Ni Complexes of an Alane/Tris(phosphine) Ligand Built Around a Strongly Lewis Acidic Tris(N-pyrrolyl)aluminum

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Ni Complexes of an Alane/Tris(phosphine) Ligand Built Around a Strongly Lewis Acidic Tris(N-pyrrolyl)aluminum

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Abstract. Syntheses of a new tripodal alane/tris(phosphine) ligand (AlP_3) based on 2-(diisopropylphosphino)pyrrole, and AlP_3-supported Ni complexes are reported. The central tris(pyrrolyl)aluminum moeity acts as a stronger Lewis acid towards Ni that other related group 13 element-centered tripodal ligands, as demonstrated by the binding of H_2 to Ni and ease of reduction.

Z-type ligand is a term that arose to describe the binding of typical σ-Lewis acids to transition metal centers functioning as Lewis bases.[1] Such M→Z complexes have attracted considerable attention because of the potential for the modulation of the properties of the transition metal center via changes in the nature of the Z-Lewis acid, including for applications in catalysis.[2-7] Z-ligands are often incorporated into polydentate chelates.[1,2] The ZL_3 type, combining a central Z site with three outer neutral donors has been commonly explored (**A**, **B**, **C**, Figure 1).[8-15] The known ZL_3 ligands typically position the Z and the L sites in a 1,2-relationship to each other. 1,2-Disposition on an aromatic ring such as in **B** provides significant rigidity and preorganization to the structure that is geometrically well set up for binding a transition metal.

We surmised that using a 1,2-pyrrolediyl connection presents an attractive alternative to 1,2-benzenediyl in **B**. Both are flat aromatic connectors, but N-pyrrolyl is a very electron-withdrawing substituent compared to a C-aryl,[16] introducing intrinsic electronic asymmetry. We note that the pyrrole backbone has not been widely used in ligand construction,[17-21] in contrast to the benzene ring connectors which are ubiquitous in many ligand types far beyond ZL_3. A reliable synthesis of a 2-phosphinopyrrole precursor should permit a more active exploration of these options. The only known derivative is 2-diphenylphosphinopyrole,[22-25] which was most recently used by Tonks et al.[26,27] and Johnson et al.[28] Its synthesis is not high-yielding and we have not had success in adapting it for other phosphino variations.[29] In this work, we wish to report two synthetic pathways leading to 2-(diisopropylphosphino)pyrrole (**4**, Scheme 1), as well as the straightforward use of **4** in the construction of a new AlP_3 ligand (Scheme 2) and AlP_3 complexes.[30] The AlP_3 ligand combines a central Z-type alane site with three outer phosphine donors. We were attracted to exploring AlP_3 because the pyrrolyl substituents on Al should render it more electron-poor than the C-aryl substituents on boron in **B** or the dialkylamido substituents on Al in **C**. Coupled with the absence of the extra amine donor such as in **C**, we expected that the alane site in AlP_3 should be considerably more Lewis acidic[31] than other common ZL_3 systems with a central group 13 Lewis acid.

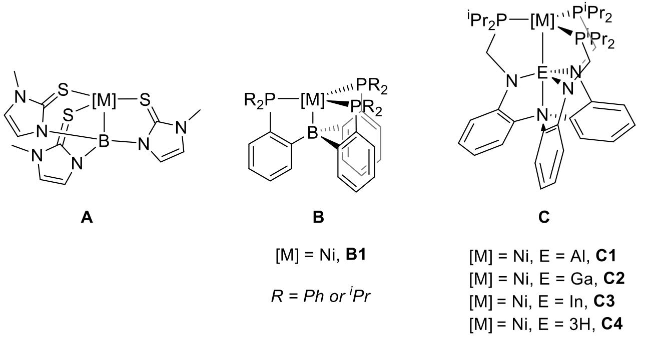

Figure 1. Key examples of transition metal complexes of ZL_3 ligands from the literature.

