiminato ligand, as well as by polar solvents (entry 3). Notably, imine insertion into the nickel-methyl bond is not observed under any conditions.

2.2. Carbon monoxide insertion with nickel complexes *8*

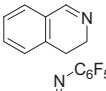
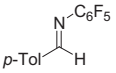
The addition of 1 atm carbon monoxide to complexes **8a–l** in the presence of imine (3 equivalents) results in the rapid insertion of CO to generate the analogous Ni–acyl complexes (Table 3) [20]. While these complexes are not sufficiently stable to be isolated, *in situ* ^{1}H NMR data is consistent with the structures of **11a–l** as

[1] ^{1}H NMR spectrum of **8m** (400 MHz, C_6D_6) (listing distinctive signals only): δ 9.80 (d, 2H, *J* = 7.7 Hz), 7.90 (s, 1H), 7.71 (d, 2H, *J* = 7.7 Hz), 7.54 (s, 1H), 6.43 (t, 2H, *J* = 7.3 Hz), 4.20 (sept., 1H, *J* = 6.6 Hz), 3.83 (sept., 1H, *J* = 6.6 Hz), 2.03 (s, 3H), 1.42 (d, 3H, *J* = 6.6 Hz), 1.24 (d, 3H, *J* = 6.6 Hz), 1.17 (d, 3H, *J* = 6.2 Hz), 0.90 (d, 3H, *J* = 6.2 Hz), −1.04 (s, 3H). (b) ^{1}H NMR spectrum of **8n** (400 MHz, C_6D_6) (listing distinctive signals only): δ 9.77 (d, 2H, *J* = 7.7 Hz), 8.14 (s, 1H), 7.75 (d, 2H, *J* = 7.7 Hz), 7.56 (s, 1H), 6.42 (t, 2H, *J* = 7.7 Hz), 4.35 (sept., 1H, *J* = 6.8 Hz), 3.87 (sept., 1H, *J* = 6.8 Hz), 2.02 (s, 3H), 1.42 (d, 3H, *J* = 7.0 Hz), 1.33 (d, 3H, *J* = 6.2 Hz), 1.19 (d, 3H, *J* = 6.6 Hz), 0.94 (d, 3H, *J* = 6.6 Hz), −0.96 (s, 3H).

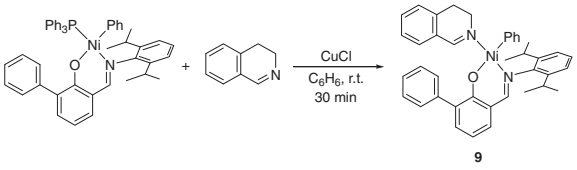
Table 1
The synthesis of (κ^2-*N*,*O*-salicylaldiminato)nickel–imine complexes.



7, 8a-o

Cpd	R^1	R^2	Imine	Yield (%)[a]
7	Ph	H		60
8a	Ph	H		91
8b	H	H		81
8c	H	F		73
8d	H	NO_2		83
8e	Ph	H		88
8f	H	H		76
8g	H	F		74
8h	H	NO_2		87
8i	Ph	H		89
8j	H	H		81
8k	H	F		78
8l	H	NO_2		92
8m	Ph	H		–
8n	Ph	H		–

[a] Isolated yields.

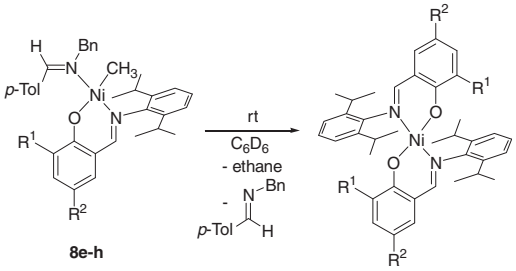


9

Scheme 3. The synthesis of the κ^2-*N*,*O*-salicylaldiminatonickel(II) complex **9**.

shown, in equilibrium with CO-coordinated complexes **12a–d**. For example, monitoring the reaction of **8j** by ^{1}H NMR spectroscopy reveals the disappearance of the Ni–CH_3 resonance after 15 min at ambient temperature, along with the appearance of two new

Table 2
Formation of bis(salicylaldiminato)nickel complexes **10a–d**.



8e-h

10a (R^1 = Ph, R^2 = H)
b (R^1 = H, R^2 = H)
c (R^1 = H, R^2 = F)
d (R^1 = H, R^2 = NO_2)

Entry	Cpd	R^1	R^2	Time (h)	Yield **10** (%)[a]
1	**8e**	Ph	H	6	84[b]
2	**8f**	H	H	61	96
3	**8f**	H	H	5	88[b,c]
4	**8g**	H	F	39	91
5	**8h**	H	NO_2	10	95

[a] General conditions: 0.02 M of **9** in d_6-benzene at 25 °C, monitored *in situ* by ^{1}H NMR.
[b] Isolated yield.
[c] In d_3-acetonitrile.

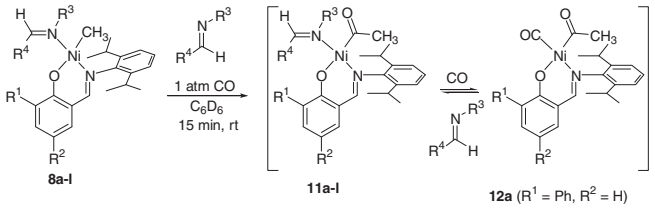
Ni–$COCH_3$ singlets at δ 1.92 ppm (**11j**) and δ 2.49 ppm (**12b**) in a 7–1 ratio. Complex **11j** also contains a coordinated monodentate imine ligand [^{1}H NMR: δ 8.63 (s, 1H)], which ^{1}H-NOE NMR studies confirm is *cis* to the nickel-acyl ligand. The CO-coordinated complex **12b** is observed regardless of the monodentate imine in the starting material, consistent with CO occupying the fourth coordination site.

The ratio of complexes **11** and **12** varies with the coordination ability of the imine, and the steric and electronic properties of the salicylaldiminato ligand (Table 3). Increasing the steric bulk on the salicylaldiminato ligand favors the generation of **12** (e.g. entries 1, 5, 9). However, electron withdrawing substituents on the ligand framework, which presumably increases the Lewis acidity of the metal center, favors imine coordination (entries 3, 4). In general, the *cis*-tethered imine dihydroisoquinoline more strongly favors imine coordination relative to the more sterically encumbered *trans*-disubstituted imines (entries 9–12). As anticipated from a dynamic equilibrium between **11** and **12**, the ratio of imine coordinated complex **11** increased with the addition of excess imine (entries 13–15).

