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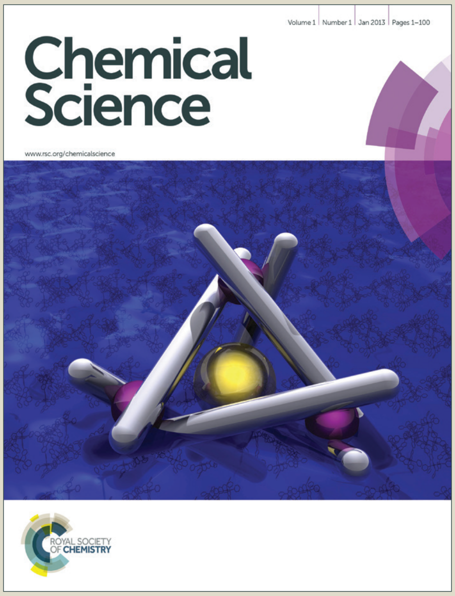

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ARTICLE

Transmethylation of a Four-Coordinate Nickel(I) Monocarbonyl Species with Methyl Iodide

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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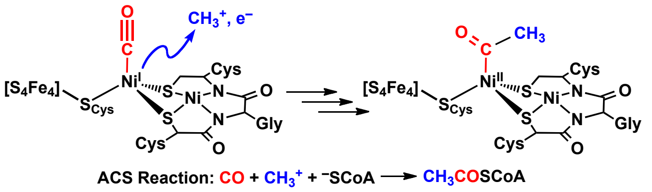
Three distinct oxidation states of nickel carbonyl species, formally Ni(II), +1 and 0, (compound **1**, **2** and **3**) have been realized using the (PNP)Ni scaffold ($PNP^- = N[2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3]_2^-$). X-ray diffraction studies of these carbonyl complexes show a geometrical change about the nickel center from square planar (**1**) to pyramidal (**2**) and pseudotetrahedral (**3**). Interestingly, the Ni-C bond distance of **2** is longer than that of **1** and **3** due to the electron population of the antibonding d_{x2-y2} orbital. Different reactivity of these nickel carbonyl species was clearly observed. Reaction of the monovalent nickel carbonyl species (**2**) with CH_3I revealed the formation of $(PNP)NiCOCH_3$ (**4**) via C-C bond coupling while the zerovalent congener (**3**) showed the oxidative ligand substitution reaction.

Introduction

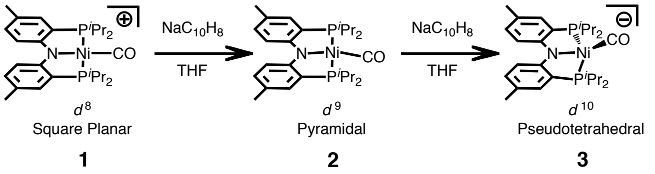
Carbon monoxide is a key natural small molecule utilized in various organometallic reactions. In particular, numerous carbonylation reactions mediated by transition metal catalysts are widely used in industrial processes such as hydroformylation and the Monsanto Process.[1] As those processes commonly employ rare and expensive transition metals such as Rh, Ru and Ir,[1] the utilization of an earth-abundant transition metals is recently drawing much attention due to its potential economic advantages. For the group 10 elements, while important examples of catalytic carbonylation employing Pd and Pt are acknowledged, there are some cases that involve a zero-valent nickel species.[2] In fact, nickel(I) monocarbonyl species are relatively uncommon and its reactivity is therefore, still unexplored *vide infra*. Monovalent nickel species are suggested to play an important role in the chemical and electrochemical catalytic C-C bond formation of various organic substrates.[3] In fact, biological transmethylation occurs via the formation of a nickel-monocarbonyl species at the active site of acetyl-CoA synthase (ACS) (Scheme 1).[4]



Scheme 1 The active site of acetyl-CoA synthase (ACS) and its C-C bond formation reaction.

