Inorg. Chem. **2003**, *42*, 5471–5473

Inorganic Chemistry Communication

Amido Phosphine Complexes of Zinc

Lan-Chang Liang,*,† Wei-Ying Lee,† and Chen-Hsiung Hung‡

Department of Chemistry and Center for Nanoscience & Nanotechnology,
National Sun Yat-sen University, Kaohsiung 80424, Taiwan, and Department of Chemistry,
National Changhua University of Education, Changhua 50058, Taiwan

Received June 5, 2003

The first examples of amido phosphine complexes of zinc have been prepared. Addition of *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylaniline (H[NP]) to $ZnMe_2$ or $ZnEt_2$ in diethyl ether at –35 °C generated the monomeric, three-coordinate [NP]ZnR (R = Me, Et), while the metathesis reaction of $ZnCl_2$ with [NP]Li-$(THF)_2$ in diethyl ether at –35 °C produced homoleptic $[NP]_2Zn$.

Amido phosphine ligands are versatile hybrid ligands that allow for the preparation of a wide range of transition metal, main-group metal, and f-element complexes.[1−4] Recent progress in this area has resulted in unusual chemical transformations, particularly in dinitrogen chemistry.[3,4] We were attracted to the development of new amido phosphine ligands with the potentially robust and rigid *o*-phenylene backbone.[5] The bidentate ligands of this type are 2-(diphenylphosphino)aniline derivatives. We note that although 2-(diphenylphosphino)aniline and its N-alkyl derivatives (usually small or primary alkyls) have been popular ligands in the past three decades,[6−9] the N-arylated compounds are notably absent. These compounds can be regarded as derivatives of phosphine-functionalized biaryl amide, whose electronic and steric properties are anticipated to be finely controllable by exchanging substituents at both donor atoms. In this contribution, we present a potentially general strategy for the synthesis of these new ligands by giving a sterically demanding example, *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylanilide ($[NP]^-$), and demonstrate its coordination chemistry with zinc, which led to the isolation of rarely encountered monomeric, three-coordinate zinc complexes.[10−17] Low coordinate zinc complexes supported by sterically demanding ligands have recently shown remarkably catalytic activity for polymerization of lactide and copolymerization of epoxides and carbon dioxide.[16−20] To the best of our knowledge, these compounds are the first examples of amido phosphine complexes of zinc, despite a number of amido phosphine ligands available to date.

As summarized in Scheme 1, the synthesis of the ligand precursor is straightforward. The synthetic strategy takes advantage of the fact that aryl fluoride compounds are virtually inactive to the well-developed palladium-catalyzed aryl amination reactions[21,22] but reactive to the nucleophilic phosphanylation.[23] These reactions proceed cleanly from commercially available starting materials to generate the desired H[NP] in high overall yield on a scale of 15 g.

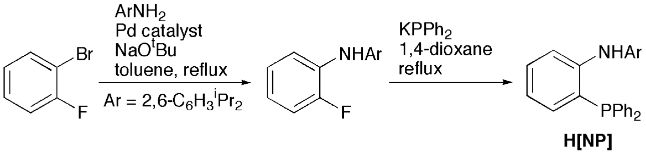
---

* To whom correspondence is addressed. E-mail: lcliang@mail.nsysu.edu.tw. Fax: +886-7-5253908.
† National Sun Yat-sen University.
‡ National Changhua University of Education.

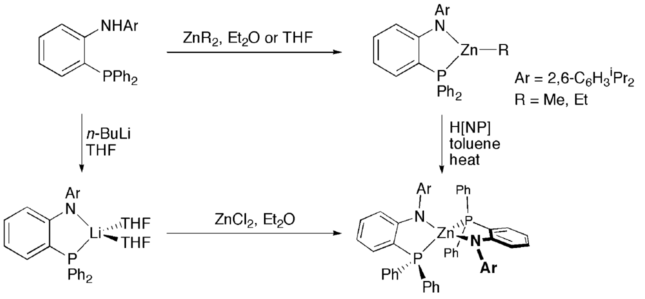
(1) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839−2845.
(2) Schrock, R. R.; Seidel, S. W.; Schrodi, Y.; Davis, W. M. *Organometallics* **1999**, *18*, 428−437.
(3) Fryzuk, M. D.; Mackay, B. A.; Johnson, S. A.; Patrick, B. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3709−3712.
(4) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.
(5) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007−3009.
(6) Crociani, L.; Tisato, F.; Refosco, F.; Bandoli, G.; Corain, B. *Eur. J. Inorg. Chem.* **1998**, 1689−1697 and references therein.
(7) Fritz, H. P.; Gordon, I. R.; Schwarzhans, K. E.; Venznzi, L. M. *J. Chem. Soc.* **1965**, 5210−5216.
(8) Hedden, D.; Roundhill, D. M. *Inorg. Chem.* **1985**, *24*, 4152−4158.
(9) Rauchfuss, T. B.; Patino, F. T.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 652−656.
(10) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908−909.
(11) Gruff, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1989**, *111*, 8762−8763.
(12) Bochmann, M.; Bwembya, G. C.; Grinter, R.; Powell, A. K.; Webb, K. J.; Hursthouse, M. B.; Malik, K. M. A.; Mazid, M. A. *Inorg. Chem.* **1994**, *33*, 2290−2296.
(13) Looney, A.; Han, R. Y.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274−288.
(14) Darensbourg, D. J.; Zimmer, M. S.; Rainey, P.; Larkins, D. L. *Inorg. Chem.* **1998**, *37*, 2852−2853.
(15) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785−2794.
(16) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229−3238.
(17) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738−8749.
(18) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577−7579.
(19) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487−12496.
(20) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845−11854.
(21) Wolfe, J. P.; Wagaw, S.; Marcoux, J. F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805−818.
(22) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860.
(23) Hingst, M.; Tepper, M.; Stelzer, O. *Eur. J. Inorg. Chem.* **1998**, 73−82.

