

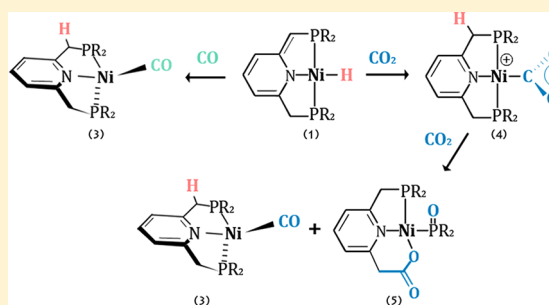
Metal–Ligand Cooperation as Key in Formation of Dearomatized Ni^{II}–H Pincer Complexes and in Their Reactivity toward CO and CO₂

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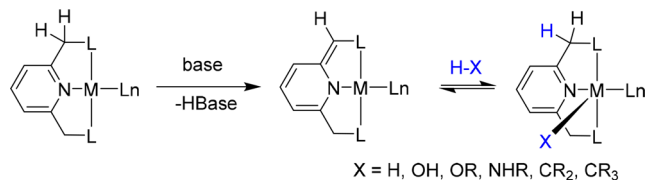
Supporting Information

ABSTRACT: The unique synthesis and reactivity of [(^RPNP*)NiH] complexes (**1a,b**), based on metal–ligand cooperation (MLC), are presented (^RPNP* = deprotonated PNP ligand, R = ⁱPr, ^tBu). Unexpectedly, the dearomatized complexes **1a,b** were obtained by reduction of the dicationic complexes [(^RPNP)Ni(MeCN)](BF₄)₂ with sodium amalgam or by reaction of the free ligand with Ni⁰(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 CO₂ via MLC to form a rare example of η¹ binding of CO₂ to nickel, complexes **4a,b**. An unusual CO₂ 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^tPr₂NC₂O₂)Ni(P(O)ⁱPr₂)] (**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



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}–H²⁹ and C_{sp3}–H³⁰ bonds, and it is a key step in the design of several environmentally benign catalytic reactions.^{7–11}

Due to the importance of CO₂ as a potential C1 building block,^{31,32} we have explored the reactivity of dearomatized pincer complexes toward CO₂. It was found that MLC is also involved in the activation of CO₂ 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

CO₂. Recently, we reported the reductive cleavage of CO₂ by dearomatized (^tBu-PNP)Ir–H and (^tBu-PNP)Rh–H complexes via MLC (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)-pyridine),^{38,39} leading to the design of a cycle of photocarbonylation of benzene.³⁹

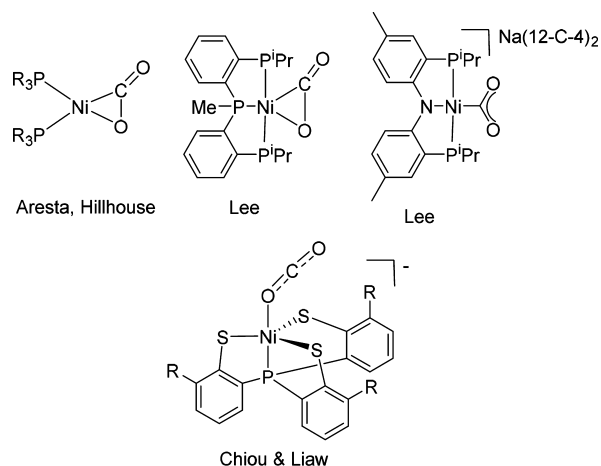
Herein we report a rare case of Ni(η¹-CO₂-κC) complexes, obtained by direct coordination of free CO₂ to lutidine-based Ni–hydride complexes [(^R-PNP*)NiH] (^R-PNP* = dearomatized PNP ligand, R = ^tBu, ⁱPr) involving metal–ligand cooperation.