The nickel(I)-CO species has been proposed as a potential active species in the so-called "paramagnetic mechanism".[4] According to this mechanism transmethylation occurs at the nickel(I) site between a carbonyl ligand and a methyl cation transferred from CH_3-cob(III)alamin.[4] However, the chemical validity has not been evaluated in terms of the reactivity of monovalent nickel monocarbonyl adducts. With these in mind, we are interested in generating a series of low-valent nickel monocarbonyl species where we can investigate their chemical validity in C-C bond formation with iodoalkanes.

Here, we report three distinct oxidation states of nickel monocarbonyl, formally Ni(I) and Ni(0) along with a previously reported divalent nickel monocarbonyl adduct (**1**) supported by an anionic pincer-type PNP ligand ($PNP^- = N[2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3]_2$) (Scheme 2).[5] The geometrical and electronic differences of these carbonyl complexes have been explored via XRD crystallography with a theoretical evaluation using DFT calculations. Those three carbonyl species show different products from the reaction with iodoalkanes. Under treatment of methyl iodide, a monovalent (PNP)NiCO (**2**) reveals C-C bond formation while a nickel(0) monocarbonyl species (**3**) favors ligand substitution. This is the first case where the methylation of a monovalent nickel carbonyl species results in a nickel acetyl formation.



Scheme 2 Synthesis of cationic $\{Ni\text{-}CO\}^+$ (**1**), neutral Ni-CO (**2**) and anionic $\{Ni\text{-}CO\}^-$ (**3**) species.

Results and discussion

I. Syntheses of Nickel(I/0) Monocarbonyl Complexes

In order to establish the low-valent chemistry of a nickel monocarbonyl species, we decided to utilize a (PNP)Ni scaffold in which a four coordinate nickel center can be stabilized. We sought to investigate how the reactivity of the nickel monocarbonyl species can be controlled via the variation of the number of *d* electrons resulting in geometric alteration from a square planar to pseudotetrahedral geometry. Square planar nickel(II) monocarbonyl species {(PNP)NiCO}{BF_4} (**1**) was recently reported by our group.[5] The corresponding monovalent nickel carbonyl species (**2**) was produced from the chemical reduction of **1**, accomplished by addition of 1 equivalent of sodium naphthalide in THF (Scheme 2). This paramagnetic species (PNP)NiCO with one naphthalene molecule (**2**•$C_{10}H_8$) was synthesized in good yield (82%). Due to its paramagnetic nature, **2** does not show a ^{31}P NMR spectroscopic signal (Fig. 1). According to the results of an Evans' method[6] for magnetic moment determination (μ_{eff} = 1.54 μ_B, C_6D_6), together with X-band EPR data of a frozen solution of **2** (g = 2.08, 2.02, 2.02 in toluene at 20 K, Fig. 1), an S = ½ spin state for **2** is assured. Since there is a greater back-donating capacity for the monovalent nickel ion of **2**, compared to Ni^{II}-CO (**1**), the C-O vibrational frequency for **2** is lower than that for **1** (ν_{CO} = 1927 cm^{-1}; $\Delta\nu_{CO}$ = –144 cm^{-1}, Table 1).

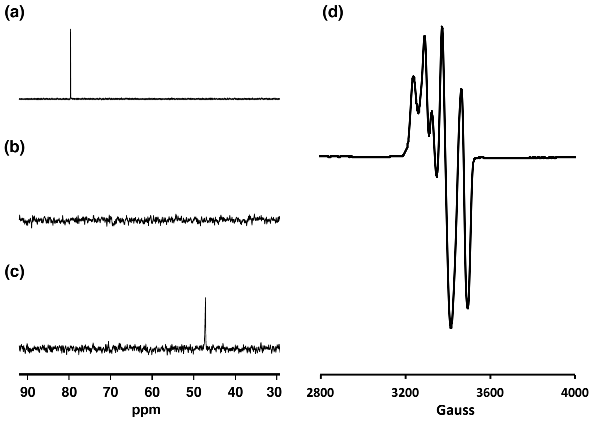


Fig. 1 ^{31}P NMR spectra of (a) {(PNP)NiCO}{BF_4} (**1**, 79.65 ppm)[5] (b) (PNP)NiCO (**2**, no signal) (c) {Na(12-C-4)$_2$}{(PNP)NiCO} (**3'**, 47.20 ppm). (d) X-band EPR spectrum of **2** (20 K, toluene).

