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Article

Metal−Ligand Cooperation as Key in Formation of Dearomatized Ni(II)−H Pincer Complexes and in Their Reactivity toward CO and CO2

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S *Supporting Information*

ABSTRACT: The unique synthesis and reactivity of [(^{R}PNP*)NiH] complexes (**1a,b**), based on metal−ligand cooperation (MLC), are presented (^{R}PNP* = deprotonated PNP ligand, R = ^{i}Pr, ^{t}Bu). Unexpectedly, the dearomatized complexes **1a,b** were obtained by reduction of the dicationic complexes [(^{R}PNP)Ni(MeCN)](BF$_4$)$_2$ with sodium amalgam or by reaction of the free ligand with Ni^0(COD)$_2$. Complex **1b** reacts with CO via MLC, to give a rare case of a distorted-octahedral PNP-based pincer complex, the Ni(0) complex **3b**. Complexes **1a,b** also react with CO$_2$ via MLC to form a rare example of η^1 binding of CO$_2$ to nickel, complexes **4a,b**. An unusual CO$_2$ cleavage process by complex **4b**, involving C−O and C−P cleavage and C−C bond formation, led to the Ni−CO complex **3b** and to the new complex [(P^{i}Pr$_2$NC$_2$O$_2$)Ni(P(O)^{i}Pr$_2$)] (**5b**). All complexes have been fully characterized by NMR and X-ray crystallography.
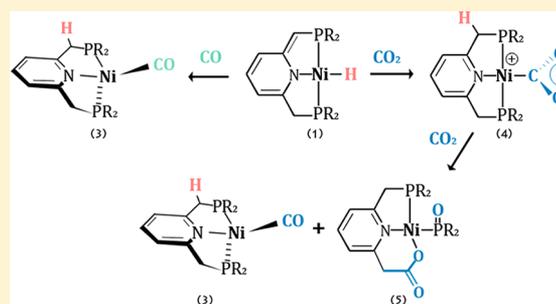
Late-transition-metal complexes of electron-donating and bulky "pincer" ligands have found important applications in synthesis, bond activation, and catalysis.[1−6] The lutidine-based pincer ligands (Scheme 1) are highly electron donating ligands with a relatively low trans influence of the pyridinic nitrogen and benzylic "arms" amenable to deprotonation.

Scheme 1. H−X Bond Activation by Aromatization/Dearomatization MLC Reactivity

X = H, OH, OR, NHR, CR$_2$, CR$_3$
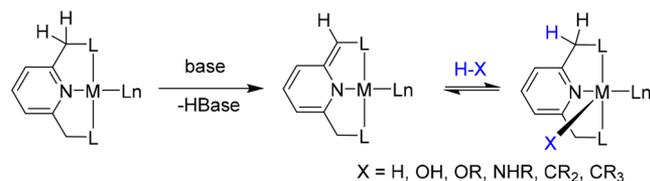
In recent years our group has developed a novel mode of metal−ligand cooperation (MLC), involving aromatization/dearomatization of lutidine-based pincer complexes (Scheme 1).[7−12] This mode of reactivity enabled the activation of various substrates such as alcohols,[13−17] amines,[18−21] nitriles,[22,23] boranes,[24] dihydrogen,[25−27] and dioxygen,[28] as well as activation of C$_{sp2}$−H[29] and C$_{sp3}$−H[30] bonds, and it is a key step in the design of several environmentally benign catalytic reactions.[7−11]

Due to the importance of CO$_2$ as a potential C1 building block,[31,32] we have explored the reactivity of dearomatized pincer complexes toward CO$_2$. It was found that MLC is also involved in the activation of CO$_2$ by dearomatized lutidine-based complexes of Fe,[33] Ru,[34,35] Re,[36] Ni,[37] and Ir,[38] reversibly forming a new C−C bond between the ligand backbone and

CO$_2$. Recently, we reported the reductive cleavage of CO$_2$ by dearomatized (^{t}Bu-PNP)Ir−H and (^{t}Bu-PNP)Rh−H complexes via MLC (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)-pyridine),[38,39] leading to the design of a cycle of photo-carbonylation of benzene.[39]

Herein we report a rare case of Ni(η^1-CO$_2$-κC) complexes, obtained by direct coordination of free CO$_2$ to lutidine-based Ni−hydride complexes [(R-PNP*)NiH] (R-PNP* = dearomatized PNP ligand, R = ^{t}Bu, ^{i}Pr) involving metal−ligand cooperation.