2.3. Imine insertion with neutral nickel–acyl complexes

The *in situ* generation of nickel–acyl imine complexes **11a–l** provides the ability to compare their insertion propensity to the analogous cationic nickel complexes **1**, which have been previously shown to undergo insertion of imine into the nickel–acyl bond to afford chelated amides (Scheme 1). As shown in Table 4, the neutral nickel-acyl complexes of *N*-methyl and *N*-benzyl substituted imines **11a–h** do not undergo imine insertion, and instead eliminate the acyl and phenolic salicylaldiminato ligands over the course of 5 h at ambient temperature to form esters **13a–d** (Table 4). The latter are observed along with uncoordinated imine and the bis(salicylaldiminato)nickel complexes **10** [21]. This reaction occurs regardless of the substituents on the chelating salicylaldiminato ligand. The addition of excess imine is found to partially inhibit the formation of esters **13** (entries 9 and 10), suggesting

Table 3
In situ Generation of nickel–acyl complexes.[a]



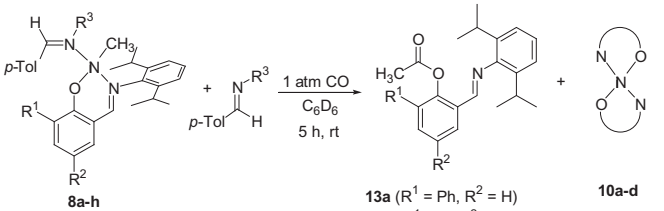
8a-l **11a-l**

12a (R^1 = Ph, R^2 = H)
b (R^1 = H, R^2 = H)
c (R^1 = H, R^2 = F)
d (R^1 = H, R^2 = NO_2)

Entry	Cpd	R^1	R^2	Imine	[Imine] (M)	Ratio **11**:**12**[b]
1	**8a**	Ph	H		0.15	1.2:1
2	**8b**	H	H		0.15	1.9:1
3	**8c**	H	F		0.15	7.8:1
4	**8d**	H	NO_2		0.15	5.5:1
5	**8e**	Ph	H		0.15	1.2:1
6	**8f**	H	H		0.15	2.0:1
7	**8g**	H	F		0.15	3.1:1
8	**8h**	H	NO_2		0.15	3.2:1
9	**8i**	Ph	H		0.15	5.4:1
10	**8j**	H	H		0.15	7.3:1
11	**8k**	H	F		0.15	11.5:1
12	**8l**	H	NO_2		0.15	6.9:1
13	**8b**	H	H		2.5	>20:1
14	**8f**	H	H		2.5	>20:1
15	**8j**	H	H		2.5	>20:1

[a] General conditions: 0.05 M **8**, 1 atm of CO at 25 °C in d_6-benzene, 15 min, rt.
[b] *In situ* ratio measured by ^{1}H NMR.

Table 4
Ester Formation from imine nickel–acyl complexes.[a]



8a-h **13a** (R^1 = Ph, R^2 = H) **10a-d**
b (R^1 = H, R^2 = H)
c (R^1 = H, R^2 = F)
d (R^1 = H, R^2 = NO_2)

Entry	R^1	R^2	R^3	[Imine] (M)	Yield **13** (%)[b]	Yield **10**[b] (%)
1	Ph	H	Me	0.15	89	–
2	H	H	Me	0.15	86	13
3	H	F	Me	0.15	84	13
4	H	NO_2	Me	0.15	41	42
5	Ph	H	Bn	0.15	90	–
6	H	H	Bn	0.15	87	11
7	H	F	Bn	0.15	78	21
8	H	NO_2	Bn	0.15	76	23
9	H	H	Me	2.5	33	62
10	H	H	Bn	2.5	40	56

[a] 1 atm of CO at 25 °C in d_6-benzene with 0.05 M **8**.
[b] Yields determined by *in situ* ^{1}H NMR analysis.

that the formation of esters **13** may proceed via the equilibrium generation CO-coordinated complex **12**.

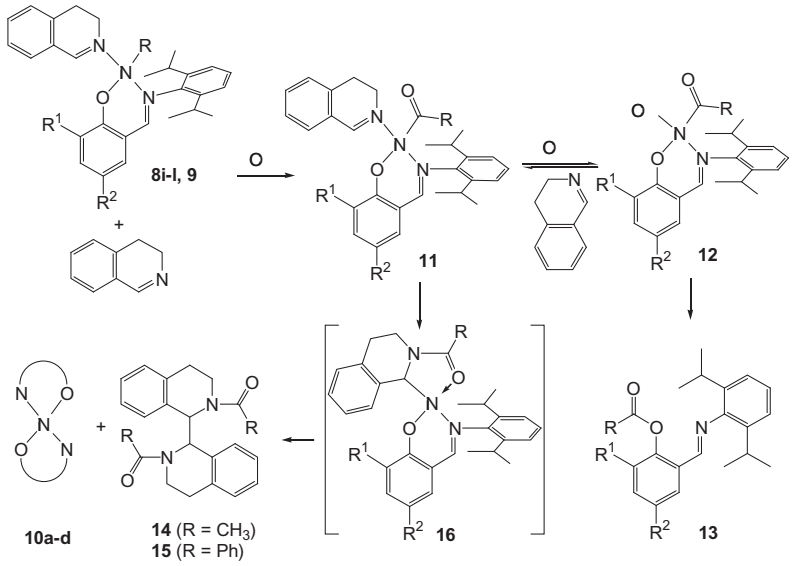
The lack of imine insertion with *in situ* generated nickel-acyl complexes **11a–l** may result from the lower electrophilicity of the acyl ligand inhibiting reaction with the imine [11]. However, it is also plausible that these bulky *trans*-disubstituted imines simply cannot complete with the less sterically encumbered phenolic unit for coupling with the nickel–acyl ligand. In considering the latter, we postulated that the less sterically encumbered *cis*-tethered imines in **11i–l** may be able to more effectively complete with ester formation. As shown in Table 5, the reaction of *in situ* generated nickel-acyl complex **11j** in the presence of 3,4-dihydroisoquinoline forms only small amounts of ester **13a** (14%, entry 1). In addition, a second organic product is observed forming in 77% yield, which has been characterized to be the 1,2-diamide **14**. 1,2-Diamide **14** formation presumably arises via the formation of an amide-bound nickel complex such as **16**, which can disproportionate to generate **14** and the observed nickel complex **10b** (80% yield). This disproportionation is analogous to established bimolecular coupling of nickel-alkyl ligands to form alkanes [22]. The other 3,4-dihydroisoquinoline complexes **8i**,**k**,**l** show similar results, with each forming 1,2-diamide **14** as the major product. The nickel-phenyl substituted complex **9** also forms the benzoyl-substituted diamide **15** (entry 9).

In order to further probe for the intermediacy of the imine insertion product **16** in diamide formation, the reaction of **8j** was monitored *in situ* by ^{1}H NMR spectroscopy in d_6-benzene. This shows the build-up of an intermediate to a maximum of 30% yield over the course of the reaction. This compound displays a new methyl resonance at δ 0.65 (s, 3H), and along with signals for both the salicylaldiminato and dihydroisoquinoline units.[2] However, the methine hydrogen in the dihydroisoquinoline is shifted upfield (δ 5.42, from δ 8.63 in **8j**), suggesting reduction of the C=N π-bond. The latter is similar to related signals of imine insertion products [11], and consistent with the preliminary assignment of this intermediate as the nickel-chelated amide complex **16j**. Further monitoring the reaction by ^{1}H NMR spectroscopy shows the disappearance of **16j** coincides with the growth of **14**. The disproportionation of complex **16j** to for the diamide could proceed via a number of pathways, including radical, ionic or bimetallic mechanisms. While at present we have no conclusive data on the mechanism of 1,2-diamide formation, it is notable that the addition of radical traps [23] does not alter product distribution, arguing against a radical pathway (Scheme 4).

The generation of 1,2-diamides **14** suggests that, provided the imine is sufficiently nucleophilic to compete with ester reductive

[2] NMR data for complex **16j**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.61 (s, 1H, *HC*=N), 5.42 (s, 1H, NiC(*H*)NCOCH$_3$), 4.05 (m, 2H, *CH*(CH$_3$)$_2$), 2.35-2.20 (m, 2H, NC*H*$_2$CH$_2$), 2.10-1.97 (m., 2H, NCH$_2$C*H*$_2$), 1.43 (d, 3H, CH(C*H*$_3$)$_2$), 1.28 (d, 3H, CH(C*H*$_3$)$_2$), 1.14–1.10 (m, 6H, CH(CH$_3$)$_2$), 0.65 (s, 3H, NiC(H)NCOC*H*$_3$).