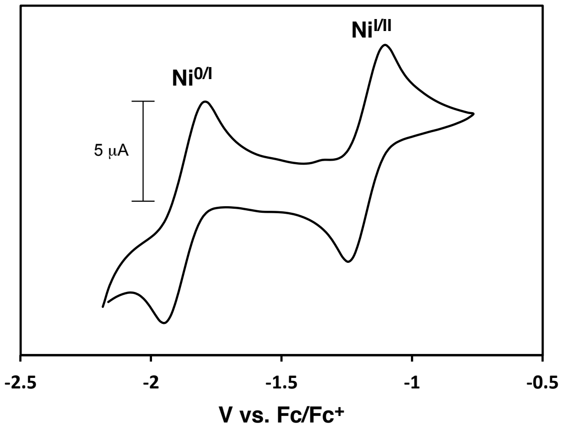


Fig. 2 Cyclic voltammogram of (PNP)NiCO (**2**); scan rate = 100 mV/s. Ni$^{I/II}$ couple at –1.20 V and Ni$^{0/I}$ couple at –1.87 V vs. Fc/Fc$^+$ were observed in THF with 0.1 M {*n*-Bu_4N}{PF_6}.

The existence of an anionic species, {(PNP)NiCO}$^-$ (**3**) was gleaned by cyclic voltammetric analysis carried out on (PNP)NiCO (**2**). Two reversible one-electron redox couples are observed at –1.20 and –1.87 V vs. Fc/Fc$^+$ in THF solvent (Fig. 2). Based on these observations, we attempted a chemical generation of the anionic nickel carbonyl species by addition of 1 equivalent of sodium naphthalide to **2**. A diamagnetic nickel carbonyl species (PNP)Ni(CO)Na (**3**) is produced, possessing a ^{31}P NMR spectroscopic signal at 46.59 ppm in C_6D_6/THF solution. To eliminate the effect of a sodium cation, 2 equivalent of 12-crown-4 was added to the solution of **3** to yield {Na(12-C-4)$_2$}{(PNP)NiCO} (**3'**) which gives a new ^{31}P-NMR signal at 47.20 ppm. Further, this complex displays a new carbonyl vibration, dramatically shifted from that for its precursor Ni(I) species **2** ($\Delta\nu_{CO}$ = –108 cm^{-1}, Table 1 and Supporting Information). These data indicate that this new anionic species possesses a very electron rich zero-valent nickel ion, which displays a much higher back-donation capability. Regeneration of **2** from **3** was also accomplished by addition of 1 equivalent of silver trifluoromethanesulfonate (74% yield, Supporting Information).

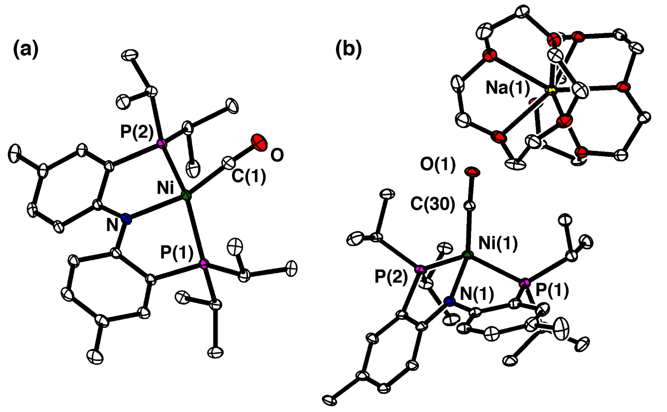


Fig. 3 Displacement ellipsoid (50%) representations of (a) (PNP)NiCO (**2**), (b) {Na(12-C-4)$_2$}{(PNP)NiCO} (**3'**). Hydrogen atoms and molecules of co-crystallization are omitted for clarity. See Table 1 and Supporting Information for details.