CO$_2$ coordination to Ni complexes is well known,[40] and Ni complexes serve as efficient catalysts in CO$_2$ activation and utilization as a C1 building block,[31,41] mainly in CO$_2$ hydrogenation[42−45] and carboxylation.[46−56] The first structurally characterized metal−CO$_2$ complex was (PCy$_3$)$_2$Ni(η^2-CO$_2$), reported by Aresta et al. in 1975 (Scheme 2).[57] Since then, several similar Ni(η^2-CO$_2$) complexes have been reported,[58,59] including a unique five-coordinated Ni(η^2-CO$_2$) complex.[60] A unique coordination mode of μ-η^2,η^2-CO$_2$ in a dinuclear Ni complex was reported by Sadighi and co-workers,[61] and a rare case of Ni^{III}(η^1-(CO$_2$)$^{\bullet}$-κO) was reported by Chiou, Liaw, and co-workers.[62] Recently a rare case of Ni^{II}(η^1-CO$_2$-κC) was reported by Lee[63] (Scheme 2).

The dearomatized complex [(^{t}Bu-PNP*)NiH] (**1a**, Scheme 3), reported by van der Vlugt et al., was obtained by reaction of LiAlH$_4$ with the dearomatized complex [(^{t}Bu-PNP*)NiCl].[64] Surprisingly, we obtained the Ni(II) complex **1a** by attempting to reduce the dicationic Ni(II) complex [(^{t}Bu-PNP)Ni-

Scheme 2. Mononuclear Ni CO$_2$ Complexes

Aresta, Hillhouse   Lee   Lee

Chiou & Liaw
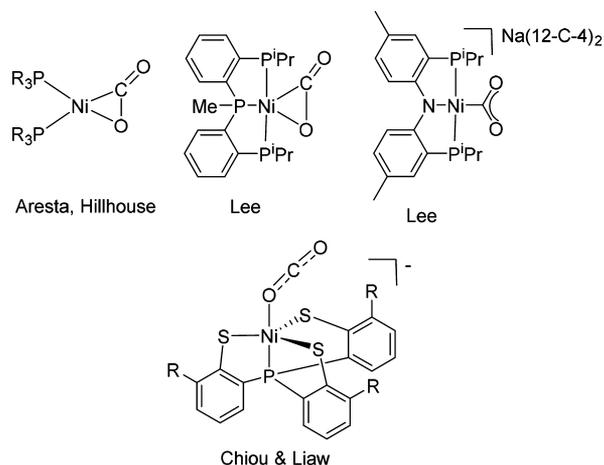
Scheme 3. Synthesis of Complexes 1a,b

2a,b   **1a,2a**: R = ^{t}Bu   **1a,b**
        1b,2b: R = ^{i}Pr
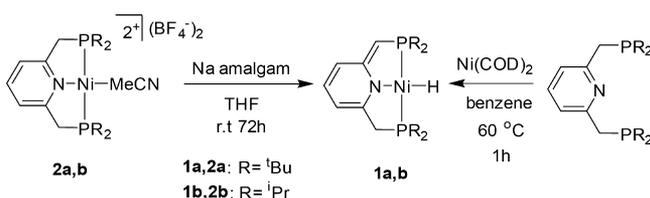
(MeCN)][(BF$_4$)$_2$[64] with sodium amalgam (Scheme 3). Single crystals of complex **1a** were obtained by slow evaporation of its benzene solution. The unreported X-ray structure of **1a** is shown in Figure 1. The new complex [(^{i}Pr-PNP)Ni(MeCN)]-
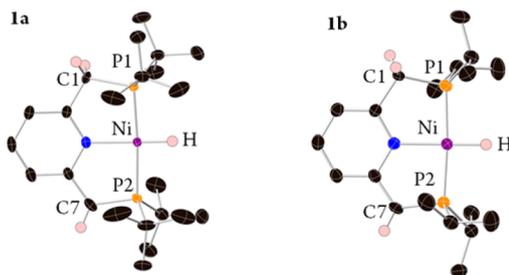
Figure 1. Single-crystal X-ray structures with thermal ellipsoids shown at the 50% probability level of complex **1a** (left) and complex **1b** (right). Hydrogen atoms, except Ni−H and side arm protons, are omitted for clarity. See the Supporting Information for a full description of the structures.