CO₂ coordination to Ni complexes is well known,⁴⁰ and Ni complexes serve as efficient catalysts in CO₂ activation and utilization as a C1 building block,^{31,41} mainly in CO₂ hydrogenation^{42–45} and carboxylation.^{46–56} The first structurally characterized metal–CO₂ complex was (PCy₃)₂Ni(η²-CO₂), reported by Aresta et al. in 1975 (Scheme 2).⁵⁷ Since then, several similar Ni(η²-CO₂) complexes have been reported,^{58,59} including a unique five-coordinated Ni(η²-CO₂) complex.⁶⁰ A unique coordination mode of μ-η²,η²-CO₂ in a dinuclear Ni complex was reported by Sadighi and co-workers,⁶¹ and a rare case of Ni^{III}(η¹-(CO₂)⁺-κO) was reported by Chiou, Liaw, and co-workers.⁶² Recently a rare case of Ni^{II}(η¹-CO₂-κC) was reported by Lee⁶³ (Scheme 2).

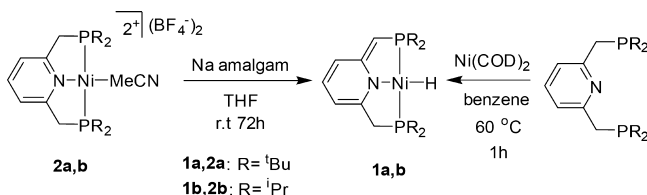
The dearomatized complex [(^tBu-PNP*)NiH] (**1a**, Scheme 3), reported by van der Vlugt et al., was obtained by reaction of LiAlH₄ with the dearomatized complex [(^tBu-PNP*)NiCl].⁶⁴ Surprisingly, we obtained the Ni(II) complex **1a** by attempting to reduce the dicationic Ni(II) complex [(^tBu-PNP)Ni-

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Scheme 2. Mononuclear Ni CO₂ Complexes

Scheme 3. Synthesis of Complexes 1a,b



(MeCN)](BF₄)₂⁶⁴ 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 [(ⁱPr-PNP)Ni(MeCN)]-

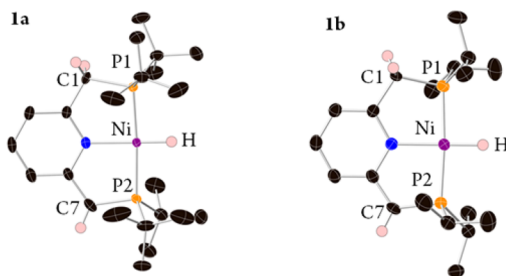


Figure 1. Single-crystal X-ray structures with thermal ellipsoids shown at the 50% probability level of complex 1a (left) and complex 1b (right). Hydrogen atoms, except Ni–H and side arm protons, are omitted for clarity. See the Supporting Information for a full description of the structures.

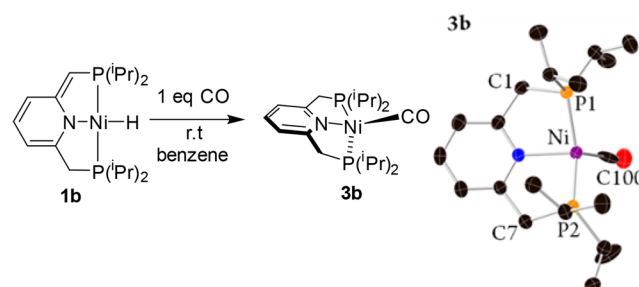
(BF₄)₂ was also prepared, and upon similar treatment with sodium amalgam the corresponding dearomatized hydrido complex 1b was obtained (Scheme 3). Crystals suitable for X-ray diffraction of 1b (Figure 1) were obtained by evaporation of its pentane solution. The X-ray structures of 1a,b reveal the expected square-planar geometry.