Table 5
Imine Insertion with neutral nickel–acyl complexes.[a]



Entry	Cpd	R^1	R^2	[Imine] (M)	Yield **14** (**15**) (%)[b]	Yield **13** (%)	Yield **10** (%)
1	**8j**	H	H	0.15	77	14	80
2	**8i**	Ph	H	0.15	74	15	–[c]
3	**8k**	H	F	0.15	75	15	85
4	**8l**	H	NO_2	0.15	82	15	84
5	**8j**	H	H	0.50	97	3	95
6	**8i**	Ph	H	0.50	94	5	–[c]
7[d]	**8j**	H	H	0.15	63	28	72
8[e]	**8j**	H	H	0.15	40	53	–[f]
9	**9**	Ph	H	0.50	25	14	78

[a] General conditions: 1 atm of CO at 25 °C in d_6-benzene with 0.05 M of **8**.
[b] 1H NMR yield.
[c] Nickel complex is paramagnetic.
[d] 3 atm CO.
[e] d_3-Acetonitrile.
[f] Precipitates in acetonitrile.

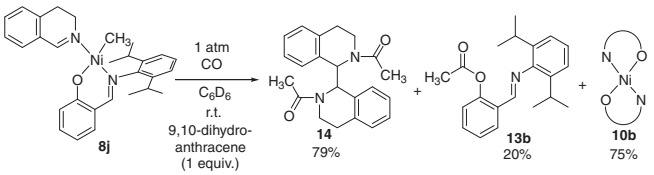
elimination, sequential CO/imine insertion is viable with neutral nickel complexes. It is notable that diamide formation, and the *in situ* generation of complex **16j**, are rapid relative to imine insertion with cationic palladium complexes (70 °C, 6 h) and similar in rate to what has been observed with cationic nickel complexes [8,11a]. The addition of excess imine increases the yield of diamide **14** (Table 5, entries 5, 6). Considering the dynamic equilibrium between **11** and **12**, this data suggests that imine insertion and 1,2-diamide product forms via imine-coordinated complexes **11**. Consistent with the latter, both increased CO pressure (entry 7), or more coordinating solvents (entry 8) favor reductive elimination to generate esters **13**.

3. Conclusions

In conclusion, we have found that neutral nickel complexes of the form (N^O)Ni(R)(R^2(H)C═NR^1) can be prepared, and undergo rapid insertion of carbon monoxide to afford the analogous nickel-acyl complexes. The latter is in dynamic equilibrium with the CO-coordinated (N^O)Ni($COCH_3$)(CO). The reductive elimination of the nickel–acyl and -phenolic ligands to form esters is the dominant reaction with bulky *trans*-disubstituted imines. However, with the *cis*-substituted 3,4-dihydroisoquinoline, imine insertion is quite rapid, leading to the formation of an intermediate (**16**) which ultimately disproportionates to form 1,2-diamides. Overall, this suggests that imine insertion into neutral nickel–acyl bonds is a viable process, and that inhibition of disproportionation could allow these products to be used in subsequent chemistry.

4. Experimental section

All manipulations were carried out in dried glassware under a dry, dioxygen-free (O_2), dinitrogen (N_2) atmosphere, using standard Schlenk or glovebox techniques and a Vacuum Atmosphere 553-2 drybox. Unless otherwise noted, all reagents were purchased from commercial sources and used without purification: carbon monoxide (Matheson, 99.98%), 9,10-dihydroanthracene (Aldrich, 97%), benzyl benzoate (Aldrich, 99 + %). All solvents were freshly distilled and de-gassed before use and stored under nitrogen over activated molecular sieves. Diethyl ether was distilled using sodium benzophenone. Pentane, benzene and toluene were distilled using CaH_2. Acetonitrile was distilled using P_4O_{10}. Deuterated solvents were dried as their protonated analogs, but vacuum



Scheme 4. Reaction of **8j** with CO in the presence of 9,10-dihydroanthracene.

transferred from the drying agent. Tolualdimines [24], 3,4-dihydroisoquinoline [25], (tmeda)Ni(CH_3)$_2$ [26], and (6-phenyl-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)Ni(Ph)(PPh_3) [19] were prepared via literature procedures. Salicylaldimines [16,19] and their salicylaldehyde precursors were also prepared as described in the literature.

Nuclear magnetic resonance (NMR) characterization was obtained on JEOL 270 MHz, Varian Mercury 200 MHz, 300 MHz, 400 MHz and Varian Unity 500 MHz spectrometers. Electrospray ionization-high resolution mass spectrometry (ESI-HRMS) analyses were preformed by Alain Lesimple, Ph.D. at the Department of Medicine, Mass Spectrometry Unit, McGill University, Montréal, Canada. **10b** [16], **14** and **15** [27] are previously reported compounds.

4.1. General procedure for the synthesis of nickel complexes **7** and **8**

(tmeda)Ni(CH_3)$_2$ (50.0 mg, 0.244 mmol) was dissolved in a 20 mL scintillation vial in benzene (5 mL) to give a yellow brown solution. In a separate vessel, imine (0.732 mmol) and salicylaldimine (0.244 mmol) were dissolved in benzene (10 mL) and the mixture was added to the nickel solution, dropwise, while stirring. The resulting dark red–brown mixture was left to stir at ambient temperature for 3 h. The solution was then filtered through Celite, the filtrate concentrated in vacuo, and the solid triturated with pentane (*ca.* 5 mL). The orange solid was collected by filtration and washed with pentane (3 × 2 mL) to afford orange powder product.

4.1.1. (6-Phenyl-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(pyridine) (**7**)

Yield: 60%. ^{1}H NMR (400 MHz, C_6D_6): δ 8.43 (d, 2H, J_{HH} = 8.2 Hz), 7.57 (s, 1H), 7.40–7.38 (m, 3H), 7.31–6.88 (m, 7H), 6.59 (br, 1H), 6.51 (t, 1H, $^2J_{HH}$ = 7.3 Hz), 6.13 (s, 2H), 4.20 (sept., 2H, J_{HH} = 6.6 Hz), 1.49 (d, 6H, J_{HH} = 6.6 Hz), 1.06 (d, 6H, J_{HH} = 6.6 Hz), −0.71 (s, 3H).

^{13}C NMR (500 MHz, C_6D_6): δ 166.4, 165.2, 151.8, 150.1, 141.1, 140.6, 135.4, 134.5, 133.8, 133.3, 131.8, 129.8, 127.4, 126.4, 125.6, 123.5, 122.9, 120.6, 114.0, 28.5, 24.8, 23.1, −7.5.

4.1.2. (6-Phenyl-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(N-methyltolualdimine) (**8a**)

Yield: 91%. ^{1}H NMR (300 MHz, C_6D_6): δ 9.47 (d, 2H, J_{HH} = 8.2 Hz), 7.61 (s, 1H), 7.55–7.52 (m, 2H), 7.35 (d, 1H, J_{HH} = 5.5 Hz), 7.10–6.89 (m, 9H), 6.86 (d, 1H, J_{HH} = 1.7 Hz), 6.45 (t, 1H, J_{HH} = 7.7 Hz), 4.22 (sept., 1H, J_{HH} = 6.9 Hz), 4.02 (sept., 1H, J_{HH} = 6.9 Hz), 3.35 (s, 3H), 2.03 (s, 3H), 1.51 (d, 3H, J_{HH} = 6.9 Hz), 1.35 (d, 3H, J_{HH} = 6.9 Hz), 1.19 (d, 3H, J_{HH} = 6.9 Hz), 1.04 (d, 3H, J_{HH} = 6.9 Hz), −1.09 (s, 3H).