N-Boc protected 2-bromopyrrole (**1**) was prepared according to a published procedure.[32] Lithium/bromine exchange presumably generated the unobserved **2** in situ, which was allowed to react with ClP^iPr_2, resulting in the formation of crude **3** (Method A, Scheme 1). Deprotection of the Boc group produced **4** in good yield, but in sub-optimal purity, which can be traced to the 87% purity of **1**. Purification of **4** can be accomplished via the synthesis of the lithio derivative **5**, which was isolated in a 60% yield. Air-free hydrolysis of **5** then gave **4**

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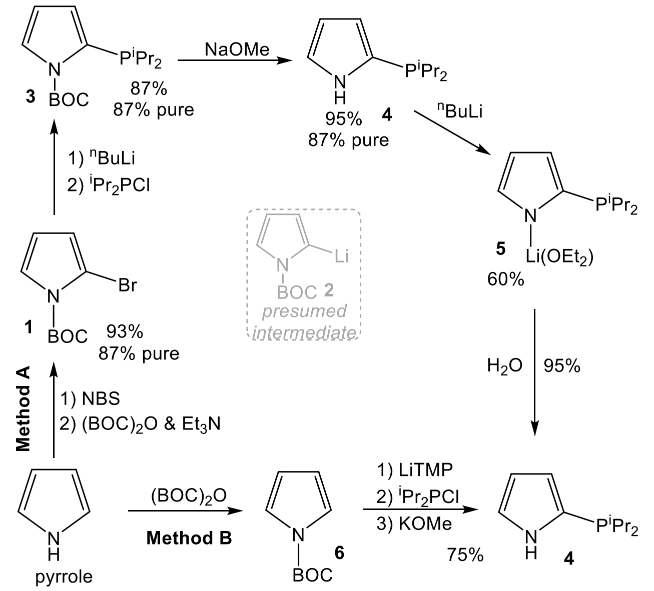
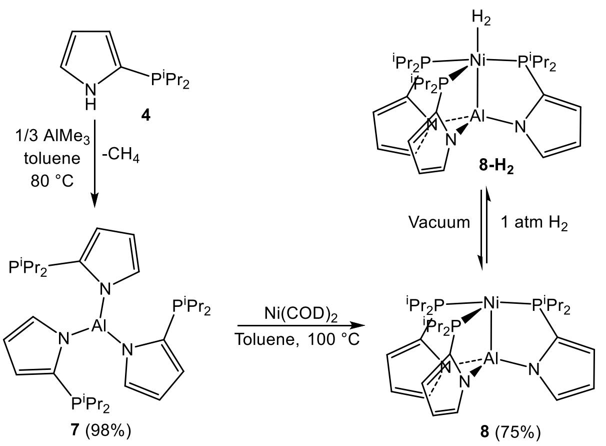
Electronic Supplementary Information (ESI) available: Details of experimental procedures and characterization. Crystallographic data: CCDC 1915840. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x of >98% purity (47% yield based on ${}^{i}Pr_2PCl$). An alternative synthesis (Method B) generates the presumed intermediate **2** via deprotonation of **6** [33] with LiTMP[23], followed by phosphination and Boc-deprotection. Distillation of the crude product, followed by recrystallization from isooctane yielded **4** in high purity and 75% yield.



Scheme 1. Synthesis of phosphinopyrrole.

The tripodal ligand AlP_3 (**7**) was synthesized via protolysis of $AlMe_3$ with 3 equiv of pyrrolylphosphine (**4**) at 80 °C for 1 h in toluene. After all the volatiles were removed under vacuum, AlP_3 was obtained as an orange oil of >95% purity (NMR evidence). Attempts to purify AlP_3 (**7**) further were hampered by its high lipophilicity and sensitivity towards water and other protic sources, but the crude material could be used effectively in the next step. Thermolysis of **7** with $Ni(COD)_2$ at 100 °C for 4 h in toluene led to the formation of $(AlP_3)Ni$ (**8**, Scheme 2), which was isolated in the form of analytically pure dark-green crystals in 75% yield after filtration and recrystallization. Both **7** and **8** displayed apparent C_{3v} symmetry in their NMR spectra at ambient temperature, although the signals of **8** appeared broadened.