Complex 1b exhibits in the ¹H NMR spectrum a hydride signal at –18.13 ppm (²J_{PH} = 65 Hz), and the ³¹P{¹H} 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 d¹⁰ ML₄ complex, Ni(0) complexes prefer to adopt a tetrahedral geometry, and Ni(0) square-planar complexes are as yet

unknown. Only one d¹⁰ 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 Ni⁰(COD)₂ complex with the R-PNP ligands (R = ^tBu, ⁱPr) 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 ^tBu-PNP ligand. However, upon addition of 1 equiv of CO to the ⁱPr-PNP complex 1b, a rapid color change occurred, yielding the unusual neutral pincer Ni(0) carbonyl complex 3b (Scheme 4). Complex 3b exhibits a

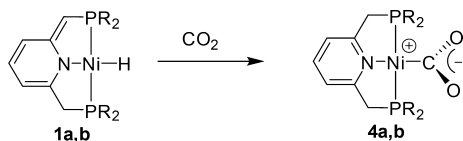
Scheme 4. Formation of the Ni(0) Complex 3b and Its Single-Crystal X-ray Structure with Thermal Ellipsoids Shown at the 50% Probability Level^a

^aHydrogen atoms are omitted for clarity. See the Supporting Information for a full structural description.

singlet peak at 68.36 ppm in the ³¹P{¹H} 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 ¹³C{¹H} NMR spectrum, at a slightly higher field in comparison to that of the recently reported nickel monocarbonyl anionic complex {Na(12-C-4)}₂{(acriPNP)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{(acriPNP)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 CO₂ to give the aromatized complexes 4a,b with a rare η¹ coordination mode of carbon dioxide (Scheme 5). While complex 1b reacts readily with CO₂ at ambient temperature with only 0.5 bar of CO₂, forming complex 4b in 82% yield (according to ³¹P

Scheme 5. Synthesis of Complexes 4a,b



4a: R = ^tBu, 8 bar CO₂, 72 hrs, 80 °C.

4b: R = ⁱPr, 0.5 bar CO₂, 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 -CO₂ coordination mode is common, the η^1 -CO₂ coordination mode is rare. It was reported for [Rh(diams)₂Cl(CO₂)],⁶⁷ [Ru(bpy)₂(CO)(CO₂)]·3H₂O,^{68,69} [Ir(dmpe)₂Cl(CO₂)],⁷⁰ and [Co(salen)K(η^1 -CO₂)(THF)].^{71,72} The only Ni- η^1 -CO₂ complex is the recently reported anionic complex [Na(12-C-4)₂][(PNP)Ni- η^1 -CO₂] (PNP = N[2-PⁱPr-2,4-Me-C₆H₃]₂),⁶³ which was obtained by a reduction of the carboxylate complex [(PNP)NiCOONa] and not by direct CO₂ 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

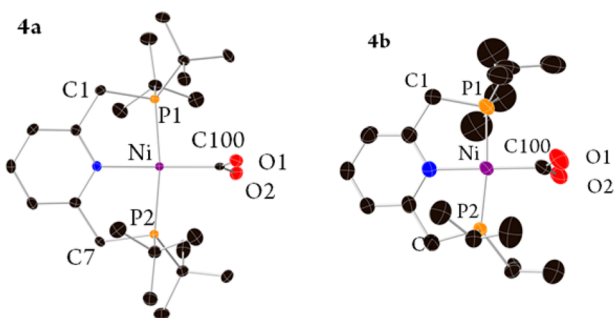


Figure 2. Single-crystal X-ray structures, with thermal ellipsoids shown at the 50% probability level, of complexes **4a** (left) and **4b** (right). Hydrogen atoms and cocrystallized solvents are omitted for clarity. See the [Supporting Information](#) for a full description of the structures.