^{13}C NMR (300 MHz, C_6D_6): δ 166.2, 165.4, 165.2, 149.9, 142.0, 141.2, 141.0, 140.7, 134.5, 133.9, 133.4, 131.8, 130.8, 129.8, 129.3, 127.3, 126.4, 126.0, 123.6, 123.4, 120.6, 114.0, 50.1, 28.5, 28.4, 25.3, 24.9, 23.4, 23.1, 21.5, −11.6.

ESI-HRMS: calculated for $C_{35}H_{41}N_2ONi^+$ (M+H$^+$) 563.25614; found 563.25585.

4.1.3. (2-((2,6-Diisopropylphenyl)iminomethyl)phenoxide)Ni(CH_3)(N-methyltolualdimine) (**8b**)

Yield: 81%. ^{1}H NMR (300 MHz, C_6D_6): δ 9.41 (d, 2H, J_{HH} = 8.0 Hz), 7.58 (s, 1H), 7.09–6.99 (m, 8H), 6.92 (d, 1H, J_{HH} = 7.0 Hz), 6.40 (t, 1H, J_{HH} = 7.0 Hz), 4.22 (sept., 1H, J_{HH} = 7.0 Hz), 4.04 (sept., 1H, J_{HH} = 7.0 Hz), 3.61 (s, 3H), 2.05 (s, 3H), 1.53 (d, 3H, J_{HH} = 6.6 Hz), 1.31 (d, 3H, J_{HH} = 7.0 Hz), 1.17 (d, 3H, J_{HH} = 7.0 Hz), 1.03 (d, 3H, J_{HH} = 6.6 Hz), −1.09 (s, 3H).

^{13}C NMR (300 MHz, C_6D_6): δ 168.4, 166.1, 165.8, 150.1, 141.8, 141.2, 141.0, 134.3, 134.1, 131.9, 131.0, 129.3, 126.4, 123.6, 123.4, 122.9, 119.9, 113.7, 50.3, 28.5, 28.4, 25.2, 24.8, 23.3, 23.1, 21.4, −11.2.

ESI-HRMS: calculated for $C_{29}H_{37}N_2ONi^+$ (M+H$^+$) 487.22518; found 487.22539.

4.1.4. (4-Fluoro-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(N-methyltolualdimine) (**8c**)

Yield: 73%. ^{1}H NMR (300 MHz, C_6D_6): δ 9.41 (d, 2H, J_{HH} = 8.2 Hz), 7.37 (s, 1H), 7.07–6.98 (m, 6H), 6.80–6.72 (m, 2H), 6.57 (dd, 1H, J_{HH} = 9.2 Hz, J_{HF} = 3.0 Hz), 4.16 (sept., 1H, J_{HH} = 6.9 Hz), 3.97 (sept., 1H, J_{HH} = 6.9 Hz), 3.56 (s, 3H), 2.04 (s, 3H), 1.51 (d, 3H, J_{HH} = 6.9 Hz), 1.30 (d, 3H, J_{HH} = 6.9 Hz), 1.14 (d, 3H, J_{HH} = 6.9 Hz), 1.02 (d, 3H, J_{HH} = 6.9 Hz), −1.09 (s, 3H).

^{13}C NMR (300 MHz, C_6D_6): δ 165.9, 165.1, 165.0, 154.2, 151.2, 149.8, 142.0, 140.9 (d, J_{CF} = 13.4 Hz), 131.7, 131.0, 129.3, 126.5, 123.8 (d, J_{CF} = 6.9 Hz), 123.5 (d, J_{CF} = 12.0 Hz), 123.1, 122.8, 117.9 (d, J_{CF} = 7.8 Hz), 116.2 (d, J_{CF} = 21.2 Hz), 50.3, 28.5, 28.4, 25.1, 24.8, 23.3, 23.1, 21.4, −10.9.

^{19}F NMR (400 MHz, C_6D_6): δ −137.9.

ESI-HRMS: calculated for $C_{29}H_{36}N_2ONiF^+$ (M+H$^+$) 505.21554; found 505.21597.

4.1.5. (4-Nitro-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(N-methyltolualdimine) (**8d**)

Yield: 83%. ^{1}H NMR (500 MHz, C_6D_6): δ 9.29 (d, 2H, J_{HH} = 7.8 Hz), 7.96 (s, 1H), 7.88 (dd, 1H, $^1J_{HH}$ = 9.6 Hz, $^2J_{HH}$ = 2.7 Hz), 7.22 (s, 1H), 7.09–6.92 (m, 6H), 6.46 (d, 1H, J_{HH} = 9.1 Hz), 4.02 (sept, 1H, J_{HH} = 6.9 Hz), 3.79 (sept, 1H, J_{HH} = 6.9 Hz), 3.42 (s, 3H), 2.03 (s, 3H), 1.48 (d, 3H, J_{HH} = 6.9 Hz), 1.27 (d, 3H, J_{HH} = 6.9 Hz), 1.08 (d, 3H, J_{HH} = 6.9 Hz), 0.99 (d, 3H, J_{HH} = 6.9 Hz), −1.05 (s, 3H).

^{13}C NMR (500 MHz, C_6D_6): δ 171.7, 166.6, 166.1, 161.5, 148.9, 142.4, 140.4, 140.3, 136.2, 131.9, 131.3, 130.7, 129.3, 129.2, 128.7, 128.4, 128.2, 128.0, 127.8, 126.7, 123.6, 123.5, 122.5, 118.4, 49.8, 48.0, 28.5, 28.4, 25.0, 24.6, 23.2, 22.9, 21.3, 21.2–10.2.

ESI-HRMS: calculated for $C_{29}H_{36}N_3O_3Ni^+$ (M+H$^+$) 532.21090; found 532.21047.

4.1.6. (6-Phenyl-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(N-benzyltolualdimine) (**8e**)

Yield: 88%. ^{1}H NMR (500 MHz, C_6D_6): δ 9.57 (d, 2H, J_{HH} = 7.3 Hz), 7.57 (s, 1H), 7.51 (s, 2H), 7.33 (d, 1H, J_{HH} = 7.3 Hz), 7.10–7.02 (m, 11H), 6.93 (d, 2H, J_{HH} = 6.4 Hz), 6.85 (d, 2H, J_{HH} = 6.9 Hz), 6.43 (t, 1H, J_{HH} = 7.3 Hz), 5.14 (d, 1H, $^2J_{HH}$ = 15.1 Hz), 4.82 (d, 1H, $^2J_{HH}$ = 15.1 Hz), 4.03 (sept., 2H, J_{HH} = 6.4 Hz), 2.03 (s, 3H), 1.42 (d, 3H, $^2J_{HH}$ = 6.9 Hz), 1.40 (d, 3H, $^2J_{HH}$ = 6.9 Hz), 1.19 (d, 3H, J_{HH} = 6.9 Hz), 1.06 (d, 3H, J_{HH} = 6.9 Hz), −1.10 (s, 3H).