Single crystals suitable for an X-ray study were obtained via vapor diffusion of pentane into a toluene solution of $(AlP_3)Ni$. An XRD study revealed an approximately C_3-symmetric structure for **8** in the solid state (Figure 2). The Ni centre is only slightly displaced from the plane defined by the three phosphorus atoms (ΣP-Ni-P = 357.4°), while the geometry of the Al center is decidedly tetrahedral with an average Ni-Al-N angle of 112.6°. The Ni-Al distance in **8** (2.2695(16) Å) can be contrasted with the much longer Ni-Al distance in Lu's **C1** (ca. 2.45 Å)[14] and the sum of the corresponding covalent radii per Alvarez et al (also 2.45 Å).[34] Furthermore, the Ni-Al distance in **8** is only ca. 0.1 Å longer than the Ni-B distance in **B1**,[12] in spite of a 0.37 Å larger covalent radius for Al vs B.[34] These data suggest a strong Ni-Al interaction. It is best viewed as σ-donation from a zerovalent Ni to the Al Lewis acid. The presence of this interaction renders the Ni center divalent because two electrons of the original d^{10} configuration at Ni are being used for Ni→Al bonding.[35] The semantics and the nuanced theoretical underpinnings of the nomenclature pertaining to the oxidation state and d^n configuration assignments in M→Z complexes have been debated and analysed elsewhere.[1-3,14,36-38]



Scheme 2. Synthesis of **7** and its complexation with Ni

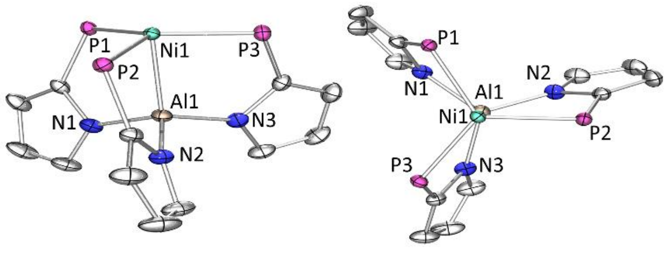
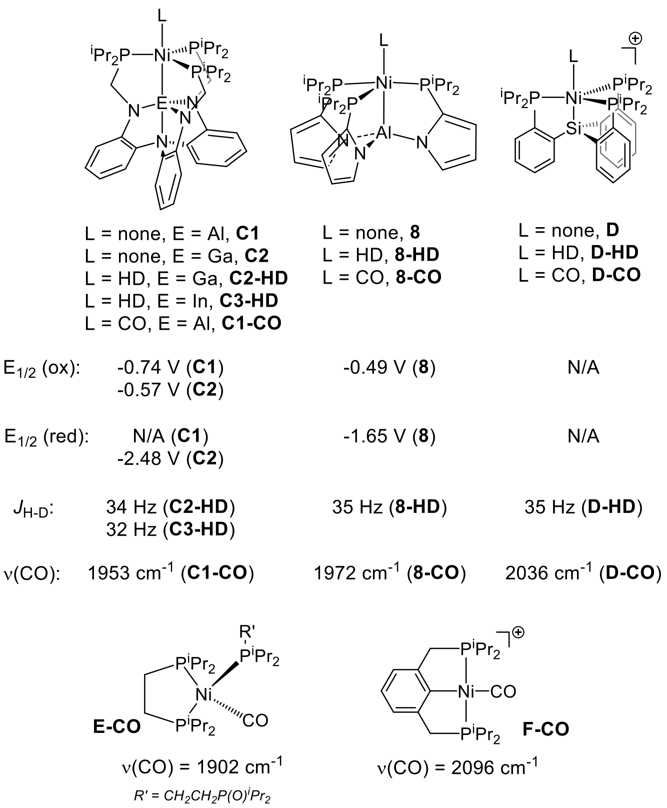