under a CO₂ 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 CO₂ plane is almost perpendicular to the pincer ligand plane. The Ni–CO₂ 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 -CO₂ complexes and longer by 0.11–0.044 Å than those reported for Ni- η^2 -CO₂.^{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 -CO₂ 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 -CO₂ coordination mode, as the Ni–O bond lengths in η^2 -CO₂ complexes are shorter by 0.8–0.5 Å.^{57,59} The bond lengths of the CO₂ ligand in complexes **4a,b** are similar to the reported bonds of the complex [Na(12-C-4)₂][(PNP)Ni- η^1 -CO₂].⁶³ In addition, the Ni–CO₂ 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 ^tBu-PNP ligand in comparison to

the ⁱPr analogue. Aresta et al., in his seminal work on (PR₃)₂Ni(η^2 -CO₂) complexes (R = (C₆H₁₁), Et, Buⁿ), also observed that steric hindrance has a great influence on the Ni–CO₂ bond strength.⁵⁸ We have previously reported that the steric difference between the ^tBu-PNP and ⁱPr analogues can lead to large differences in reactivity.⁷³ The lower steric hindrance of the ⁱPr-PNP can result in a higher degree of π back-donation from the Ni center to the CO₂ ligand,⁶³ which shortens the Ni–CO₂ 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 CO₂ at room temperature to gradually form complex **4b** (Figure 3), complex **1a** requires

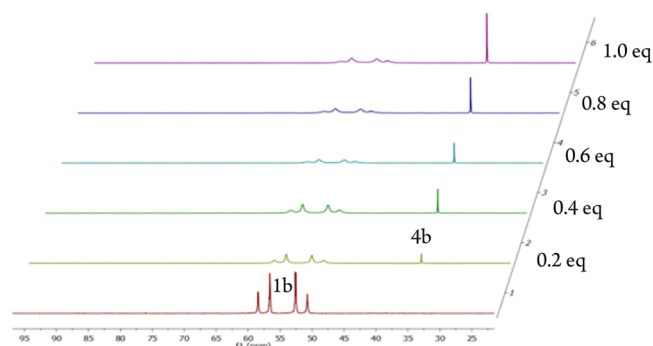


Figure 3. ³¹P{¹H} NMR (121.4 MHz) spectra representing gradual injection of about 0.2 equiv of CO₂ into a toluene solution of complex **1b** in an NMR tube equipped with a septum cap. Similar conditions with complex **1a** yielded no detectable conversion.

at least 5 bar of CO₂ 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 ¹H and ¹³C NMR spectral patterns of the ligand backbone and a singlet signal in the ³¹P{¹H} NMR spectrum at 47.65 (**4a**) and 35.46 ppm (**4b**), as expected for aromatic square-planar complexes. The CO₂ ligand gives rise to broad peaks at 174.74 and 173.25 ppm, respectively, in the ¹³C{¹H} NMR spectra, which are at a higher field in comparison to the reported chemical shifts of the CO₂ ligands in the complexes [Ru(bpy)₂(CO)(CO₂)]·3H₂O^{68,69} (203.9 ppm) and [Na(12-C-4)₂][(PNP)Ni- η^1 -CO₂]⁶³ (197.25 ppm). The reported Ni- η^2 -CO₂ 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 CO₂, an unexpected reaction was observed. According to the ³¹P{¹H} 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 CO₂, although at lower conversion. Complex **4a** demonstrated no such reactivity, despite the use of more forcing conditions of 10 bar of CO₂ 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 [(PⁱPr₂NC₂O₂)Ni(P(O)ⁱPr₂)] (**5b**, Figure 4) were obtained by layering of pentane over a dichloromethane solution. Complex

Scheme 6. CO₂ Cleavage by Complex 4b, Involving C=O and C–P Cleavage and C–C Bond Formation

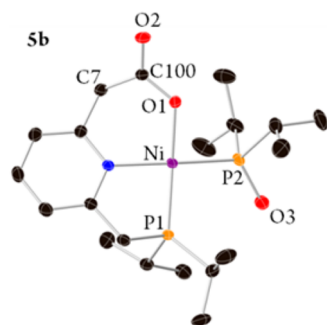
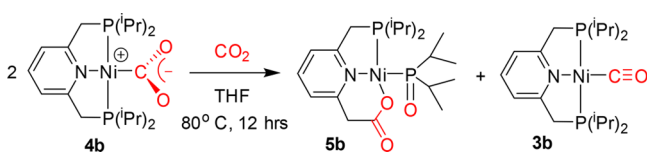


Figure 4. Single-crystal X-ray structures with thermal ellipsoids shown at the 50% probability level of complex **5b**. Hydrogen atoms are omitted for clarity. See the [Supporting Information](#) for a full description of the structure.

