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Nickel(II) Complexes of Bis(2-diphenylphosphinophenyl)amide

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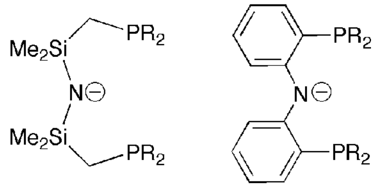
Summary: A series of nickel(II) alkyl and aryl complexes supported by the bis(2-diphenylphosphinophenyl)amide ligand, [PNP]$^-$, have been prepared, including those in which the alkyl contains β-hydrogen atoms. The stability of these compounds toward β-elimination is attributed to the rigidity and robustness of the new tridentate amido diphosphine ligand.

Chart 1



Metal complexes of "hybrid" ligands that contain both soft and hard donors have received increasing attention in recent years because of their potentials for generating unusual chemical transformations.[1] One remarkable example in this aspect is the chelating amido phosphine derivatives that contain the $-SiMe_2CH_2-$ ligand backbone as depicted in Chart 1. The tridentate ligands of this type have shown widespread reactivity with metals across the periodic table.[2−10] These ligands, however, are prone to phosphine dissociation under certain circumstances due to the flexibility of the backbone.[11] With the silyl linker, the ligands may become reactive, as cleavage of both N−Si[12] and C−H[13] bonds has been observed. In an effort to develop new chelating amido phosphine ligands that are potentially more rigid and robust, we aim to synthesize a series of *o*-phenylene derivatives.[14] To this end, we have prepared the potentially tridentate bis(2-diphenylphosphinophenyl)amide ligand, [PNP]$^-$, and explored the coordination chemistry

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(1) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.

(2) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839−2845.

(3) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1992**, *11*, 2967−2969.

(4) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J.; Thompson, R. C. *Inorg. Chem.* **1994**, *33*, 5528−5534.

(5) Fryzuk, M. D.; Mylvaganam, M.; Zaworotko, M. J.; MacGillivray, L. R. *Organometallics* **1996**, *15*, 1134−1138.

(6) Fryzuk, M. D.; Giesbrecht, G.; Rettig, S. J. *Organometallics* **1996**, *15*, 3329−3336.

(7) Fryzuk, M. D.; Giesbrecht, G. R.; Olovsson, G.; Rettig, S. J. *Organometallics* **1996**, *15*, 4832−4841.

(8) Fryzuk, M. D.; Giesbrecht, G. R.; Rettig, S. J. *Organometallics* **1997**, *16*, 725−736.

(9) Fryzuk, M. D.; Leznoff, D. B.; Ma, E. S. F.; Rettig, S. J.; Young, V. G. *Organometallics* **1998**, *17*, 2313−2323.

(10) Fryzuk, M. D.; Leznoff, D. B.; Thompson, R. C.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 10126−10135.

(11) Fryzuk, M. D.; Carter, A.; Rettig, S. J. *Organometallics* **1992**, *11*, 469−472.

(12) Ozerov, O. V.; Ferard, H. F.; Watson, L. A.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **2002**, *41*, 5615−5625.

(13) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026−2036.

(14) Liang, L.-C.; Lee, W.-Y.; Huang, M.-H.; Yin, C.-C.; Hung, C.-H. Manuscript in preparation.

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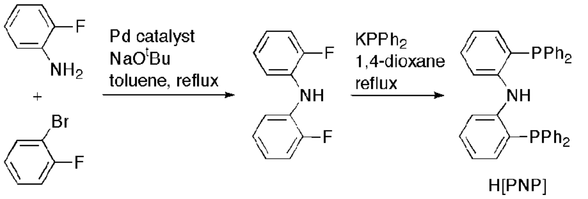
involving it. In this contribution, we present the synthesis of H[PNP] and an account of our experiments involving divalent nickel, which led to the discovery of thermally stable alkyl derivatives including those containing β-hydrogen atoms, a result that is markedly different from that found in the silyl-derived $[N(SiMe_2CH_2PR_2)_2]^-$ system.[15]

The ligand synthesis takes two straightforward steps from relatively inexpensive, commercially available starting materials. As shown in eq 1, the palladium-catalyzed cross-coupling reaction[16−18] of 2-fluoroaniline with 2-bromofluorobenzene in the presence of sodium *tert*-butoxide in refluxing toluene produces di(2-fluorophenyl)amine quantitatively. After standard workup, di(2-fluorophenyl)amine may be directly used for the subsequent nucleophilic phosphanylation[19,20] without further purification. Treatment of di(2-fluorophenyl)amine with 2 equiv of $KPPh_2$ in refluxing 1,4-dixoane generates H[PNP], which can be readily purified by recrystallization from dichloromethane or methanol. Compound H[PNP] and the fluorine precursor have been fully characterized by multinuclear NMR spectroscopy and elemental analysis. The solid-state structure of H[PNP] was determined by X-ray crystallography (see Supporting Information).