Figure 2. ORTEP drawing (50% thermal ellipsoids) of **8** showing selected atom labeling. Hydrogen atoms and isopropyl groups were omitted for clarity. Selected bond distances (Å) and angles (°): Ni1-P1, 2.2217(13); Ni1-P2 2.2227(13); Ni1-P3 2.2197(17); Ni1-Al1, 2.2695(16); Al-N1, 1.8591(19); Al1-N2, 1.8545(16); Al-N3 1.8483(19); P1-Ni1-P2, 117.61(5); P1-Ni1-Al1, 86.18(4); P2-Ni1-Al1, 84.18(3); P3-Ni1-P1, 118.91(2); P3-Ni1-P2 120.89(4); P3-Ni1-Al1 83.60(2); N1-Al1-Ni1, 106.55(5); N2-Al1-Ni1, 104.57(6); N2-Al1-N1, 112.91(7); N3-Al1-Ni1, 107.39(4); N3-Al1-N1, 113.03(6), N3-Al1-N2, 111.73(7).

Further evidence of the strong Ni→Al donation can be deduced from the electrochemical study of $(AlP_3)Ni$ (**8**). Cyclic voltammogram of **8** (Figure S30) displayed two quasi-reversible waves with $E_{1/2}$ values of -0.49 V and -1.65 V vs the Fc/Fc^+ couple. We assign these two redox events as oxidation and reduction of **8**, respectively. The contrast with the complexes by Lu et al. is instructive. Reversible oxidation was reported for **C1** (-0.74 V), **C2** (-0.57), and the Lewis-acid free complex **C4** (-1.02 V), indicating that **8** is more difficult to oxidize than any of these (Figure 3). A reversible reduction for **C1** was not reported, but the Ga analog **C2** displayed a reversible reduction at -2.48 V.[14,15] The overall analysis by Lu et al. suggested that Ga is more electron-withdrawing than Al with respect to Ni in their compound series.[15] Thus, the much greater ease of reduction of **8** is striking. The larger difference in the potentials for the reduction events between **8** and **C2** ($\Delta E_{1/2}$ = 0.83 V), compared to a modest difference in potentials for the oxidation event ($\Delta E_{1/2}$ = 0.08 V) is likely a reflection of that the Ni→Al interaction is much more influential on the LUMO than on the HOMO of an $(L_3Z)Ni$ molecule.[14]

Lu et al. investigated the binding of H_2 to Ni in their series of compounds **C1-C3**, including demonstrating that catalysis of olefin and CO_2 hydrogenation was possible.[5,15] Notably, they observed little to no binding of H_2 to **C1** at RT, and only to the Ga and In analogs **C2** and **C3**.[39] Binding of H_2 to **B1** was also not detected.[40] In contrast, the dark-green solution of **8** in C_6D_6 turned pale green immediately when it was exposed to 1 atm H_2. NMR spectroscopy indicated the formation of a new complex **8-H$_2$**, with a broad resonance at -2.1 ppm in the ^1H NMR spectrum, and new, considerably shifted resonances in the $^{31}P\{^1H\}$ (24.3 ppm vs 13.0 ppm for **8** and ^{27}Al NMR spectra (138.0 ppm vs 104.4 ppm for **8**). Variable temperature NMR experiments showed that below -20 °C, the resonance for the Ni-bound H_2 shifted to ca. -2.5 ppm, the signal for free H_2 appeared, and no trace of **8** was evident. This suggests that **8-H$_2$** constitutes ca. 90% of the mixture at RT and is in rapid equilibrium with **8** and free H_2. At temperatures below -20 °C, however, the formation of **8-H$_2$** is complete under 1 atm of H_2. Collecting NMR spectra at temperatures down to -75 °C did not allow for an unambiguous T_{1min} value, but the lowest obtained values of <25 ms were consistent with a classical dihydrogen complex.[41] This was corroborated by the J_{H-D} = 35 Hz determined for **8-HD** isotopomer prepared from **8** and HD gas.[42] This value can be compared against those for the HD adducts of **C2** (34 Hz) and **C3** (32 Hz) analysed by Lu et al (Figure 3).[39,43] The slightly higher value in **8-HD** suggests less back-donation to HD from Ni and is consistent with the notion of a more electron-poor Ni center in **8-HD**. However, all these values are near the upper limit for HD complexes, and are similar to that observed by Peters et al. in the closely related **D-HD** (Figure 3).[40]