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 CO₂ 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 CH₂ signals of the benzylic positions, in which only one is coupled to a phosphorus atom, were observed in the ¹H and ¹³C{¹H} NMR.

Apparently, two molecules of CO₂ are involved, one leading to C–P cleavage followed by C–C bond formation, generating a carboxylate ligand, while the second molecule oxidizes the ⁱPr₂P fragment to the ⁱPr₂P=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 CO₂ molecules to give the Ir(III) carbonyl phosphoryl complex [Ir(depe)(CO)(Ph₂PO)(dbuCO₂)], 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 past⁷⁵ and also more in recent studies.^{76,77} Complexes bearing phosphoryl ligands (R₂P=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 [(ⁱPrPNP)Ni(CO)] pincer complex. Notably, complexes **1a,b** react with CO₂ via MLC to form rare examples of η¹ binding of

CO₂ to nickel, complexes **4a,b**. Upon heating under a CO₂ atmosphere, the CO₂ complex **4b** undergoes an unexpected CO₂ 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 Ni⁰CO 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](https://doi.org/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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■ REFERENCES

- (1) Maser, L.; Vondung, L.; Langer, R. *Polyhedron* **2018**, *143*, 28–42.
- (2) Albrecht, M.; Lindner, M. M. *Dalton Trans.* **2011**, *40*, 8733–8744.
- (3) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750–3781.
- (4) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759–1792.
- (5) van Koten, G. *J. Organomet. Chem.* **2017**, *845*, 4–18.
- (6) Morales-Morales, D.; Jensen, C. M. *The Chemistry of Pincer Compounds*, 1st ed.; Elsevier: Oxford, U.K., 2007.
- (7) Khusnutdinova, J. R.; Milstein, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236–12273.
- (8) Milstein, D. *Philos. Trans. R. Soc., A* **2015**, *373*, 20140189.
- (9) Zell, T.; Milstein, D. *Acc. Chem. Res.* **2015**, *48*, 1979–1994.
- (10) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588–602.
- (11) Gunanathan, C.; Milstein, D. *Top. Organomet. Chem.* **2011**, *37*, 55–84.
- (12) Milstein, D. *Top. Catal.* **2010**, *53*, 915–923.
- (13) Montag, M.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2012**, *134*, 10325–10328.
- (14) Zhang, J.; Leitun, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841.
- (15) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790–792.