(1)

Addition of *n*-butyllithium to H[PNP] in THF at −35 °C affords in 78% yield the lithium amide complex $[PNP]Li(THF)_2$ as a pale yellow crystalline solid, which is stable under an inert atmosphere and can be easily manipulated in the drybox. The ^1H NMR spectrum of the lithium complex indicates 2 equiv of coordinated THF molecules. The phosphorus donors of $[PNP]Li(THF)_2$ in C_6D_6 appear as a broad singlet resonance at −14.44 ppm in the $^{31}P\{^1H\}$ NMR spectrum at room temperature, a value relatively downfield as compared to the protonated compound H[PNP] at −18.62 ppm and the silyl-derived $LiN(SiMe_2CH_2PPh_2)_2$ at −23.20 ppm.[15] The absence of internuclear coupling between phosphorus and lithium-7 ($I = 3/2$, natural abundance 92.6%) is consistent with no or extremely weak phosphine coordination. Accordingly, the $^7Li\{^1H\}$ NMR spectrum at room temperature reveals a broad singlet at 2.42 ppm instead of the expected triplet resonance.

The solid-state structure of $[PNP]Li(THF)_2$ confirms the tridentate feature of this new amido diphosphine ligand. An X-ray study of $[PNP]Li(THF)_2$ showed it to be a five-coordinate species with distorted trigonal bipyramidal geometry about the lithium center, as depicted in Figure 1. The tridentate ligand coordinates to the lithium atom in a meridional fashion. The bond distances between the lithium atom and the two phosphorus donors in $[PNP]Li(THF)_2$ (2.80 Å average) are slightly longer than those found in $\{[LiN(SiMe_2CH_2P^iPr_2)_2]_2\}LiCl$[8] by ca. 0.20 Å. The Li(1)−N(1), Li(1)−O(1), and Li(1)−O(2) distances are all unexceptional. The bond angles about Li(1) are in the range 73.09(15)−146.01(18)°, corresponding to N(1)−Li(1)−P(1) and P(1)−Li(1)−P(2), respectively. The two oxygen atoms lie perfectly on the equatorial plane with the three equatorial angels ranging from 102.3(2)° to 139.7(3)°. The two phosphorus donors are both distorted from the ideal tetrahedral geometry. The two phenyl groups on each phosphorus atom are oriented such that they are virtually perpendicular to each other, with one roughly being axial and the other equatorial. The two phenylene rings of the backbone are tilted with respect to the coordination plane due to the steric repulsion between the two CH groups ortho to the amido nitrogen atom. The dihedral angle defined by the two phenylene planes in $[PNP]Li(THF)_2$ is 38.95°, which is larger than the corresponding angle in H[PNP] by 7.20° (see Supporting Information). This is perhaps the consequence of the decrease in C−N−C angles of the ligand backbone from 125.5(3)° to 117.1(2)° upon lithiation of H[PNP]. With the rigid framework of the ligand, the P(1)−Li(1)−P(2) angle is therefore much smaller than the ideal angle of 180°.

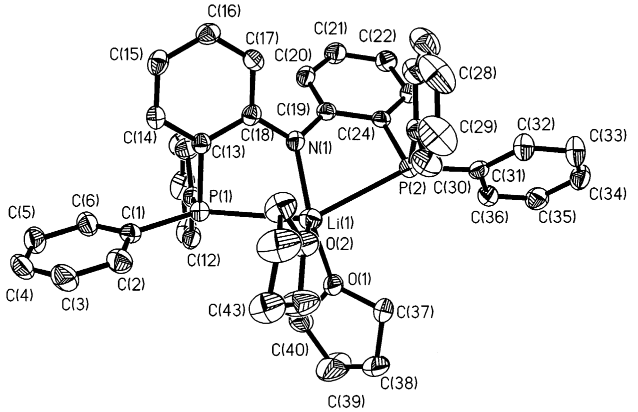


Figure 1. Molecular structure of $[PNP]Li(THF)_2$. Selected bond distances (Å) and angles (deg): Li(1)−O(2) 1.955(5), Li(1)−O(1) 1.969(5), Li(1)−N(1) 2.039(5), Li(1)−P(2) 2.779(5), Li(1)−P(1) 2.824(5), O(2)−Li(1)−O(1) 102.3(2), O(2)−Li(1)−N(1) 118.0(2), O(1)−Li(1)−N(1) 139.7(3), O(2)−Li(1)−P(2) 105.4(2), O(1)−Li(1)−P(2) 95.26(18), N(1)−Li(1)−P(2) 73.35(15), O(2)−Li(1)−P(1) 94.92(18), O(1)−Li(1)−P(1) 106.85(19), N(1)−Li(1)−P(1) 73.09(15), P(2)−Li(1)−P(1) 146.01(18), C(18)−N(1)−C(19) 117.1(2), C(18)−N(1)−Li(1) 118.2(2), C(19)−N(1)−Li(1) 124.6(2).

