Inorg. Chem. **2005**, *44*, 5147–5151

Inorganic Chemistry Article

Zirconium and Hafnium Complexes Containing Bidentate Diarylamido–Phosphine Ligands

Pin-Shu Chien and Lan-Chang Liang*

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

Received April 18, 2005

The first examples of mononuclear, structurally characterized triarylphosphine complexes of zirconium and hafnium are reported. The metathetical reactions of $MCl_4(THF)_2$ (M = Zr, Hf) with $[^iPrNP]Li(THF)_2$ ($[^iPrNP]^-$ = *N*-(2-(diphenylphosphino)phenyl)-2,6-diisopropylanilide) or $[MeNP]Li(THF)_2$ ($[MeNP]^-$ = *N*-(2-(diphenylphosphino)-phenyl)-2,6-dimethylanilide) in toluene at –35 °C produced the corresponding $[^iPrNP]MCl_3(THF)$ and $[MeNP]_2MCl_2$, respectively, in high yield. In contrast, attempts to prepare $[MeNP]MCl_3(THF)$ and $[^iPrNP]_2MCl_2$ led to the concomitant formation of mono- and bis-ligated complexes, from which purification proved rather ineffective. The solution and solid-state structures of $[^iPrNP]MCl_3(THF)$ and $[MeNP]_2MCl_2$ were studied by multinuclear NMR spectroscopy and X-ray crystallography. The geometry of these six-coordinate complexes is best described as a distorted octahedron in which the chloride ligands in $[^iPrNP]MCl_3(THF)$ adopt a virtually meridional coordination mode whereas those in $[MeNP]_2MCl_2$ are trans to each other.

Introduction

The search for appropriate methods to effectively activate and/or functionalize dinitrogen under mild conditions has continued to attract considerable attention in recent years.[1−6] Significant progress has been made, particularly in the past decade, with metal complexes incorporating (chelating) amide[7−9] or cyclopentadienyl[10,11] ligands. For instance, Fryzuk and co-workers have shown that zirconium complexes supported by multidentate amido phosphine ligands that contain the $-CH_2SiMe_2-$ backbone are capable of dinitrogen activation,[12−15] from which hydrogenation rather than more frequently encountered displacement of the dinitrogen ligand may become feasible.[9,16] One notable drawback in this ligand system, however, is perhaps the participation of the $-CH_2SiMe_2-$ backbone under certain circumstances.[17] To diminish the possibility of such undesired reactivity, we have recently developed a series of *o*-phenylene-derived amido−phosphine ligands (Figure 1) that are relatively more rigid and robust, as has been demonstrated in the group 10 metal chemistry.[18−21] In an effort to extend the territory of ligands of this type involving early transition metals and to pursue our interests in dinitrogen fixation chemistry, we have set out to prepare group 4 metal complexes and study their reactivity. In this contribution, we aim to demonstrate the synthetic possibility and establish the structural characterization of zirconium and hafnium

---

* Author to whom correspondence should be addressed. E-mail: lcliang@mail.nsysu.edu.tw. Fax: +886-7-5253908.

(1) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200*, 379.
(2) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385.
(3) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. Catal.* **2003**, *345*, 1061.
(4) Hidai, M. *Coord. Chem. Rev.* **1999**, *185−186*, 99.
(5) Richards, R. L. *Coord. Chem. Rev.* **1996**, *154*, 83.
(6) Bazhenova, T. A.; Shilov, A. E. *Coord. Chem. Rev.* **1995**, *144*, 69.
(7) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76.
(8) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.
(9) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.
(10) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.
(11) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351.
(12) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 8185.
(13) Cohen, J. D.; Fryzuk, M. D.; Loehr, T. M.; Mylvaganam, M.; Rettig, S. J. *Inorg. Chem.* **1998**, *37*, 112.
(14) Cohen, J. D.; Mylvaganam, M.; Fryzuk, M. D.; Loehr, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 9529.
(15) Fryzuk, M. D.; Haddad, T. S.; Mylvaganam, M.; McConville, D. H.; Rettig, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 2782.
(16) Basch, H.; Musaev, D. G.; Morokuma, K.; Fryzuk, M. D.; Love, J. B.; Seidel, W. W.; Albinati, A.; Koetzle, T. F.; Klooster, W. T.; Mason, S. A.; Eckert, J. *J. Am. Chem. Soc.* **1999**, *121*, 523.
(17) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026.
(18) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007.
(19) Liang, L.-C.; Lee, W.-Y.; Yin, C.-C. *Organometallics* **2004**, *23*, 3538.
(20) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813.
(21) Liang, L.-C.; Chien, P.-S.; Huang, M.-H. *Organometallics* **2005**, *24*, 353.