^{13}C NMR (500 MHz, C_6D_6): δ 166.1, 165.0, 164.8, 161.1, 149.8, 142.0, 141.1, 140.9, 135.7, 134.3, 133.7, 133.6, 132.0, 130.9, 130.6, 129.9, 129.4, 129.2, 128.6, 127.9, 127.4, 126.9, 126.3, 125.8, 123.4, 123.3, 120.3, 113.7, 65.7, 65.1, 28.3, 25.2, 24.9, 23.3, 23.1, 22.6, 21.4, 21.2, −11.1.

ESI-HRMS: calculated for $C_{41}H_{45}N_2ONi^+$ (M+H$^+$) 639.28774; found 639.28799.

4.1.7. (2-((2,6-Diisopropylphenyl)iminomethyl)phenoxide)Ni(CH_3)(N-benzyltolualdimine) (**8f**)

Yield: 76%. ^{1}H NMR (500 MHz, C_6D_6): δ 9.39 (d, 2H, J_{HH} = 7.8 Hz), 7.55 (s, 1H), 7.37 (d, 1H, J_{HH} = 6.9 Hz), 7.13–6.96 (m, 11H), 6.92 (d, 2H, J_{HH} = 6.4 Hz), 6.42 (t, 1H, J_{HH} = 6.9 Hz), 5.40 (d, 1H, $^2J_{HH}$ = 14.2 Hz), 4.97 (d, 1H, $^2J_{HH}$ = 14.2 Hz), 4.00 (sept., 1H, $^2J_{HH}$ = 6.9 Hz), 3.94 (sept., 1H, $^2J_{HH}$ = 6.9 Hz), 2.03 (s, 3H), 1.34 (d, 3H, $^2J_{HH}$ = 6.9 Hz), 1.32 (d, 3H, $^2J_{HH}$ = 6.9 Hz), 1.13 (d, 3H, J_{HH} = 6.9 Hz), 1.05 (d, 3H, J_{HH} = 6.9 Hz), −1.27 (s, 3H).

^{13}C NMR (500 MHz, C_6D_6): δ 168.1, 166.1, 165.4, 149.8, 141.8, 141.1, 140.9, 136.6, 134.2, 134.0, 132.1, 131.0, 130.4, 129.4, 129.1, 128.7, 126.9, 126.2, 123.4, 123.2, 122.8, 119.8, 113.6, 66.4, 28.2, 25.2, 25.0, 23.3, 23.2, 21.4, −9.9.

ESI-HRMS: calculated for $C_{35}H_{41}N_2ONi^+$ ($M+H^+$) 563.25689; found 563.25669.

*4.1.8. (4-Fluoro-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(N-benzyltolualdimine) (**8g**)*

Yield: 74%. ^{1}H NMR (200 MHz, C_6D_6): δ 9.38 (d, 2H, J_{HH} = 7.3 Hz), 7.34 (s, 1H), 7.06–7.00 (m, 11H), 6.80–6.72 (m, 2H), 6.57 (d, 1H, J_{HH} = 7.3 Hz), 5.32 (d, 1H, $^2J_{HH}$ = 14.3 Hz), 4.91 (d, 1H, $^2J_{HH}$ = 14.3 Hz), 3.91 (sept., 2H, J_{HH} = 7.3 Hz), 2.03 (s, 3H), 1.31 (t, 6H, J_{HH} = 7.7 Hz), 1.10 (d, 3H, $^2J_{HH}$ = 6.6 Hz), 1.05 (d, 3H, $^2J_{HH}$ = 6.6 Hz), −1.26 (s, 3H).

^{13}C NMR (300 MHz, C_6D_6): δ 165.5, 165.1, 164.7, 153.5, 151.7, 149.6, 141.9, 140.8 (d, J_{CF} = 28.7 Hz), 136.5, 132.0, 131.0, 130.4, 129.1, 128.7, 128.4, 126.3, 123.7, 123.3 (d, J_{CF} = 17.7 Hz), 122.8 (d, J_{CF} = 24.4 Hz), 117.7, 116.2 (d, J_{CF} = 21.1 Hz), 66.4, 28.2, 25.1, 24.9, 23.3, 23.2, 21.4, −9.8.

^{19}F NMR (400 MHz, C_6D_6): δ −132.9.

ESI-HRMS: calculated for $C_{35}H_{40}N_2ONiF^+$ ($M+H^+$) 581.24635; found 581.24727.

*4.1.9. (4-Nitro-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(N-benzyltolualdimine) (**8h**)*

Yield: 87%. ^{1}H NMR (300 MHz, C_6D_6): δ 9.31 (d, 2H, J_{HH} = 8.2 Hz), 7.95–7.90 (m, 2H), 7.32–7.30 (m, 3H), 7.14–6.94 (m, 9H), 6.40 (d, 1H, J_{HH} = 10.4 Hz), 4.98 (d, 1H, $^2J_{HH}$ = 14.0 Hz), 4.77 (d, 1H, $^2J_{HH}$ = 14.0 Hz), 3.78 (sept., 1H, J_{HH} = 6.9 Hz), 3.69 (sept., 1H, J_{HH} = 6.9 Hz), 2.01 (s, 3H), 1.32–1.26 (m, 6H), 1.03 (d, 3H, J_{HH} = 6.9 Hz), 0.99 (d, 3H, J_{HH} = 6.9 Hz), −1.19 (s, 3H).

^{13}C NMR (300 MHz, C_6D_6): δ 171.6, 166.2, 148.9, 142.6, 140.6, 140.3, 136.2, 131.9, 131.7, 131.0, 130.4, 129.3, 128.8, 128.7, 127.9, 126.7, 123.6, 123.5, 122.6, 118.4, 66.7, 28.4, 25.1, 24.9, 23.4, 23.3, 21.5, −9.2.

ESI-HRMS: calculated for $C_{35}H_{40}N_3O_3Ni^+$ ($M+H^+$) 608.24184; found 608.24177.

*4.1.10. (6-Phenyl-2-((2,6-diisopropylphenyl)iminomethyl)-phenoxide)Ni(CH_3)(3,4-dihydroisoquinoline) (**8i**)*

Yield: 89%. ^{1}H NMR (400 MHz, C_6D_6): δ 8.27 (s, 1H), 7.59–7.57 (m, 3H), 7.41 (dd, 2H, $^1J_{HH}$ = 4.9 Hz, $^2J_{HH}$ = 2.2 Hz), 7.14–7.05 (m, 3H), 6.92–6.72 (m, 6H), 6.52–6.47 (m, 3H), 4.18 (sept., 2H, J_{HH} = 6.9 Hz), 3.58 (t, 2H, J_{HH} = 6.3 Hz), 1.91 (t, 2H, J_{HH} = 8.0 Hz), 1.52 (d, 6H, J_{HH} = 6.9 Hz), 1.07 (d, 6H, J_{HH} = 6.9 Hz), −0.74 (s, 3H).

^{13}C NMR (300 MHz, C_6D_6): δ 166.4, 165.3, 164.5, 150.2, 141.1, 141.0, 135.8, 134.5, 133.9, 133.5, 131.7, 129.9, 128.2, 127.9, 127.5, 127.2, 126.9, 126.5, 125.8, 123.6, 120.8, 113.9, 49.8, 28.5, 25.3, 24.9, 23.2, −9.8.

ESI-HRMS: calculated for $C_{35}H_{38}N_2ONi^+$ (M^+) 560.23376; found 560.23391.