(BF$_4$)$_2$ was also prepared, and upon similar treatment with sodium amalgam the corresponding dearomatized hydrido complex **1b** was obtained (Scheme 3). Crystals suitable for X-ray diffraction of **1b** (Figure 1) were obtained by evaporation of its pentane solution. The X-ray structures of **1a,b** reveal the expected square-planar geometry.

Complex **1b** exhibits in the ^{1}H NMR spectrum a hydride signal at −18.13 ppm ($^2J_{PH}$ = 65 Hz), and the ^{31}P{^{1}H} NMR spectrum exhibits an AB pattern centered at 54.72 ppm ($^2J_{PP}$ = 225.1 Hz), similar to the spectra reported for **1a**.[64]

We believe that the reduction of complexes **2a,b** leads initially to Ni(0) intermediates forced into a square-planar geometry by the relatively rigid PNP pincer ligand. As a d^{10} ML$_4$ complex, Ni(0) complexes prefer to adopt a tetrahedral geometry, and Ni(0) square-planar complexes are as yet

unknown. Only one d^{10} square-planar complex is known, a Pt(0) complex.[65] The postulated unstable Ni(0) intermediates rearrange by metal−ligand cooperation, in which proton transfer from the benzylic position of the pincer ligand to the metal center takes place, yielding the Ni(II) dearomatized hydride complexes **1a,b**. In support of this mechanism, reaction of the Ni^0(COD)$_2$ complex with the R-PNP ligands (R = ^{t}Bu, ^{i}Pr) resulted in the dearomatized complexes **1a,b** exclusively (Scheme 3).

In order to explore the possibility of reverting the metal−ligand cooperative proton transfer from the arm to the metal center, thus gaining a Ni(0) complex, complexes **1a,b** were reacted with CO. Upon treatment of complex **1a** with 1 equiv of CO no reaction was observed, likely as a result of steric congestion imposed by the bulky ^{t}Bu-PNP ligand. However, upon addition of 1 equiv of CO to the ^{i}Pr-PNP complex **1b**, a rapid color change occurred, yielding the unusual neutral pincer Ni(0) carbonyl complex **3b** (Scheme 4). Complex **3b** exhibits a

Scheme 4. Formation of the Ni(0) Complex 3b and Its Single-Crystal X-ray Structure with Thermal Ellipsoids Shown at the 50% Probability Level[a]

1b   **3b**
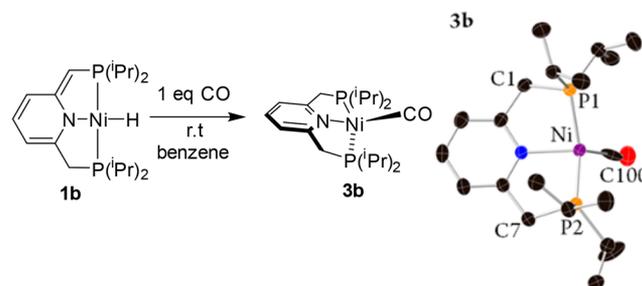
[a]Hydrogen atoms are omitted for clarity. See the Supporting Information for a full structural description.

singlet peak at 68.36 ppm in the ^{31}P{^{1}H} NMR, indicating a metal−ligand cooperative transfer of a proton from the metal back to the unsaturated arm, yielding a symmetric complex. The carbonyl ligand gives rise to a triplet peak at 204.02 ppm in the ^{13}C{^{1}H} NMR spectrum, at a slightly higher field in comparison to that of the recently reported nickel monocarbonyl anionic complex {Na(12-C-4)$_2$}{(^{acri}PNP)Ni(CO)}.[66] Slow evaporation of the benzene solution resulted in formation of single crystals suitable for X-ray diffraction (Scheme 4), and these adopt a distorted-tetrahedral geometry. The P−Ni−CO angle is the only characteristic tetrahedral angle (111.3(2)°), while the N−Ni−P and the N−Ni−CO angles are 85.0(1) and 125.8(2)°, respectively. The Ni−CO and C−O bond distances are 1.862(6) and 1.030(6) Å, respectively, and the CO IR band appears at 1888 cm^{-1} in benzene solution. In comparison, the recently reported monocarbonyl Ni(0) anionic complex [Na(12-C-4)2][(^{acri}PNP)Ni(CO)], which also adopts a distorted-tetrahedral geometry due to the rigid PNP ligand, exhibits Ni−CO and C−O bond lengths of 1.77(1) and 1.18(1) Å, respectively, and an IR CO band appears at 1828 cm^{-1}, indicating a higher degree of π back-donation from the low-valent nickel center in comparison with **3b**.[66]