10.1021/ic0346228 CCC: $25.00

Scheme 1



Scheme 2



Compound H[NP] and its fluorine precursor were both characterized by multinuclear NMR spectroscopy and elemental analysis. The solid-state structure of H[NP] was determined by X-ray crystallography (see Supporting Information).

Addition of ZnR$_2$ (R = Me, Et) to an ethereal (diethyl ether or THF) solution of H[NP] at −35 °C led to the elimination of corresponding alkanes and the formation of [NP]ZnR as colorless crystals (Scheme 2). The formation of monomeric, coordinatively unsaturated [NP]ZnR is remarkable, particularly for *small alkyl* derivatives, as these reactions were conducted in strong coordinating solvents. Three-coordinate zinc complexes that are not associated with coordinating solvents are extremely rare.[24] Compounds [NP]ZnMe and [NP]ZnEt are extremely sensitive to moist air, affording exclusively H[NP] according to the ^{31}P{^{1}H} NMR spectroscopy. However, they are thermally stable at 100 °C for >3 days under inert atmosphere (40 mM in toluene). As expected, the isopropylmethyl groups in both [NP]ZnMe and [NP]ZnEt are diastereotopic as evidenced by ^{1}H and ^{13}C NMR spectroscopy, implying restricted rotation about the N−Ar bond. The ^{31}P{^{1}H} NMR spectra of [NP]ZnMe and [NP]ZnEt reveal a singlet resonance for the phosphorus donor at −27.34 and −27.15 ppm, respectively, which is shifted relatively upfield from that of H[NP] at −20.11 ppm. A similar upfield change in the ^{31}P chemical shift is also observed for (2,6-^{t}Bu$_2$C$_6$H$_3$O)$_2$Zn(PCy$_3$) (−2.1 ppm)[14] and [(μ-Cl)(ZnLCl)$_2$][ClO$_4$] (−3.2 ppm, L = *N*-(diphenylphosphinopropyl)-1,4,7-triazacyclononane)[25] as compared to the corresponding free phosphines. The coordination of the phosphorus donor of [NP]$^-$ to Zn is further supported by the ^{13}C{^{1}H} and DEPT ^{13}C NMR spectroscopy. For instance, the C$_\alpha$ atom in [NP]ZnEt appears as a doublet resonance at 1.82 ppm with $^2J_{CP}$ of 36 Hz.

Crystallographically characterized phosphine derivatives of group 12 metals are rare.[14,19,25] Single crystals of [NP]ZnEt suitable for an X-ray diffraction study were grown from a concentrated diethyl ether solution at −35 °C. As depicted in Figure 1, [NP]ZnEt exists as a monomeric, three-coordinate species with the zinc atom surrounded by one ethyl group and the nitrogen and phosphorus donors of the amido phosphine ligand. The Zn(1)−N(1), Zn(1)−P(2), and Zn(1)−C(31) distances are all unexceptional. The zinc atom is slightly displaced from the N-phenylene-P plane by 0.1392 Å. The binding angle of the amido phosphine ligand is 85.04(12)°. The sum of the bond angles about Zn(1) equals 359.81°, indicating a trigonal planar geometry at zinc. The N−Zn−C$_\alpha$ angle is ca. 6.33° larger than P−Zn−C$_\alpha$, likely as a reflection of significant steric repulsion imposed by the 2,6-diisopropylphenyl group at the nitrogen donor, which is ca. 0.534 Å closer to Zn than is phosphorus. The diisopropylphenyl ring is approximately perpendicular to the phenylene backbone of the amido phosphine ligand. In contrast to that found in the solid-state structure of H[NP], the phosphorus atom in [NP]ZnEt adopts a distorted tetrahedral geometry where the two phenyl substituents are evenly displaced with respect to the phenylene backbone. As a result, the ethyl group is oriented such that the interligand repulsion in [NP]ZnEt is minimized as much as it can be.