Table 1 (PNP)Ni carbonyl species (**1**, **2** and **3'**).

	ν_{CO} (cm^{-1})	C-O (Å)	Ni-C (Å)	Ni-N (Å)	N-Ni-C (°)
{NiCO}$^+$ 1[4]	2071	1.133(2)	1.746(2)	1.866(1)	172.36(6)
NiCO 2	1927	1.149(2)	1.776(2)	1.964(1)	153.25(8)
{NiCO}$^-$ 3'	1819	1.174(4) 1.173(4)	1.719(3) 1.713(4)	2.039(3) 2.066(3)	128.7(1) 128.7(1)

While nickel monocarbonyl species are uncommon, structurally characterized monocarbonyl nickel(I) and nickel(0) complexes do exist.[7,8] However, there is no report to-date showing a nickel monocarbonyl species stabilized and isolated in three distinct oxidation states. Here, solid-state structures were successfully obtained for all three of these carbonyl adducts **1**,[5] **2** and **3'** (See Fig. 3, Table 1 and Supporting Information) which were further accompanied by physical/spectroscopic data. Inevitably, there is dramatic alteration in the CO vibrational frequency when comparing the (PNP)Ni compounds that exist in three distinct formal oxidation states (II, I and 0), C-O bond distances consistently increase from 1.133(2) to 1.149(2) and 1.174(4) Å, respectively. Interestingly, the Ni-C bond distance in **2,** however, is slightly more elongated than that in **1** (1.776(2) vs. 1.746(2), respectively). Of course, it is common for electron-rich metals to favor the formation of strong π-backbonding into the antibonding orbital of the CO ligand, resulting in shorter metal-carbon bonds but longer C-O bonds.[9] Yet, compensating for this behavior is the fact that nickel complex reduction places additional electrons in metal-orbitals with antibonding character leading to weaker Ni-C σ-bonding.[7b,10] Caulton and coworkers recently reported that reversible binding of CO occurs at a *monovalent* nickel ion supported by a ligand similar to the one employed here [PNP’ = (^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N].[7b,10] Due to the antibonding character of the SOMO of the square planar nickel(I) ion, nickel reversibly bind CO in contrast to the planar d^8 $[(PNP')Ni^{II}(CO)]^+$ complex or (PNP’)Co(CO).[7b,10] DFT calculations with Mülliken population analysis determinations carried out on compound **2**, show that ~71% of the unpaired spin is located on the nickel center (Fig. 4 and Supporting Information). However, a Ni(I) carbonyl or Ni(0) carbonyl species here does not allow for CO dissociation under vacuum. We do not have any evidence that our PNP-nickel complexes form overall three-coordinate species; such an entity was in fact detected in the case of Caulton’s PNP’-Ni complex.[7b,10] Mindiola group has also suggested a putative Ni(I) species in the generation of Ni(I) dimer $[Ni(\mu_2\text{-}PNP)]_2$ but did not further investigate on producing a carbonyl species while its congener $[Co(\mu_2\text{-}PNP)]_2$ does produce a [(PNP)CoCO] species.[11] According to our current investigation, $(PNP)Ni^I$ or Ni^0 does not form either three coordinate species or a dimer in the presence of its forth CO ligand.

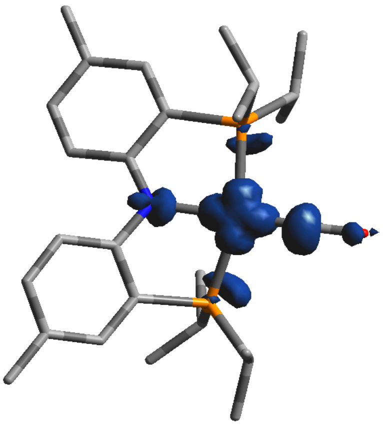
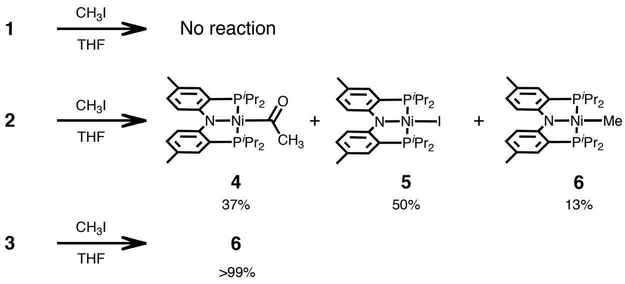