The dearomatized hydride complexes **1a,b** react with CO$_2$ to give the aromatized complexes **4a,b** with a rare η^1 coordination mode of carbon dioxide (Scheme 5). While complex **1b** reacts readily with CO$_2$ at ambient temperature with only 0.5 bar of CO$_2$, forming complex **4b** in 82% yield (according to ^{31}P

Scheme 5. Synthesis of Complexes 4a,b
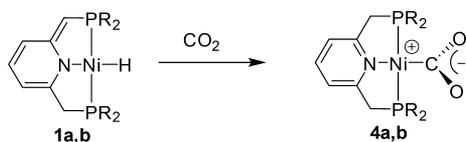
4a: R = ^{t}Bu, 8 bar CO_2, 72 hrs, 80 °C.
4b: R = ^{i}Pr, 0.5 bar CO_2, 8 hrs, room temperature.

NMR) after 8 h, the conversion of **1a** to **4a** requires the more forcing conditions of 8 bar, 80 °C, and 72 h, yielding 60% of the product.

Whereas the η^2-CO_2 coordination mode is common, the η^1-CO_2 coordination mode is rare. It was reported for [Rh-(diars)$_2$Cl(CO_2)],[67] [Ru(bpy)$_2$(CO)(CO_2)]·3H_2O,[68,69] [Ir-(dmpe)$_2$Cl(CO_2)],[70] and [Co(salen)K(η^1-CO_2)(THF)].[71,72] The only Ni-η^1-CO_2 complex is the recently reported anionic complex [Na(12-C-4)$_2$][(PNP)Ni-η^1-CO_2] (PNP = N[2-P^{i}Pr$_2$-4-Me-C_6H_3]$_2$),[63] which was obtained by a reduction of the carboxylate complex [(PNP)NiCOONa] and not by direct CO_2 coordination, unlike complexes **4a,b**.

Crystals suitable for X-ray diffraction of **4a,b** (Figure 2) were obtained from the crude reaction mixture in a pressure flask
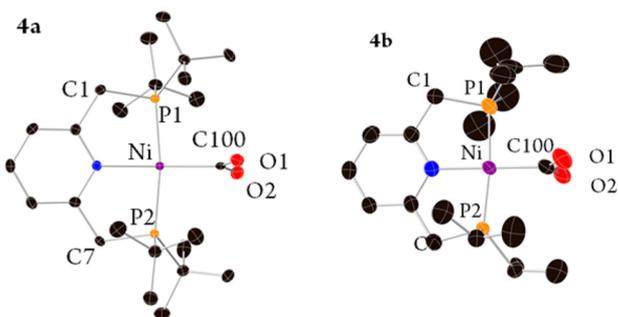
Figure 2. Single-crystal X-ray structures, with thermal ellipsoids shown at the 50% probability level, of complexes **4a** (left) and **4b** (right). Hydrogen atoms and cocrystallized solvents are omitted for clarity. See the Supporting Information for a full description of the structures.

under a CO_2 atmosphere. Both complexes exhibit a distorted-square-planar geometry with P−Ni−P angles of 171.39(3) and 173.4(1)° and N−Ni−C angles of 179.0(1) and 178.6(2)° for complexes **4a,b**, respectively. The CO_2 plane is almost perpendicular to the pincer ligand plane. The Ni−CO_2 bond lengths in complexes **4a,b** are 1.950(3) and 1.912(4) Å, respectively, which are in the range of reported η^1-CO_2 complexes and longer by 0.11−0.044 Å than those reported for Ni−η^2-CO_2.[57,59] The two C−O bond lengths are similar (1.244(3), 1.254(3) Å in **4a** and 1.240(5), 1.250(5) Å in **4b**), unlike the C−O bonds in reported Ni−η^2-CO_2 complexes, in which the difference in length is 0.06 Å.[59,60] In addition, the large and similar distances between the oxygen atoms and the metal center (2.737(2), 2.721(1) Å in **4a** and 2.749(3), 2.637(3) Å in **4b**) also indicate an η^1-CO_2 coordination mode, as the Ni−O bond lengths in η^2-CO_2 complexes are shorter by 0.8−0.5 Å.[57,59] The bond lengths of the CO_2 ligand in complexes **4a,b** are similar to the reported bonds of the complex [Na(12-C-4)$_2$][(PNP)Ni-η^1-CO_2].[63] In addition, the Ni−CO_2 bond length in complex **4a** is longer by 0.04 Å in comparison with **4b**. This elongation is probably due to the more sterically demanding ^{t}Bu-PNP ligand in comparison to