Exposure of a C_6D_6 solution of **8** to 1 atm of CO resulted in complete conversion to the new complex **8-CO** (Figure 3). Its ν(CO) value can be used to compare the capacity of the Ni center for π-back-donation in the three locally isoelectronic systems **C1-CO**,[44] **8-CO**, and **D-CO**[40] (Figure 3). The ν(CO) values for these three complexes lie in between the values for complexes **E-CO** and **F-CO** (Figure 3), which possess the more traditional, four-coordinate geometries about zerovalent Ni (**E-CO**, tetrahedral)[45] and low-spin divalent Ni (**F-CO**, square-planar).[46] The values for **C1-CO** and **8-CO** are closer to the value of the zerovalent **E-CO**, whereas the value for **D-CO** is closer to **F-CO**. However, it must be noted that the difference between **8-CO** and **D-CO** (74 cm^{-1}) is similar to the differences between **8-CO** and **E-CO** (70 cm^{-1}), or **D-CO** and **F-CO** (60 cm^{-1}). Thus, the triad of **C1**/**8**/**D** can be viewed as part of a continuum of possible structures in which Ni is rendered to be more electron-poor by the donation to a progressively stronger Lewis acid: base-stabilized tris(amido)alane in **C1**, tris(pyrrolyl)alane in **8**, and formally triarylsilylium cation in **D**.



L = none, E = Al, **C1**
L = none, E = Ga, **C2**
L = HD, E = Ga, **C2-HD**
L = HD, E = In, **C3-HD**
L = CO, E = Al, **C1-CO**

L = none, **8**
L = HD, **8-HD**
L = CO, **8-CO**

L = none, **D**
L = HD, **D-HD**
L = CO, **D-CO**

$E_{1/2}$ (ox):	-0.74 V (**C1**) -0.57 V (**C2**)	-0.49 V (**8**)	N/A
$E_{1/2}$ (red):	N/A (**C1**) -2.48 V (**C2**)	-1.65 V (**8**)	N/A
J_{H-D}:	34 Hz (**C2-HD**) 32 Hz (**C3-HD**)	35 Hz (**8-HD**)	35 Hz (**D-HD**)
ν(CO):	1953 cm^{-1} (**C1-CO**)	1972 cm^{-1} (**8-CO**)	2036 cm^{-1} (**D-CO**)

ν(CO) = 1902 cm^{-1}
ν(CO) = 2096 cm^{-1}
$R' = CH_2CH_2P(O)^iPr_2$

Figure 3. Comparison of selected properties of **8** and its HD and CO adducts with literature examples.

All in all, our observations indicate with that the central Lewis acid in AlP_3 (**7**) is considerably stronger than the Z fragments in other common group 13-centered ZL_3 ligands. The greater degree to which the alane site in **8** withdraws electron density from Ni is consistent with the short Al-Ni distance, ease of reduction of $(AlP_3)Ni$ (**8**), and the ability of Ni in **8** to bind H_2.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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[1] A. Amgoune and D. Bourissou, *Chem. Commun.,* 2011, **47**, 859– 871.

[2] D. You and F. P. Gabbaï, *Trends Chem.,* 2019, **1**, 485-496.

[3] J. S. Jones and F. P. Gabbaï, *Acc. Chem. Res.,* 2016, **49**, 857–867.

[4] W. H. Harman, T.-P. Lin and J. C. Peters, *Angew. Chem., Int. Ed.,* 2014, **53**, 1081−1086.

[5] R. C. Cammarota, M. V. Vollmer, J. Xie, J. Ye, J. C. Linehan, S. A. Burgess, A. M. Appel, L. Gagliardi and C. C. Lu, *J. Am. Chem. Soc.,* 2017, **139**, 14244–14250

[6] J. S. Anderson, J. Rittle and J. C. Peters, *Nature*, 2013, **501**, 84–87.