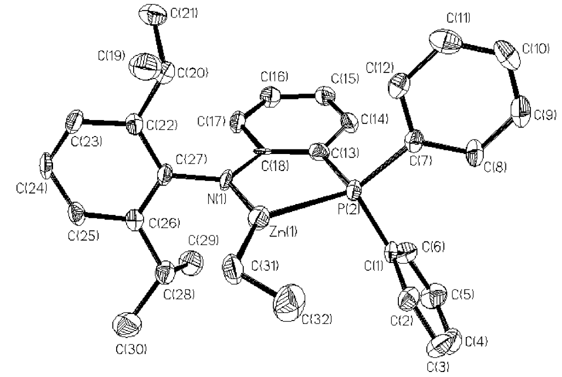


Figure 1. Molecular structure of [NP]ZnEt. Selected bond distances (Å) and angles (deg): N(1)−Zn(1) 1.911(4), P(2)−Zn(1) 2.4450(14), Zn(1)−C(31) 1.956(5), N(1)−Zn(1)−C(31) 140.55(19), N(1)−Zn(1)−P(2) 85.04(12), C(31)−Zn(1)−P(2) 134.22(16).

Addition of n-BuLi to H[NP] dissolved in THF at −35 °C followed by concentration of the reaction solution resulted in the crystallization of the solvated lithium amide, [NP]Li(THF)$_2$, in 90% yield (Scheme 2). The ^{1}H, ^{31}P{^{1}H}, and ^{7}Li{^{1}H} NMR spectra at room temperature are conclusive to elucidate the chelating feature of the amido phosphine ligand. Again, the isopropylmethyl groups in [NP]Li(THF)$_2$ are diastereotopic but shifted relatively downfield in the ^{1}H NMR spectroscopy as compared to that of H[NP]. The ^{31}P{^{1}H} NMR spectrum at room temperature reveals a ∼1:1:1:1 quartet resonance centered at −11.99 ppm, consistent with the coordination of the phosphorus donor to the quadrupolar lithium-7 center ($I = {}^3/_2$, natural abundance 92.6%). The coupling constant $^1J_{LiP}$ of 38 Hz in [NP]Li(THF)$_2$ is comparable to those found for the lithium phosphide derivatives such as [Li(tmeda)]$_2$[1,2-C$_6$H$_4$(PPh)$_2$] (35 Hz)[26] and [Li(tmeda)]$_2$[1,2-C$_6$H$_4$(PSiMe$_3$)$_2$] (38 Hz).[26] The lithium metal

---

(24) Prust, J.; Stasch, A.; Zheng, W.; Roesky, H. W.; Alexopoulos, E.; Usón, I.; Böhler, D.; Schuchardt, T. *Organometallics* **2001**, *20*, 3825−3828.

(25) Ellis, D.; Farrugia, L. J.; Hickman, d. T.; Lovatt, P. A.; Peacock, R. D. *Chem. Commun.* **1996**, 1817−1818.

(26) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Yin, P. *J. Chem. Soc., Dalton Trans.* **1995**, 3925−3932.

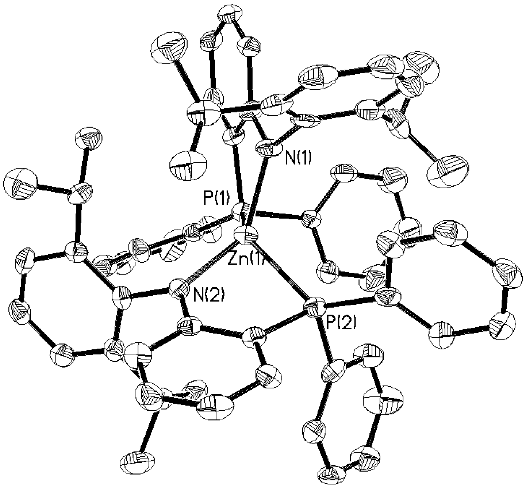


Figure 2. Molecular structure of $[NP]_2Zn$. Selected bond distances (Å) and angles (deg): Zn(1)−N(1) 1.971(5), Zn(1)−N(2) 1.974(5), Zn(1)−P(2) 2.4387(19), Zn(1)−P(1) 2.4545(19), N(1)−Zn(1)−N(2) 135.1(2), N(1)−Zn(1)−P(2) 113.39(15), N(2)−Zn(1)−P(2) 83.15(15), N(1)−Zn(1)−P(1) 84.24(15), N(2)−Zn(1)−P(1) 118.21(16), P(2)−Zn(1)−P(1) 129.41(7).

of $[NP]Li(THF)_2$ appears as a doublet resonance at 1.37 ppm in the $^{7}Li\{^{1}H\}$ NMR spectrum with the same coupling constant as that observed in the $^{31}P\{^{1}H\}$ NMR spectrum.