Fig. 4 Mülliken atomic spin density plots derived from the single-point DFT calculation of (PNP)NiCO (**2**); Ni: 71.2%; P1: 2.8%; P2: 4.8%; N: 6.5%; C: 7.8%. Lobal representations correspond to the spin density by the number with 0.004 isocontours. Gaussian09; B3LYP, lanl2dz for nickel and 6-31+G** for all other atoms.

The geometry about the nickel center dramatically changes for the three complexes, *viz*. tetracoordinate Ni(II) complex **1** is nearly planar,[5] Ni(I) compound **2** has a pyramidal geometry with the metal ion out of the ligand plane and Ni(0) complex **3** possesses pseudotetrahedral coordination (Fig. 3 and Table 1, see especially the N-Ni-C angle variations). Thus, with the PNP ligand we have employed and the various nickel complexes generated we present a notable system in which straightforward electron occupation affects the metal complex geometry and their reactivity, *vide infra*.

II. Reaction of Nickel Monocarbonyl Complexes with CH_3I

In order to understand the reactivity of the nickel monocarbonyl species **1**, **2** and **3**, we employed a series of alkyl iodides. Due to the relevance of the C-C bond formation to the ACS chemistry, we examined which oxidation states of nickel carbonyl species can generate acyl products such as (PNP)NiCOCH$_3$ (**4**). While {(PNP)NiCO}{BF$_4$} (**1**) does not show any reactivity toward iodomethane, (PNP)Ni(CO)Na (**3**) displays an instantaneous reaction with ~1.3 equivalent of iodomethane in THF at –35 °C showing a color change from orange to red (Scheme 3 and Table 2). The resulting product reveals a methyl signal at –0.30 ppm (t, J = 8.8 Hz) in ^{1}H NMR spectrum, which is identified as (PNP)NiCH$_3$ (**6**) previously reported by Ozerov and coworkers (Scheme 3 and Fig. 5).[12]



Scheme 3

The same reaction conducted with a monovalent nickel (PNP)NiCO (**2**), however, revealed favorable production of the acetyl moiety over ligand substitution (Scheme 3). Upon addition of 1.1 equivalent of iodomethane to the THF solution of **2** an immediate color change from green to greenish yellow occurred. The resulting solution possesses three diamagnetic species $(PNP)Ni^{II}COCH_3$ (**4**, 37%), $(PNP)Ni^{II}I$[13] (**5**, 50%) and $(PNP)Ni^{II}CH_3$ (**6**, 13%), confirmed by both ^{1}H and ^{31}P NMR data (Scheme 3 and Table 2). In a slow reaction (40 hrs at room temperature), the acyl product, **4** was independently synthesized from the reaction of (PNP)NiCH$_3$ (**6**) with CO (g) in good yield (81%) (Supporting Information). The carbonyl vibration of **4** was detected at 1616 cm^{-1}, clearly shifted from the vibration of precursor **2** (1927 cm^{-1}, Supporting Information). The solid-state structure of **4** clearly shows an acetyl moiety bearing a C−O bond (1.225(2) Å) in a distorted-square-planar nickel complex (∠N-Ni-C = 178.57(6)° and ∠P-Ni-P = 167.72(2)°) (Fig. 5).