*4.1.11. (2-((2,6-Diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(3,4-dihydroisoquinoline) (**8j**)*

Yield: 81%. ^{1}H NMR (300 MHz, C_6D_6): δ 8.43 (s, 1H), 7.53 (s, 1H), 7.18 (dt, 1H, $^1J_{HH}$ = 5.2 Hz, $^2J_{HH}$ = 1.6 Hz), 7.09–7.06 (m, 3H), 7.00 (d, 1H, J_{HH} = 8.5 Hz), 6.91 (dd, 1H, $^1J_{HH}$ = 7.3 Hz, $^2J_{HH}$ = 1.6 Hz), 6.84 (t, 1H, J_{HH} = 7.1 Hz), 6.72 (t, 1H, J_{HH} = 7.1 Hz), 6.53–6.42 (m, 3H), 4.16 (sept., 2H, J_{HH} = 6.9 Hz), 3.78 (t, 2H, J_{HH} = 7.4 Hz), 2.10 (t, 2H, J_{HH} = 7.7 Hz), 1.51 (d, 6H, J_{HH} = 6.9 Hz), 1.04 (d, 6H, J_{HH} = 6.9 Hz), −0.73 (s, 3H).

^{13}C NMR (300 MHz, C_6D_6): δ 168.1, 166.1, 164.3, 150.3, 141.2, 135.7, 134.3, 134.1, 131.8, 127.3, 127.1, 126.4, 123.6, 122.9, 120.1, 113.7, 49.8, 28.5, 25.7, 24.9, 23.2, −9.1.

ESI-HRMS: calculated for $C_{29}H_{34}N_2ONi^+$ (M^+) 484.20246; found 484.20286.

*4.1.12. (4-Fluoro-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(3,4-dihydroisoquinoline) (**8k**)*

Yield: 78%. ^{1}H NMR (500 MHz, C_6D_6): δ 8.39 (s, 1H), 7,33 (s, 1H), 7.10–7.05 (m, 3H), 6.90 (dt, 1H, $^1J_{HH}$ = 4.6 Hz, $^2J_{HF}$ = 1.4 Hz), 6.83 (dt, 1H, $^1J_{HH}$ = 8.7 Hz, $^2J_{HF}$ = 1.4 Hz), 6.76–6.70 (m, 2H), 6.57 (dd, 1H, $^1J_{HH}$ = 8.9 Hz, $^2J_{HF}$ = 3.2 Hz), 6.51 (d, 1H, J_{HH} = 6.9 Hz), 6.46 (d, 1H, J_{HH} = 7.3 Hz), 4.10 (sept., 2H, J_{HH} = 6.9 Hz), 3.73 (t, 2H, J_{HH} = 7.8 Hz), 2.08 (t, 2H, J_{HH} = 7.8 Hz), 1.50 (d, 6H, J_{HH} = 6.9 Hz), 1.03 (d, 6H, J_{HH} = 6.9 Hz), −0.73 (s, 3H).

^{13}C NMR (500 MHz, C_6D_6): δ 165.1, 164.6, 164.3, 153.5, 151.7, 150.0, 140.8, 135.6, 131.7, 127.1 (d, J_{CF} = 24.5 Hz), 126.4, 123.7, 123.6, 123.5, 123.0, 122.8 (d, J_{CF} = 24.0 Hz), 118.0 (d, J_{CF} = 8.2 Hz), 116.3 (d, J_{CF} = 21.6 Hz), 49.7, 29.1, 28.4, 25.5, 24.7, 24.3, 23.6, 23.1, −9.0.

^{19}F NMR (400 MHz, C_6D_6): δ −132.6.

ESI-HRMS: calculated for $C_{29}H_{33}FN_2ONi^+$ (M^+) 502.19304; found 502.19362.

*4.1.13. (4-Nitro-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-Ni(CH_3)(3,4-dihydroisoquinoline) (**8l**)*

Yield: 92%. ^{1}H NMR (500 MHz, C_6D_6): δ 8.21 (s, 1H), 8.04 (d, 1H, J_{HH} = 9.2 Hz), 7.98 (s, 1H), 7.18–7.02 (m, 4H), 6.84 (t, 1H, J_{HH} = 6.9 Hz), 6.71 (t, 1H, J_{HH} = 7.3 Hz), 6.50–6.45 (m, 3H), 3.96 (sept., 2H, J_{HH} = 6.4 Hz), 3.59 (t, 2H, J_{HH} = 7.8 Hz), 2.03 (t, 2H, J_{HH} = 8.2 Hz), 1.47 (d, 6H, J_{HH} = 6.4 Hz), 1.00 (d, 6H, J_{HH} = 6.4 Hz), −0.70 (s, 3H).

^{13}C NMR (500 MHz, C_6D_6): δ 171.5, 166.1, 164.8, 149.2, 140.4, 136.2, 135.5, 132.1, 131.9, 128.7, 127.7, 127.2, 127.1, 126.8, 123.6, 122.5, 118.5, 49.6, 28.5, 25.4, 24.6, 23.1, −8.2.

ESI-HRMS: calculated for $C_{29}H_{33}N_3NiO_3^+$ (M^+) 529.18754; found 529.18743.

*4.2. Synthesis of complex **9***

(6-Phenyl-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)Ni(Ph)(PPh_3) (150.0 mg, 0.199 mmol) and 3,4-dihydroisoquinoline (31.4 mg, 0.239 mmol) were dissolved in benzene (*ca.* 10 mL). In a second vessel, a slurry of CuCl (29.6 mg, 0.239 mmol) in benzene (*ca.* 2 mL) was prepared, and added to the mixture with stirring. After 30 min at room temperature, the solution was filtered through Celite. The filtrate was concentrated in vacuo, then dissolved in minimal pentane for crystallization at −40 °C. Yellow crystals were then collected by filtration and washed with cold pentane (3 × 2 mL) (104.2 mg, 84% yield).

^{1}H NMR (400 MHz, C_6D_6): δ 8.35 (s, 1H), 7.67–7.59 (m, 5H), 7.42 (d, 2H, J_{HH} = 4.9 Hz), 6.93–6.39 (m, 13H), 4.13 (sept., 2H, J_{HH} = 6.9 Hz), 3.42 (t, 2H, J_{HH} = 6.3 Hz), 1.81 (t, 2H, J_{HH} = 6.6 Hz), 1.39 (d, 6H, J_{HH} = 6.9 Hz), 1.01 (d, 6H, J_{HH} = 6.9 Hz).

^{13}C NMR (300 MHz, C_6D_6): δ 167.5, 165.1, 164.8, 150.9, 150.8, 140.7, 140.6, 136.7, 135.8, 134.8, 134.7, 134.5, 134.1, 133.8, 133.7, 133.5, 131.9, 129.9, 129.7, 128.8, 128.7, 128.2, 127.5, 127.1, 126.8, 126.4, 125.0, 124.9, 123.0, 122.2, 120.7, 114.4, 49.8, 28.8, 25.6, 25.2, 22.8.

ESI-HRMS: calculated for $C_{40}H_{40}N_2NiO^+$ (M^+) 622.24941; found 622.24933.

*4.3. Stability of complexes **8e**–**h** in benzene*

A typical experiment is as follows. A.J. Young tube was charged with a 0.02 M solution of nickel complex **8e** (6.4 mg, 0.010 mmol) in C_6D_6 (0.50 mL). Benzyl benzoate was added as the internal standard. The formation of *bis*-salicylaldiminatonickel(II) complexes **10a** was monitored by ^{1}H NMR spectroscopy at 25 °C. The decomposition time was determined by measuring both the disappearance of **8e** and the appearance of uncoordinated imine.