Lithium amides are convenient starting materials for metathetical reactions with transition metal halides. With the hybrid characteristic, the tridentate $[PNP]^-$ ligand is expected to adopt a wide variety of metals. Following the lead of the X-ray structure of $[PNP]Li(THF)_2$, where the tridentate ligand is meridional, it is anticipated that square-planar, monoalkyl complexes of $[PNP]^-$ should impose the alkyl group to occupy a position trans to the amido nitrogen donor, thereby concomitantly experiencing the two chemically equivalent phosphorus donors in the cis positions. Our experi-

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[15] Fryzuk, M. D.; Macneil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918−930.

[16] Wolfe, J. P.; Wagaw, S.; Marcoux, J. F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805.

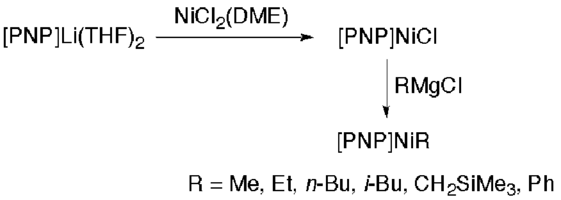
[17] Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852.

[18] Sadighi, J. P.; Harris, M. C.; Buchwald, S. L. *Tetrahedron Lett.* **1998**, *39*, 5327.

[19] Haenel, M. W.; Oevers, S.; Bruckmann, J.; Kuhnigk, J.; Kruger, C. *Synlett* **1998**, 301.

[20] Hingst, M.; Tepper, M.; Stelzer, O. *Eur. J. Inorg. Chem.* **1998**, 73.

ments on divalent nickel chemistry provide such evidence. The reaction of [PNP]Li(THF)$_2$ with NiCl$_2$(DME) in THF at −35 °C produces in 94% yield the diamagnetic [PNP]NiCl (eq 2). The chloride compound is a green, crystalline solid that is both air and water stable. Treatment of 1 equiv of Grignard reagents to [PNP]NiCl in THF at −35 °C generates quantitatively the corresponding alkyl and aryl complexes, [PNP]NiR (R = Me, Et, *n*-Bu, *i*-Bu, CH$_2$SiMe$_3$, Ph). These hydrocarbyl compounds are diamagnetic, red solids that are thermally stable in the absence of air. The stability of the ethyl, *n*-butyl, and isobutyl complexes toward β-elimination is particularly surprising, as the synthesis of the corresponding compounds supported by the closely related [N(SiMe$_2$CH$_2$PPh$_2$)$_2$]$^-$ ligand was not successful.[15] In particular, a solution of [PNP]NiEt in C$_6$D$_6$ (11 mM) did not decompose at 70 °C over a course of several hours, as indicated by the ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. We tentatively ascribe this unusual result to the rigid and robust feature of the *o*-phenylene-derived [PNP]$^-$ ligand, in which the phosphine dissociation, if any, is not significant.



(2)

Solution NMR studies of these nickel(II) complexes are all consistent with a square-planar geometry, with the [PNP]$^-$ ligand being in a meridional coordination mode. The diagnostic evidence is the presence of virtual triplet[21,22] resonances for the aromatic carbons of the ligand backbone in the ^{13}C{^{1}H} NMR spectroscopy. The C$_\alpha$ atom in all alkyl complexes appears as a triplet resonance with a $^2J_{CP}$ of ca. 20 Hz in the ^{13}C{^{1}H} NMR spectroscopy (Table 1). The ^{1}H NMR spectra also reveal the expected triplet resonances for the H$_\alpha$ atoms in [PNP]NiMe and [PNP]NiCH$_2$SiMe$_3$. The ^{31}P{^{1}H} NMR spectra show a sharp singlet resonance in all cases at ca. 25 ppm, a relative downfield resonance as compared to [PNP]NiCl that gives a signal at 18.77 ppm.

Table 1. Selected NMR Data of [PNP]NiX[a]

X	δ			*J*
	H$_\alpha$	C$_\alpha$	P	PC$_\alpha$
Cl			18.77	
Me	0.13	−15.37	27.61	21.87
Et	1.07	−2.80	26.42	19.48
n-Bu	1.07	5.24	27.06	19.10
i-Bu	1.02	18.53	26.80	19.54
CH$_2$SiMe$_3$	−0.08	−12.97	23.90	18.83
Ph		151.00	24.45	28.15

[a] All spectra were recorded in C$_6$D$_6$, chemical shifts in ppm, coupling constants in Hz.

In summary, we have developed a protocol to prepare the new monoanionic tridentate bis(2-diphenylphosphinophenyl)amide ligand and its lithium and divalent nickel derivatives. The nickel(II) chemistry established in this study is notably different from that found in the [N(SiMe$_2$CH$_2$PPh$_2$)$_2$]$^-$ system, likely as a consequence of the rigidity and robustness of the ligand employed in the former. The stability of the alkyl complexes toward β-elimination is particularly remarkable. Studies directed to delineate the reactivity of the metal complexes described here and the chemistry involving the heavier members of group 10 metals will be the subjects of further reports.

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Supporting Information Available: Text giving experimental details, ORTEP diagram of H[PNP], and all structural parameters for both H[PNP] (CCDC No. 197884) and [PNP]Li(THF)$_2$ (CCDC No. 197883). This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001; pp 260−262.

(22) Brookes, P. R.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1079.