[7] J. T. Moore and C. C. Lu, *J. Am. Chem. Soc.,* 2020, **142**, 11641–11646.

[8] M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Organometallics,* 2004, **23**, 913–916.

[9] D. J. Mihalcik, J. L. White, J. M. Tanski, L. N. Zakharov, G. P. A. Yap, C. D. Incarvito, A. L. Rheingold and D. Rabinovitch, *Dalton Trans.,* 2004, 1626–1634.

[10] K. Pang, J. M. Tanski and G. Parkin, *Chem. Commun.,* 2008, 1008–1010.

[11] S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, *Angew. Chem., Int. Ed*., 2008, ***47***, 1481-1484.

[12] M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, *J. Am. Chem. Soc.,* 2008, ***130***, 16729-16738.

[13] M.-E. Moret, L. Zhang and J. C. Peters, *J. Am. Chem. Soc.,* 2013, ***135***, 3792.

[14] P. A. Rudd, S. Liu, L. Gagliardi, V. G. Young and C. C. Lu, *J. Am. Chem. Soc.,* 2011, **133**, 20724.

[15] R. C. Cammarota and C. C. Lu, *J. Am. Chem. Soc.*, 2015, **137**, 12486–12489.

[16] K.G. Moloy and J. L. Petersen, *J. Am. Chem. Soc.,* 1995, **117**, 7696–7710.

[17] W. Weng, S. Parkin and O. V. Ozerov, *Organometallics,* 2006, **25**, 5345–5354.

[18] E. R. King and T. A. Betley, *J. Am. Chem. Soc.,* 2009, **131**, 14374–14380.

[19] S. M. Cohen and S.R. Halper, *Inorg. Chim. Acta,* 2002, **341**, 12–16.

[20] W. Weng, C.-H. Chen, B. M. Foxman and, O. V. Ozerov, *Organometallics,* 2007, **26**, 3315-3320.

[21] S. Li, Y. Wang, W. Yang, K. Li, H. Sun, X. Li, O. Fuhr and D. Fenske, *Organometallics,* 2020, **39**, 757−766.

[22] A. J. Arce, A. J. Deeming, Y. De Sanctis, S. K. Johal, C. M. Martin, M. Shinhmar, D. M. Speel and A. Vassos, *Chem. Commun.,* 1998, **2**, 233

[23] M. F. Semmelhack, A. Chlenov and D. M. Ho, *J. Am. Chem. Soc.,* 2005, **127**, 7759-7773.

[24] A. J. Deeming and M. K. Shinhmar, *J. Organomet. Chem.,* 1999, **592**, 235-239.

[25] P. L. Dunn, A. H. Reath, L. J. Clouston, V. G. Young and I. A. Tonks, *Polyhedron,* 2014, **84**, 111.

[26] P. L. Dunn, E. P. Beaumier and I. A. Tonks, *Polyhedron,* 2020, ***181***, 114471.

[27] P. L. Dunn, S. Chatterjee, S. N. MacMillan, A. J. Pearce, K. M. Lancaster and I. A. Tonks, *Inorg. Chem.*, 2019, ***58***, 11762.

[28] H. D. Fokwa, J. F. Vidlak, S. C. Weinberg, I. D. Duplessis, N. D. Schley, and M. W. Johnson, *Dalton Trans*. **2020**, *49*, 9957-9960.

[29] Closely related 2-indolylphosphines have been used in constructing polydentate ligands: (a) L. J. Murphy, H. Hollenhorst, R. McDonald, M. Ferguson, M. D. Lumsden and L. Turculet, *Organometallics*, 2017, **36**, 3709-3720. (b) J. Wassenaar and J. N. Reek, *Dalton Trans*. 2007, **34**, 3750– 3753.

[30] For an early example of a Ni complex of an alane/tris(phosphine) ligand Al(CH$_2$PMe$_2$)$_3$ (the extent of any Ni-Al interaction is unknown), see: H. H. Karsch, and A. Appelt, J. Organomet. Chem., 1986, **314**, C5-C8.