*4.3.1. Bis(6-phenyl-2-((2,6-diisopropylphenyl)iminomethyl)-phenoxide)nickel (**10a**) [16]*

Due to the paramagnetic nature of this complex, NMR characterization could not be achieved.

ESI-HRMS: calculated for $C_{50}H_{53}N_2O_2Ni^+$ ($M+H^+$) 771.34593; found 771.34550.

*4.3.2. Bis(2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)nickel (**10b**)*

^{1}H NMR (300 MHz, C_6D_6): δ 7.19 (t, 2H, J_{HH} = 2.1 Hz), 7.06 (m, 6H), 6.75 (t, 2H, J_{HH} = 4.9 Hz), 6.65 (d, 2H, J_{HH} = 6.4 Hz), 6.22 (t, 2H, J_{HH} = 6.7 Hz), 5.92 (d, 2H, J_{HH} = 8.5 Hz), 4.38 (sept., 4H, J_{HH} = 6.7 Hz), 1.46 (d, 12H, J_{HH} = 7.0 Hz), 1.11 (d, 12H, J_{HH} = 7.0 Hz).

^{13}C NMR (300 MHz, C_6D_6): δ 164.6, 164.2, 146.4, 142.3, 134.4, 132.8, 126.3, 123.1, 121.5, 119.7, 115.2, 29.3, 24.4, 23.7.

ESI-HRMS: calculated for $C_{38}H_{45}N_2O_2Ni^+$ ($M+H^+$) 619.28288; found 619.28290.

*4.3.3. Bis(4-fluoro-2-((2,6-diisopropylphenyl)iminomethyl)-phenoxide)nickel (**10c**)*

^{1}H NMR (300 MHz, C_6D_6): δ 7.16 (t, 2H, J_{HH} = 7.7 Hz), 7.00 (d, 4H, J_{HH} = 7.7 Hz), 6.82 (s, 2H), 6.47 (dt, 2H, J_{HH} = 8.7 Hz, J_{HF} = 3.0 Hz), 6.28 (dd, 2H, J_{HH} = 8.7 Hz, J_{HF} = 3.0 Hz), 5.69 (dd, 2H, J_{HH} = 9.2 Hz, J_{HF} = 4.4 Hz), 4.28 (sept., 4H, J_{HH} = 6.7 Hz), 1.43 (d, 12H, J_{HH} = 6.9 Hz), 1.09 (d, 12H, J_{HH} = 6.9 Hz).

^{13}C NMR (300 MHz, C_6D_6): δ 163.9, 160.6, 155.0, 151.9, 146.0, 142.0, 126.5, 123.2, 123.1, 122.9, 122.3 (d, J_{CF} = 7.4 Hz), 118.1 (d, J_{CF} = 8.3 Hz), 115.5 (d, J_{CF} = 22.1 Hz), 29.3, 24.3, 23.7.

^{19}F NMR (400 MHz, C_6D_6): δ −130.4.

ESI-HRMS: calculated for $C_{38}H_{43}N_2O_2NiF_2^+$ ($M+H^+$) 655.26400; found 655.26406.

*4.3.4. Bis(4-nitro-2-((2,6-diisopropylphenyl)iminomethyl)phenoxide)-nickel (**10d**)*

^{1}H NMR (300 MHz, C_6D_6): δ 7.57 (d, 2H, J_{HH} = 2.7 Hz), 7.45 (dd, 2H, $J_{HH}{}^1$ = 9.2 Hz, $J_{HH}{}^2$ = 2.7 Hz), 7.14 (m, 4H), 6.95 (m, 4H), 6.56 (s, 2H), 4.00 (sept., 4H, J_{HH} = 7.0 Hz), 1.35 (d, 12H, J_{HH} = 7.0 Hz), 1.06 (d, 12H, J_{HH} = 7.0 Hz).

^{13}C NMR (300 MHz, C_6D_6): δ 167.4, 165.0, 144.7, 141.6, 137.8, 130.5, 129.0, 127.1, 118.0, 29.3, 24.1, 23.5.

ESI-HRMS: calculated for $C_{38}H_{42}N_4O_6NiNa^+$ ($M+Na^+$) 731.23506; found 731.23501.

*4.4. Reactions of **8** with carbon monoxide*

A 25 mL reaction bomb was charged with the appropriate amount of complex **8** (0.0618 mmol) and imine (0.185 mmol) dissolved in benzene (10 mL). The solution was placed under 1 atm of carbon monoxide and stirred at ambient temperature for 5 h. The carbon monoxide atmosphere was removed by a freeze–pump–thaw process. The resulting solution was concentrated in vacuo and then stirred in acetonitrile, causing the *bis*-salicylaldiminatonickel complex **10** to precipitate. The solids were removed by filtration and the filtrate was concentrated in vacuo. Purification of the organic products was achieved via silica gel chromatography using a 60:40 hexanes/dichloromethane mixture as the eluent. When 3,4-dihydroisoquinoline is the reaction substrate, a mixture of 60:40 hexanes/dichloromethane incorporating 3% triethylamine and 3% methanol was used as the eluent.

*4.4.1. Acetic acid 3-((2,6-diisopropylphenyl)iminomethyl)-biphenyl-2-yl ester (**13a**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.18 (dd, 1H, $^1J_{HH}$ = 8.2 Hz, $^2J_{HH}$ = 1.6 Hz), 7.55–7.36 (m, 6H), 7.18–7.10 (m, 4H), 2.96 (sept., 2H, J_{HH} = 6.9 Hz), 1.98 (s, 3H), 1.16 (d, 12H, J_{HH} = 6.9 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ 169.0, 157.5, 149.3, 148.0, 137.6, 137.1, 136.2, 133.7, 128.9, 128.4, 127.9, 127.8, 126.7, 124.3, 123.1, 27.9, 23.5, 20.5.

ESI-HRMS: calculated for $C_{27}H_{30}NO_2^+$ ($M+H^+$) 400.22686; found 400.22711

*4.4.2. Acetic acid 2-((2,6-diisopropylphenyl)iminomethyl)-phenyl ester (**13b**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.17 (dd, 1H, $^1J_{HH}$ = 7.9 Hz, $^2J_{HH}$ = 1.5 Hz), 7.53 (dt, 1H, $^1J_{HH}$ = 7.3 Hz, $^2J_{HH}$ = 1.8 Hz), 7.39 (t, 1H, J_{HH} = 6.2 Hz), 7.19–7.12 (m, 4H), 2.95 (sept., 2H, J_{HH} = 7.0 Hz), 2.27 (s, 3H), 1.16 (d, 12H, J_{HH} = 7.0 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ 169.0, 157.2, 150.6, 149.3, 137.6, 132.1, 128.7, 128.0, 126.4, 124.3, 123.1, 123.0, 27.8, 23.4, 20.7.

ESI-HRMS: calculated for $C_{21}H_{26}NO_2^+$ ($M+H^+$) 324.19577; found 324.19581.

*4.4.3. Acetic acid 2-((2,6-diisopropylphenyl)iminomethyl)-4-fluoro-phenyl ester (**13c**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, 1H, J_{HF} = 2.2 Hz), 7.90 (dd, 1H, $^1J_{HH}$ = 8.9 Hz, $^2J_{HH}$ = 3.0 Hz), 7.26–7.13 (m, 5H), 2.92 (sept., 2H, J_{HH} = 6.9 Hz), 2.28 (s, 3H), 1.17 (d, 12H, J_{HH} = 6.9 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ 169.2, 162.1, 158.9, 156.1, 148.9, 146.5, 137.5, 129.6 (d, J_{CF} = 7.8 Hz), 124.6 (d, J_{CF} = 5.1 Hz), 124.5, 123.1, 119.0 (d, J_{CF} = 23.5 Hz), 114.4 (d, J_{CF} = 24.4 Hz), 27.9, 23.5, 20.7.