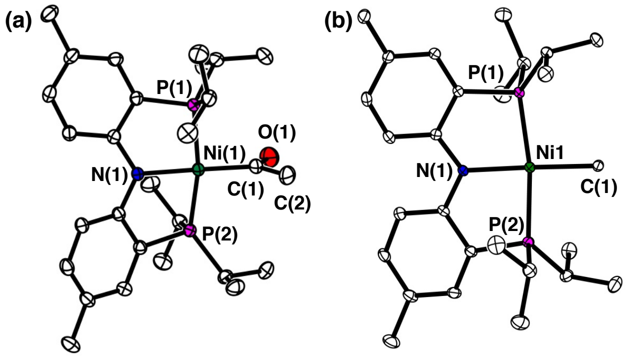


Fig. 5 Displacement ellipsoid (50%) representations of (PNP)NiCOCH$_3$ (**4**) and (PNP)NiCH$_3$ (**6**). Hydrogen atoms and molecules of co-crystallization are omitted for clarity. See Table 3 and Supporting Information for details.

Table 2 Reactions of **2** and **3** with iodoalkanes.[14]

	Reagent	NiCOR	NiR	NiI
2	MeI	37%	13%	50%
	EtI	48%	2%	50%
	^{n}PrI	49%	1%	50%
	^{i}PrI	50%	Not detected	50%
	^{t}BuI	45%	Not detected	55%
3	MeI	Not detected	>99%	Not detected
	EtI	73%	25%	Not detected
	^{n}PrI	92%	8%	Not detected
	^{i}PrI	>99%	Not detected	Not detected
	^{t}BuI	97%	Not detected	3%

Generation of (PNP)Ni^{II}COCH$_3$ (**4**) from the reaction of a monovalent nickel carbonyl species, **2** with a methylating agent has not been previously reported in organonickel chemistry. Most examples involve the conversion of a nickel alkyl species to acyl products via the migratory insertion of CO to the Ni-C bond. As a closely related example, Liang and coworkers recently reported the formation of an acyl product (PNP*)Ni^{II}-COR (PNP* = [N(o-C$_6$H$_4$PR$_2$)$_2$]$^{-}$, R = Me or Et) from the reaction of a corresponding nickel alkyl species with CO.[15] Limberg and coworkers recently reported a single example of the formation of a nickel(II)-acetyl complex [L^{tBu}NiC(O)CH$_3$] (L^{tBu} = HC{C(tBu)NC$_6$H$_3$(iPr)$_2$}$_2$$^{-}$) from the corresponding nickel(0) monocarbonyl species upon treatment with MeI.[16] In fact, the mechanism of ACS might involve a monovalent nickel-CO species according to the recent report.[4] A random binding of the substrates, CO and CH$_3$$^{+}$, occurs at the Ni$_p$ site in the A cluster followed by the formation of the proposed intermediates, Ni-CO and Ni-Me. The details (discrete fundamental steps) of the enzymatic mechanism, including details about the reactivity of important proposed intermediates such as methyl-nickel and nickel-carbonyl species are still not fully understood. To the best of our knowledge, this is the first example of C-C bond formation of Ni^{I}-CO with an alkyl cation.

Table 3 Physical parameters for the NiR and NiCOR species.

	^{31}P (ppm)	ν_{CO} (cm^{-1})	C-O (Å)	Ni-C (Å)
NiMe (**6**)	35.47	–	–	2.004(2)
NiEt	32.03	–	–	1.963(5)
Ni^{n}Pr	32.26	–	–	1.980(8), 1.97(2)^{a}
NiCOMe(**4**)	35.95	1616	1.225(2)	1.865(2)
NiCOEt	35.56	1616	–	–
NiCO^{n}Pr	35.11	1616	1.215(6)	1.869(4)
NiCO^{i}Pr	33.97	1610	1.221(3)	1.873(2)
NiCO^{t}Bu	31.36	1606	1.217(2)	1.886(1)

^{a} n-propyl group was disordered over two distinct positions.