the ^{i}Pr analogue. Aresta et al., in his seminal work on (PR$_3$)$_2$Ni(η^2-CO_2) complexes (R = (C_6H_{11}), Et, Bu^n), also observed that steric hindrance has a great influence on the Ni−CO_2 bond strength.[58] We have previously reported that the steric difference between the ^{t}Bu-PNP and ^{i}Pr analogues can lead to large differences in reactivity.[73] The lower steric hindrance of the ^{i}Pr-PNP can result in a higher degree of π back-donation from the Ni center to the CO_2 ligand,[63] which shortens the Ni−CO_2 bond length. This is in line with the differences in reaction conditions for the synthesis of complexes **4a,b** and the differences in reactivity of complexes **1a,b** toward CO. According to NMR studies, whereas complex **1b** reacts with substoichiometric amounts of CO_2 at room temperature to gradually form complex **4b** (Figure 3), complex **1a** requires
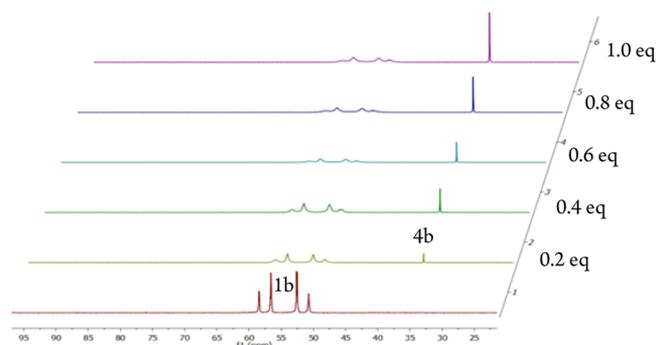
Figure 3. ^{31}P{^{1}H} NMR (121.4 MHz) spectra representing gradual injection of about 0.2 equiv of CO_2 into a toluene solution of complex **1b** in an NMR tube equipped with a septum cap. Similar conditions with complex **1a** yielded no detectable conversion.

at least 5 bar of CO_2 to achieve detectable conversion. In addition, while the formation of **4b** under these conditions requires several minutes, detectable formation of **4a** requires at least 12 h.

Complexes **4a,b** exhibit symmetric ^{1}H and ^{13}C NMR spectral patterns of the ligand backbone and a singlet signal in the ^{31}P{^{1}H} NMR spectrum at 47.65 (**4a**) and 35.46 ppm (**4b**), as expected for aromatic square-planar complexes. The CO_2 ligand gives rise to broad peaks at 174.74 and 173.25 ppm, respectively, in the ^{13}C{^{1}H} NMR spectra, which are at a higher field in comparison to the reported chemical shifts of the CO_2 ligands in the complexes [Ru(bpy)$_2$(CO)(CO_2)]·3H_2O[68,69] (203.9 ppm) and [Na(12-C-4)$_2$][(PNP)Ni-η^1-CO_2][63] (197.25 ppm). The reported Ni−η^2-CO_2 complexes give rise to a signal at 164 ppm.[59,60]

Although complex **4b** is stable at room temperature, when a THF solution of **4b** is heated to 80 °C under 5 bar of CO_2, an unexpected reaction was observed. According to the ^{31}P{^{1}H} NMR spectrum, full conversion to two products took place, giving rise to a singlet signal at 68.3 ppm, assigned as complex **3b**, and a pair of doublets at 64.3 and 102.9 ppm ($^2J_{PP}$ = 90 Hz), assigned as complex **5b** (Scheme 6). Complexes **3b** and **5b** were obtained from complex **4b** also at ambient temperature under 5 bar of CO_2, although at lower conversion. Complex **4a** demonstrated no such reactivity, despite the use of more forcing conditions of 10 bar of CO_2 at 353 K for 7 days.