[31] M. Layh, W. Uhl, G. Bouhadir and D. Bourissou, in *The Chemistry of Organoaluminum Compounds*, ed. L. Micouin, I. Marek and Z. Rappoport, John Wiley and Sons, Hoboken, NJ, 2017, pp. 379–424

[32] S.J. Mishra, S. Ghosh, A. R. Stothert, C. A. Chad A. Dickey and B. S. J. Blagg, *ACS Chem. Biol.,* 2017, **12**, 244-253

[33] H. Salman, Y. Abraham, S. Tal, S. Meltzman, M. Kapon, N. Tessler, S. Speiser and Y. Eichen, *Eur. J. Org. Chem*., 2005, **11**, 2207-2212.

[34] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans*., 2008, **21**, 2832

[35] G. Parkin, *J. Chem. Educ.*, 2006, ***83***, 791.

[36] A. F. Hill, *Organometallics,* 2006, **25**, 4741–4743.

[37] G. Parkin, *Organometallics,* 2006, **25**, 4744–4747.

[38] J. B. Bonanno, T. P. Henry, P. T. Wolczanski, A. W. Pierpont and T. R. Cundari, *Inorg. Chem.,* 2007, **46**, 1222–1232.

[39] R. C. Cammarota, J. Xie, S. A. Burgess, M. V. Vollmer, K. D. Vogiatzis, J. Ye, J. C. Linehan, A. M. Appel, C. Hoffmann, X. Wang, V. G. Young, Jr. and C. C. Lu, *Chem. Sci*., 2019, **10**, 7029–7042.

[40] C. Tsay and J. C. Peters, *Chem. Sci*., 2012, **3**, 1313-1318. Four-coordinate **D** was not isolated, it is only referred to here for comparison.

[41] P. J. Desrosiers, L. Cai, Z. Lin, R. Richards and J. Halpern, *J. Am. Chem. Soc.,* 1991, **113**, 4173– 4184.

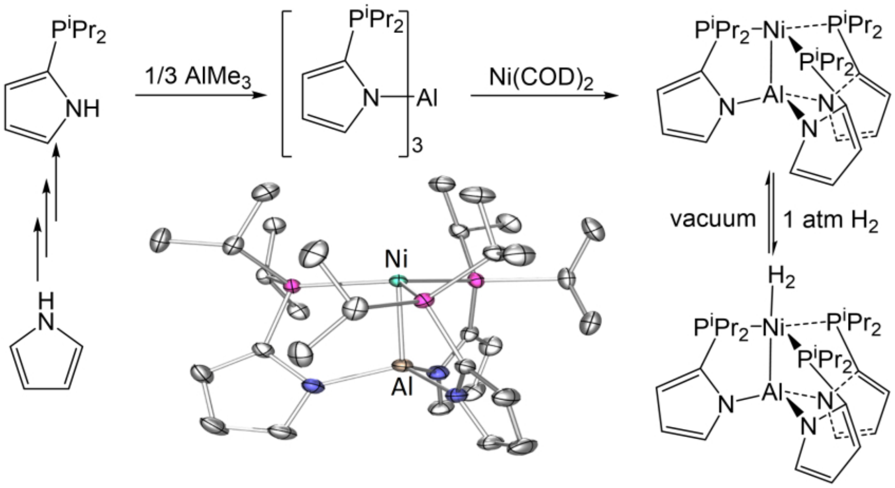
[42] R. H. Crabtree, *Chem. Rev.,* 2016, **116**, 8750-8769.

[43] R. C. Cammarota, L. J. Clouston, and C. C. Lu, *Coord. Chem. Rev*., 2017, **334**, 100-111.

[44] M. V. Vollmer, R. C. Cammarota and C. C. Lu, *Eur. J. Inorg. Chem*. 2019, **2019**, 2140-2145.

[45] L. González-Sebastián, M. Flores-Alamoa and J. J. García, *Dalton. Trans*., 2011, **40**, 9116-9122.

[46] G. M.Lee, I. Korobkov and R. T. Baker, *J. Organomet. Chem*., 2017, **847**, 270-277.



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