- (16) Fogler, E.; Garg, J. A.; Hu, P.; Leitun, G.; Shimon, L. J. W.; Milstein, D. *Chem. - Eur. J.* **2014**, *20*, 15727–15731.
- (17) Hu, P.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *ACS Catal.* **2014**, *4*, 2649–2652.
- (18) Gunanathan, C.; Gnanaprakasam, B.; Iron, M. A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 14763–14765.
- (19) Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 16756–16758.
- (20) Feller, M.; Diskin-Posner, Y.; Shimon, L. J. W.; Ben-Ari, E.; Milstein, D. *Organometallics* **2012**, *31*, 4083–4101.
- (21) Bauer, J. O.; Leitun, G.; Ben-David, Y.; Milstein, D. *ACS Catal.* **2016**, *6*, 8415–8419.
- (22) Vogt, M.; Nerush, A.; Iron, M. A.; Leitun, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2013**, *135*, 17004–17018.
- (23) Nerush, A.; Vogt, M.; Gellrich, U.; Leitun, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2016**, *138*, 6985–6997.
- (24) Anaby, A.; Butschke, B.; Ben-David, Y.; Shimon, L. J. W.; Leitun, G.; Feller, M.; Milstein, D. *Organometallics* **2014**, *33*, 3716–3726.
- (25) Zhang, J.; Leitun, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113–1115.
- (26) Schwartsburd, L.; Iron, M. A.; Konstantinovskii, L.; Ben-Ari, E.; Milstein, D. *Organometallics* **2011**, *30*, 2721–2729.
- (27) Langer, R.; Leitun, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 2120–2124.
- (28) Feller, M.; Ben-Ari, E.; Diskin-Posner, Y.; Carmieli, R.; Weiner, L.; Milstein, D. *J. Am. Chem. Soc.* **2015**, *137*, 4634–4637.
- (29) Ben-Ari, E.; Leitun, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 15390–15391.
- (30) Schwartsburd, L.; Iron, M. A.; Konstantinovskii, L.; Diskin-Posner, Y.; Leitun, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2010**, *29*, 3817–3827.
- (31) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 5933.
- (32) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G. O.; Perez-Ramirez, J. *Energy Environ. Sci.* **2013**, *6*, 3112–3135.
- (33) Rivada-Wheelaghan, O.; Dauth, A.; Leitun, G.; Diskin-Posner, Y.; Milstein, D. *Inorg. Chem.* **2015**, *54*, 4526–4538.
- (34) Vogt, M.; Gargir, M.; Iron, M. A.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *Chem. - Eur. J.* **2012**, *18*, 9194–9197.
- (35) Huff, C. A.; Kampf, J. W.; Sanford, M. S. *Organometallics* **2012**, *31*, 4643–4645.
- (36) Vogt, M.; Nerush, A.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *Chem. Sci.* **2014**, *5*, 2043–2051.
- (37) Vogt, M.; Rivada-Wheelaghan, O.; Iron, M. A.; Leitun, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **2013**, *32*, 300–308.
- (38) Feller, M.; Gellrich, U.; Anaby, A.; Diskin-Posner, Y.; Milstein, D. *J. Am. Chem. Soc.* **2016**, *138*, 6445–6454.
- (39) Anaby, A.; Feller, M.; Ben-David, Y.; Leitun, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2016**, *138*, 9941–9950.
- (40) Paparo, A.; Okuda, J. *Coord. Chem. Rev.* **2017**, *334*, 136–149.
- (41) Guo, C.-X.; Yu, B.; Ma, R.; He, L.-N. *Curr. Green Chem.* **2015**, *2*, 14–25.
- (42) Burgess, S. A.; Kendall, A. J.; Tyler, D. R.; Linehan, J. C.; Appel, A. M. *ACS Catal.* **2017**, *7*, 3089–3096.
- (43) Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, *5*, 863–864.
- (44) Chakraborty, S.; Patel, Y. J.; Krause, J. A.; Guan, H. *Polyhedron* **2012**, *32*, 30–34.
- (45) Chakraborty, S.; Zhang, J.; Patel, Y. J.; Krause, J. A.; Guan, H. *Inorg. Chem.* **2013**, *52*, 37–47.
- (46) Cao, T.; Ma, S. *Org. Chem. Front.* **2016**, *3*, 1711–1715.
- (47) Diccianni, J. B.; Heitmann, T.; Diao, T. *J. Org. Chem.* **2017**, *82*, 6895–6903.