Complex **3b** was extracted from the reaction mixture with pentane, and the two products, **3b** and **5b**, were isolated and fully characterized. Crystals suitable for X-ray diffraction of [(P^{iPr2}NC$_2$O$_2$)Ni(P(O)^{i}Pr$_2$)] (**5b**, Figure 4) were obtained by layering of pentane over a dichloromethane solution. Complex

Scheme 6. CO$_2$ Cleavage by Complex 4b, Involving C=O and C−P Cleavage and C−C Bond Formation
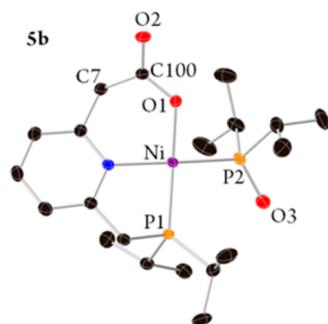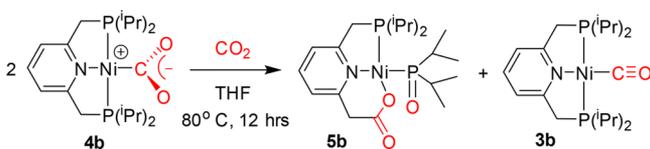
Figure 4. Single-crystal X-ray structures with thermal ellipsoids shown at the 50% probability level of complex **5b**. Hydrogen atoms are omitted for clarity. See the Supporting Information for a full description of the structure.

5b exhibits a distorted-square-planar geometry with P(1)−Ni−O(1) angle of 167.04(6)° and N−Ni−P(2) angle of 170.51(6)°. The C=O(2) and C−O(1) bond lengths are 1.229(3) and 1.296(3) Å, respectively, both longer than the free CO$_2$ bond length by 0.07−0.14 Å, and the C(7)−C(100) bond length is in the range of a single C−C bond, 1.519(4) Å. The NMR data of **5b** fit well with its X-ray structure, and two distinguishable CH$_2$ signals of the benzylic positions, in which only one is coupled to a phosphorus atom, were observed in the ^{1}H and ^{13}C{^{1}H} NMR.

Apparently, two molecules of CO$_2$ are involved, one leading to C−P cleavage followed by C−C bond formation, generating a carboxylato ligand, while the second molecule oxidizes the ^{i}Pr$_2$P fragment to the ^{i}Pr$_2$P=O ligand. The resulting CO is then trapped by another molecule of the starting complex to form the carbonyl complex **3b**. Similar reactivity was reported recently for the Ir(I) complex [Ir(depe)(dbuP)] (depe = 1,2-bis(diethylphosphino)ethane, dbuP = 1,8-diazabicyclo[5.4.0]-undec-7-ene).[74] The Ir(I) complex reacts with two CO$_2$ molecules to give the Ir(III) carbonyl phosphoryl complex [Ir(depe)(CO)(Ph$_2$PO)(dbuCO$_2$)], with a carboxylate incorporation into the dbuP ligand. In both complexes, the reported Ir complex and complex **4b**, four new bonds were formed, M−C, M−O, C−C, and P−O, and two bonds were cleaved, C=O and P−C. P−C bond cleavage has attracted much attention in the past[75] and also more in recent studies.[76,77] Complexes bearing phosphoryl ligands (R$_2$P=O)$^−$ are not common; examples were reported for Au,[78] Ru,[79] Ir,[80] and Pd.[81,82] Ni and Ru bis(phosphinite) pincer complexes were reported to decompose to phosphoryl complexes due to P−O bond cleavage under basic or wet conditions.[83,84]

In summary, unexpected synthetic and reactivity pathways involving metal−ligand cooperation (MLC) of the (PNP*)-Ni^{II}−H pincer complexes **1a,b** are presented. While complex **1a** does not react with CO, the less bulky complex **1b** reacts with CO via MLC to give a rare case of a distorted-tetrahedral [(^{i}PrPNP)Ni(CO)] pincer complex. Notably, complexes **1a,b** react with CO$_2$ via MLC to form rare examples of η^1 binding of CO$_2$ to nickel, complexes **4a,b**. Upon heating under a CO$_2$ atmosphere, the CO$_2$ complex **4b** undergoes an unexpected CO$_2$ cleavage as well as P−C cleavage, followed by C−C bond formation by carboxylation of the PNP ligand, leading to the formation of the Ni^{II}PO complex **5b** and the Ni^{0}CO complex **3b**. Further studies are aimed at understanding of the MLC mechanisms of these unusual transformations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00160.

    Experimental procedures and IR and NMR spectra of complexes **1a,b**−**5a,b** (PDF)

Accession Codes

CCDC 1831348−1831353 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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