III. Reaction of Nickel Monocarbonyl Complexes with RI

Interestingly, our results show that C-C bond formation between a nickel carbonyl and a methyl group selectively occurs at a nickel(I) center, while the nickel(0) version favors ligand substitution. In order to investigate the possible steric effects on the acylation, a series of iodoalkanes were treated with both nickel(0) and nickel(I) carbonyl species. Upon addition of 1.1–1.3 equivalent of RI (R = Me, Et, ^{n}Pr, ^{i}Pr and ^{t}Bu) to (PNP)Ni(CO)Na (**3**) at –35 °C, the reaction mixture revealed an immediate color change to brighter orange. The solution possesses two diamagnetic species, NiCOR and NiR in different ratios depending on the R group (Table 2). The same reaction was conducted with (PNP)NiCO (**2**) revealing the product mixture of NiR and NiCOR in different ratios, along with a ~50% yield of (PNP)NiI (**5**) (Table 2). These results with both species, **2** and **3** show that a relatively bulky R group favors the formation of an acyl moiety (Table 2). According to the space filling models of **2** and **3**, both nickel centers are sterically hindered by isopropyl groups and the backbone phenyl groups of a PNP ligand (Figure 6). This affects the reactivity of both nickel(I) and nieckel(0) carbonyl species toward alkyl iodide. The formation of (PNP)NiCOR species is dominant when a relatively more bulky R group such as ^{i}PrI and ^{t}BuI are utilized, whereas smaller R-groups favor the formation of corresponding nickel alkyl species. Currently, our results clearly reveal that a smaller methyl iodide or a methyl radical species can *possibly* access the nickel center to generate (PNP)NiCH$_3$ species; 13% in **2** and >99% in **3**, in which the origin of the clear reactivity differences of **2** and **3** can be assured to be electronic and not steric. All NiR and NiCOR complexes were fully characterized by various spectroscopic methods and X-ray crystallography. Selected data are listed in Table 3.

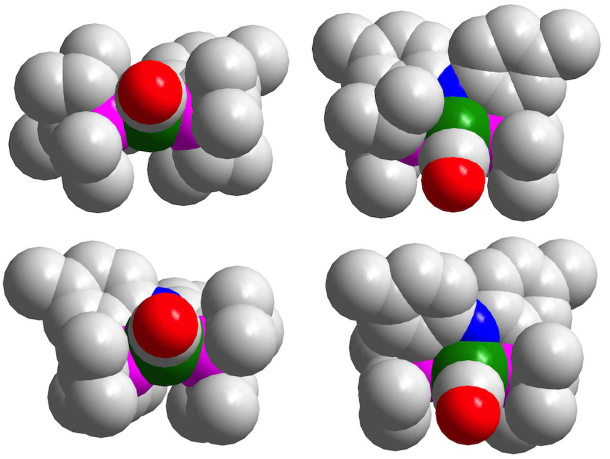
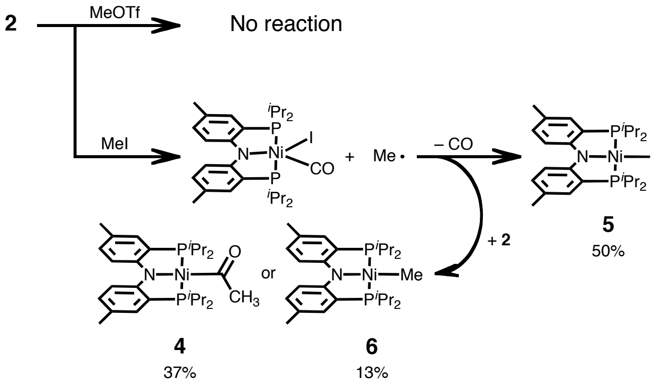


Fig. 6 Space-filling models of (PNP)NiCO (**2**, top) and (PNP)Ni(CO)Na (**3**, bottom).