- (48) Cao, T.; Yang, Z.; Ma, S. *ACS Catal.* **2017**, *7*, 4504–4508.
- (49) Cao, T.; Ma, S. *Org. Lett.* **2016**, *18*, 1510–1513.
- (50) Makida, Y.; Marelli, E.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2014**, *50*, 8010–8013.
- (51) Correa, A.; León, T.; Martín, R. *J. Am. Chem. Soc.* **2014**, *136*, 1062–1069.
- (52) Juliá-Hernández, F.; Gaydou, M.; Serrano, E.; van Gemmeren, M.; Martín, R. *Top. Curr. Chem.* **2016**, *374*, 1–38.
- (53) Zhang, Y.; Riduan, S. N. *Angew. Chem., Int. Ed.* **2011**, *50*, 6210–6212.
- (54) Correa, A.; Martín, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 6201–6204.
- (55) Ochiai, H.; Jang, M.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 2681–2683.
- (56) Mori, M. *Eur. J. Org. Chem.* **2007**, *2007*, 4981–4993.
- (57) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, *0*, 636–637.
- (58) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, *7*, 708–711.
- (59) Anderson, J. S.; Iluc, V. M.; Hillhouse, G. L. *Inorg. Chem.* **2010**, *49*, 10203–10207.
- (60) Kim, Y.-E.; Kim, J.; Lee, Y. *Chem. Commun.* **2014**, *50*, 11458–11461.
- (61) Lee, C. H.; Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 13802–13803.
- (62) Chiou, T.-W.; Tseng, Y.-M.; Lu, T.-T.; Weng, T.-C.; Sokaras, D.; Ho, W.-C.; Kuo, T.-S.; Jang, L.-Y.; Lee, J.-F.; Liaw, W.-F. *Chem. Sci.* **2016**, *7*, 3640–3644.
- (63) Yoo, C.; Lee, Y. *Chem. Sci.* **2017**, *8*, 600–605.
- (64) van der Vlugt, J. I.; Lutz, M.; Pidko, E. A.; Vogt, D.; Spek, A. L. *Dalton Trans.* **2009**, *6*, 1016–1023.
- (65) Takeuchi, K.; Taguchi, H.-o.; Tanigawa, I.; Tsujimoto, S.; Matsuo, T.; Tanaka, H.; Yoshizawa, K.; Ozawa, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 15347–15350.
- (66) Sahoo, D.; Yoo, C.; Lee, Y. *J. Am. Chem. Soc.* **2018**, *140*, 2179–2185.
- (67) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914–5915.
- (68) Tanaka, H.; Nagao, H.; Peng, S. M.; Tanaka, K. *Organometallics* **1992**, *11*, 1450–1451.
- (69) Tanaka, H.; Tzeng, B. C.; Nagao, H.; Peng, S. M.; Tanaka, K. *Inorg. Chem.* **1993**, *32*, 1508–1512.
- (70) Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 2391–2392.
- (71) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405–7407.
- (72) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082–5092.
- (73) Feller, M.; Diskin-Posner, Y.; Leitun, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2013**, *135*, 11040–11047.
- (74) Langer, J.; Hamza, A.; Pápai, I. *Angew. Chem., Int. Ed.* **2018**, *57*, 2455–2458.
- (75) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171–185.
- (76) Cao, J.; Huang, X.; Wu, L. *Chem. Commun.* **2013**, *49*, 7747–7749.
- (77) Zhou, Y.; Gan, Z.; Su, B.; Li, J.; Duan, Z.; Mathey, F. *Org. Lett.* **2015**, *17*, 5722–5724.
- (78) Hollatz, C.; Schier, A.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 1333–1338.
- (79) Sylvain, R.; Vendier, L.; Bijani, C.; Santoro, A.; Puntoriero, F.; Campagna, S.; Sutra, P.; Igau, A. *New J. Chem.* **2013**, *37*, 3543–3548.
- (80) Weismann, J.; Scharf, L. T.; Gessner, V. H. *Organometallics* **2016**, *35*, 2507–2515.
- (81) Li, P.; Li, Q.-S.; Xu, F.-B.; Song, H.-B.; Zhang, Z.-Z. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, m1825–m1826.
- (82) Kanada, J.; Tanaka, M. *Adv. Synth. Catal.* **2011**, *353*, 890–896.
- (83) Zhang, J.; Medley, C. M.; Krause, J. A.; Guan, H. *Organometallics* **2010**, *29*, 6393–6401.
- (84) Salem, H.; Shimon, L. J. W.; Diskin-Posner, Y.; Leitun, G.; Ben-David, Y.; Milstein, D. *Organometallics* **2009**, *28*, 4791–4806.