The metathesis reaction of $[NP]Li(THF)_2$ (1 or 2 equiv) with $ZnCl_2$ suspended in diethyl ether at −35 °C generated the homoleptic $[NP]_2Zn$. Pale-yellow crystals of $[NP]_2Zn$ were grown from a concentrated diethyl ether solution at −35 °C. An X-ray study of $[NP]_2Zn$ revealed a distorted tetrahedral geometry for the zinc atom (Figure 2) with the dihedral angle between the two N−Zn−P planes of 74.6°. The averaged binding angle of the amido phosphine ligands is 83.695°, a value relatively smaller than that of [NP]ZnEt. In sharp contrast to that observed for [NP]ZnEt, the zinc center in $[NP]_2Zn$ is markedly displaced by 0.7017 and 0.6685 Å, respectively, out of the N-phenylene-P planes. The Zn−P distances of 2.4466 Å (average) in $[NP]_2Zn$ are similar to that found for [NP]ZnEt, whereas the Zn−N distances of 1.9725 Å (average) are slightly longer as compared to that of [NP]ZnEt. This is perhaps the consequence of significant steric repulsion between the two ligands, particularly for the two diisopropylphenyl groups.

The solution NMR spectroscopic data of $[NP]_2Zn$ are consistent with a bis-ligand complex that has a tetrahedral geometry. The phosphorus atoms appear as a sharp singlet resonance at −22.93 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum, a value that is also shifted upfield from those of H[NP] and $[NP]Li(THF)_2$. The ^{1}H NMR spectrum reveals two septet and four doublet resonances for the isopropyl methine and methyl groups, respectively, again indicating restricted rotation about the N−Ar bonds. Like [NP]ZnR, $[NP]_2Zn$ is thermally stable (at 100 °C) but extremely moisture-sensitive.

Attempts to spectroscopically observe the presumed [NP]-ZnCl intermediate from the reaction of $[NP]Li(THF)_2$ (1 equiv) with $ZnCl_2$ by periodically monitoring the reaction aliquot were not successful. The formation of bis-ligand complexes of zinc instead of mono-ligand derivatives is also reported for systems employing salicylaldiminate,[27] tris(3,5-dimethylpyrazolyl)hydroborate,[13] and iminophosphoranate[28,29] ligands.

In view of the facile formation of $[NP]_2Zn$ by the metathetical reaction and [NP]ZnR by the alkane elimination, we attempted the reactions of [NP]ZnR with H[NP]. We found that [NP]ZnR did not react with H[NP] at room temperature at all, even after a prolonged reaction time. When the reaction temperature was increased to 100 °C, $[NP]_2Zn$ was produced cleanly as indicated by the $^{31}P\{^{1}H\}$ NMR spectroscopy.

In summary, we have prepared a new amido phosphine ligand with significant steric demand that allows for the preparation of low coordinate zinc complexes. The isolation of monomeric, coordinatively unsaturated [NP]ZnMe and [NP]ZnEt species that do not adopt strong coordinating solvents is particularly unusual. The homoleptic $[NP]_2Zn$ is a four-coordinate species where the interligand repulsion is significant as indicated by solution NMR spectroscopy and X-ray crystallography. Chemistry involving the reactivity of these new molecules in stoichiometric and catalytic transformations will be the subjects of further reports.

Acknowledgment. We thank the National Science Council (NSC 91-2113-M-110-019-) of Taiwan and NSYSU for financial support of this work, Ms. Chao-Lien Ho for technical assistance with NMR experiments, and Prof. Michael Y. Chiang and Mr. Jing-Yun Wu for technical assistance with X-ray crystallography.

Supporting Information Available: Text giving experimental details, ORTEP diagram of H[NP], and all structural parameters for [NP]ZnEt and $[NP]_2Zn$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0346228

---

(27) Darensbourg, D. J.; Rainey, P.; Yarbrough, J. *Inorg. Chem.* **2001**, *40*, 986−993.
(28) Wingerter, S.; Pfeiffer, M.; Nurso, A.; Lustig, C.; Stey, T.; Chandrasekhar, V.; Stalke, D. *J. Am. Chem. Soc.* **2001**, *123*, 1381−1388.
(29) Mahalakshmi, L.; Stalke, D. *Struct. Bonding* **2002**, *103*, 85−115.