According to our study, only acylation occurs with the nickel(I)-CO species (**2**) revealing a different reactivity compared with that for **3**. One possible explanation for this difference involves the reaction of nickel(I) species with methyl iodide to produce Ni(II)-I through a radical-type reaction pathway. Organonickel cross-coupling of alkyl electrophiles may be possible whereas the nickel(I) species can react with alkyl iodide to produce a nickel-iodide and alkyl radical.[3e,3f,17] This is in line with the observation when CH$_3$OTf was present and results in no reaction progress for the methylation of **2** (Scheme 4 and Supporting Information).[17] This indicates the reaction with CH$_3$I follows the radical pathway.[3e,3f,17] Consequently, once a methyl radical is generated, it would react with **2** to yield a mixture of products (Scheme 4). The nickel-acyl product could be generated from the migratory insertion of CO with Ni(II)-Me. However, it seems that **2** does not follow this route since migratory insertion of CO with (PNP)NiCH$_3$ is much slower (40 hrs) than that of the methylation reaction (< 1 min) for the nickel(I)-CO species (**2**) under the same conditions (Supporting Information). If binding of a methyl radical occurs at the nickel(I) center of **2** through a *radical pathway*, the formation of the five-coordinate (PNP)Ni(CO)(CH$_3$) intermediate is expected. The same species can be generated from the reaction between **3** and CH$_3$I. However, we believe that **2** follows a separate reaction pathway(s) because of the product distributions from reactions involving **2** and **3** (Table 2). To better understand this C-C bond formation, a new mechanism which involves the reaction of $Ni^{I}(CO)$ with a methyl radical to produce a known intermediate species, $Ni^{II}(CO)(CH_3)$ is proposed. A slight but significant calculated spin density (7.8%) on carbon atom at the CO ligand of **2** was found (DFT calculations, Supporting Information). Therefore, direct C-C bond formation might be an alternate possible reaction pathway. Mechanistic studies are currently under investigation to help explain such reactivity differences of nickel carbonyl species in +1 vs. 0 oxidation states.



Scheme 4

Conclusions

In summary, we have reported the synthesis and characterization of three different oxidation state of nickel carbonyl species, formally +2, +1 and 0. Although there is a dramatic change in CO vibrational frequency for three nickel monocarbonyl species, there is no significant effect on metal-ligand bond length in their solid state structures. This results from the occupation of an orbital with antibonding character which weakens the Ni-C σ-bonds. However, the nickel coordination geometry change was dramatic; $Ni^{II}CO$ is nearly square planar, $Ni^{I}CO$ has a pyramidal and $Ni^{0}CO$ possesses a pseudotetrahedral coordination environment in compensating for the electronic effects. These clearly support the presence of an additional electron occupying the d_{x2-y2} orbital, which establishes a series of consecutive electron configurations from d^8 to d^{10}. The reactivity of these three nickel carbonyl species with iodomethane was examined to compare and contrast C-C bond formation. Interestingly, C-C coupling was observed only in a $Ni^{I}CO$ species (**2**) from the reaction with MeI. This is the first case where the unique capability of a $Ni^{I}CO$ species in C-C bond formation has been recognized, in comparison with a closely related zero-valent nickel species.

Acknowledgements

This work has been supported financially by a National Research Foundation (NRF) grant funded by the Korea Government (Ministry of Education, Science, and Technology, N01110580) and by KAIST Institute for the BioCentury. We thank Dr. Y. J. Park, Dr. M. S. Seo, and Prof. W. Nam at Ewha Womans University for the data collection on their mass facilities. We also thank Dr. S. H. Kim at Korea Basic Science Institute for the EPR data collection of **2** and its interpretation. Prof. David G. Churchill and Prof. Sukbok Chang are acknowledged for insightful discussions concerning the reaction mechanism mediated by nickel.

Notes and references

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Electronic Supplementary Information (ESI) available: Characterization data for **2**–**6**, (PNP)NiR and (PNP)NiCOR; CCDC 918046 (**2•C₁₀H₈**), 918074 (**3'**), 996897 (**4**), 996898 (**6**), 996901 ((PNP)NiEt), 996902 ((PNP)NiCO^{n}Pr), 996903 ((PNP)Ni^{n}Pr), 996904 ((PNP)NiCO^{i}Pr), 996905 ((PNP)NiCO^{t}Bu); details of DFT calculations. See DOI: 10.1039/c000000x/

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A table of contents entry

Reaction of the nickel(I) carbonyl species with CH_3I revealed the formation of (PNP)$NiCOCH_3$ different from its zerovalent congener.