^{19}F NMR (400 MHz, $CDCl_3$): δ −115.3 (s).

ESI-HRMS: calculated for $C_{21}H_{25}NO_2F^+$ ($M+H^+$) 342.18631; found 342.18638.

*4.4.4. Acetic acid 2-((2,6-diisopropylphenyl)iminomethyl)-4-nitro-phenyl ester (**13d**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.05 (d, 1H, J_{HH} = 2.9 Hz), 8.37 (dd, 1H, $^1J_{HH}$ = 9.0 Hz, $^2J_{HH}$ = 2.9 Hz), 8.32 (s, 1H), 7.40 (d, 1H, J_{HH} = 8.8 Hz), 7.17 (s, 3H), 2.90 (sept., 2H, J_{HH} = 7.0 Hz), 2.32 (s, 3H), 1.17 (d, 12H, J_{HH} = 7.0 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ 168.2, 155.2, 154.6, 148.6, 146.1, 137.5, 129.2, 126.7, 124.9, 124.3, 124.2, 123.2, 28.0, 23.5, 20.8.

ESI-HRMS: calculated for $C_{21}H_{25}N_2O_4^+$ ($M+H^+$) 369.18077; found 369.18088.

*4.4.5. Benzoic acid 3-((2,6-diisopropylphenyl)iminomethyl)-biphenyl-2-yl ester (**13e**)*

^{1}H NMR (400 MHz, C_6D_6): δ 8.58 (s, 1H), 8.40 (d, 1H, J_{HH} = 8.1 Hz), 7.89 (d, 2H, J_{HH} = 7.0 Hz), 7.39 (d, 2H, J_{HH} = 7.0 Hz), 7.26 (d, 1H, J_{HH} = 7.7 Hz), 7.09–6.89 (m, 8H), 6.83 (t, 2H, J_{HH} = 7.7 Hz), 3.23 (sept., 2H, J_{HH} = 7.0 Hz), 1.13 (d, 12H, J_{HH} = 7.0 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ 164.8, 157.2, 149.2, 137.6, 136.9, 136.3, 133.8, 133.6, 130.0, 129.2, 128.9, 128.5, 128.4, 128.3, 127.7, 127.6, 124.2, 123.0, 27.8, 23.5.

ESI-HRMS: calculated for $C_{32}H_{32}NO_2^+$ ($M+H^+$) 462.24245; found 462.24276.

*4.4.6. Meso-N,N′-diacyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline (**14a**) [27]*

^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): (two conformers: A *ca.* 67%, and B *ca.* 33%) δ 7.56 (d, 2H, J_{HH} = 7.1 Hz, A), 7.30–7.07 (m, 10H), 7.01–6.94 (m, 2H), 6.47 (d, 2H, J_{HH} = 7.7 Hz, A), 6.03 (s, 2H, B), 5.86 (d, 2H, J_{HH} = 5.2 Hz, A), 5.36 (d, 2H, J_{HH} = 5.0 Hz, B), 4.89 (s, 2H, B), 4.62–4.53 (dt, $^1J_{HH}$ = 11.8 Hz, $^2J_{HH}$ = 5.2 Hz, B), 4.41–4.36 (m, 2H, A), 3.94–3.87 (m, 2H), 3.66–3.51 (m, 4H), 3.36–3.28 (m, 2H), 3.12–2.95 (m, 4H), 2.94–2.68 (m, 8H), 2.58–2.52 (m, 2H), 2.39–2.25 (m, 2H), 2.10 (d, 6H, J_{HH} = 11.5 Hz, A), 1.81 (s, 3H, B).

^{13}C NMR (300 MHz, C_6D_6): δ 171.2, 170.6, 170.5, 170.4, 135.6, 135.0, 134.9, 134.7, 134.5, 133.7, 133.5, 133.1, 129.2, 128.7,

128.4, 128.2, 127.7, 127.5, 127.4, 126.9, 126.8, 126.5, 126.1, 60.7, 60.1, 59.4, 57.2, 44.0, 42.4, 38.0, 36.6, 28.9, 28.8, 28.0, 27.9, 22.6, 22.4, 21.1, 21.0.

ESI-HRMS: calculated for $C_{22}H_{24}N_2O_2Na^+$ ($M+Na^+$) 371.17354; found 371.17268.

*4.4.7. Dl-N,N′-diacyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline (**14b**) [27]*

^{1}H NMR (400 MHz, C_6D_6): δ 6.96 (t, 2H, J_{HH} = 7.3 Hz), 6.90 (d, 2H, J_{HH} = 7.3 Hz), 6.65 (t, 2H, J_{HH} = 7.3 Hz), 5.99 (d, 2H, J_{HH} = 7.3 Hz), 5.69 (s, 2H), 3.84–3.79 (m, 2H), 3.67–3.59 (m, 2H), 2.81 (dt, 2H, $^1J_{HH}$ = 10.6 Hz, $^2J_{HH}$ = 5.9 Hz), 2.40 (dt, 2H, $^1J_{HH}$ = 15.7 Hz, $^2J_{HH}$ = 5.5 Hz), 1.79 (s, 6H).

^{13}C NMR (300 MHz, C_6D_6): δ 170.8, 135.4, 134.3, 129.7, 127.6, 127.5, 127.4, 125.3, 57.0, 44.2, 28.0, 22.3.

ESI-HRMS: calculated for $C_{22}H_{24}N_2O_2Na^+$ ($M+Na^+$) 371.17354; found 371.17273.meso, dl-*N*,*N*′-dibenzoyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline (**15**) [27a].

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.07 (m, 22H, *meso* & *dl*), 7.00 (d, 2H, J_{HH} = 6.9 Hz, *meso*), 6.93 (d, J_{HH} = 6.9 Hz, *meso*), 6.75 (d, 2H, J_{HH} = 6.9 Hz, *dl*), 6.69 (d, 2H, J_{HH} = 6.4 Hz, *dl*), 6.48 (s, 2H, *dl*), 6.41 (d, 2H, J_{HH} = 6.0 Hz, *dl*), 6.08 (d, 2H, J_{HH} = 7.8 Hz, meso), 5.25 (d, 2H, J_{HH} = 7.3 Hz, *meso*), 5.07 (s, 2H, *meso*), 4.54–4.37 (m, 2H, *dl*), 3.64–3.55 (m, 4H, *meso & dl*), 3.34–3.15 (m, 5H, *meso & dl*), 2.93–2.75 (m, 5H, *meso & dl*), 2.53–2.35 (m, 2H, *dl*).

^{13}C NMR (500 MHz, $CDCl_3$): δ 171.6, 171.3, 170.7, 137.1, 136.3, 135.9, 135.4, 134.4, 134.1, 133.6, 133.3, 129.6, 129.5, 129.4, 129.3, 129.0, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9, 127.5, 127.0, 126.9, 126.8, 126.7, 126.5, 126.5, 126.2, 126.0, 61.3, 60.1, 57.5, 55.1, 43.0, 38.5, 38.1, 29.2, 28.7, 27.6, 27.1.

ESI-HRMS: calculated for $C_{32}H_{28}N_2O_2Na^+$ ($M+Na^+$) 495.20430; found 495.20489.

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Appendix A. Supplementary material

^{1}H and ^{13}C NMR spectra of isolated products are available. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.024

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