10.1021/ic050599+ CCC: $30.25

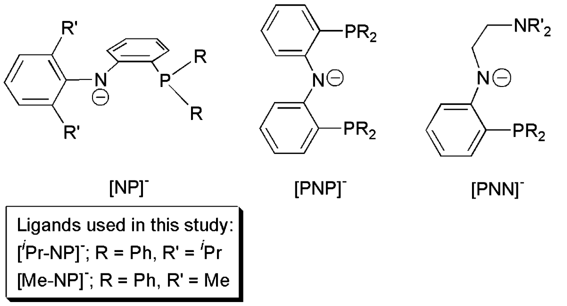

Figure 1. *o*-Phenylene-derived chelating amido−phosphine ligands.

complexes containing bidentate diarylamido−phosphine ligands *N*-(2-(diphenylphosphino)phenyl)-2,6-diisopropylanilide ([^{i}PrNP]$^-$) and *N*-(2-(diphenylphosphino)phenyl)-2,6-dimethylanilide ([MeNP]$^-$). To the best of our knowledge, compounds described herein represent the first examples of mononuclear, structurally characterized zirconium and hafnium complexes of triarylphosphines reported to date.[22]

Results and Discussion

Addition of 1 equiv of [^{i}PrNP]Li(THF)$_2$[23] to ZrCl$_4$(THF)$_2$[24] suspended in toluene at −35 °C led to the formation of [^{i}PrNP]ZrCl$_3$(THF) as yellow crystals in 72% yield. An analogous reaction employing HfCl$_4$(THF)$_2$[24] yielded [^{i}PrNP]HfCl$_3$(THF). The ^{31}P{^{1}H} NMR spectra of [^{i}PrNP]ZrCl$_3$(THF) and [^{i}PrNP]HfCl$_3$(THF) reveal a singlet resonance for the phosphorus donor at 1.95 and 4.09 ppm, respectively. These signals are shifted relatively downfield from those of H[^{i}PrNP] (−20.11 ppm) and [^{i}PrNP]Li(THF)$_2$ (−11.99 ppm),[23] consistent with the phosphorus coordination to the electron-deficient group 4 metals. The ^{1}H NMR spectra of [^{i}PrNP]ZrCl$_3$(THF) and [^{i}PrNP]HfCl$_3$(THF) indicate the presence of 1 equiv of coordinated THF molecule. As noted previously in the [^{i}PrNP]$^-$ chemistry of the main-group (e.g., Li, Al, and Zn)[23,25] and late transition metals (e.g., Ni and Pd),[19,21] the two isopropyl groups in [^{i}PrNP]ZrCl$_3$(THF) and [^{i}PrNP]HfCl$_3$(THF) are chemically equivalent, and the isopropylmethyl moieties are diastereotopic as evidenced by the ^{1}H and ^{13}C NMR spectroscopy. This phenomenon is indicative of restricted rotation about the N−Ar bond due likely to the steric crowding imposed by the *o*-isopropyl substituents. Attempts to prepare [^{i}PrNP]$_2$MCl$_2$ from the reactions of MCl$_4$(THF)$_2$ (M = Zr, Hf) with 2 equiv of [^{i}PrNP]Li(THF)$_2$ produced the corresponding [^{i}PrNP]MCl$_3$(THF), even after an extended period of time, along with a few new compounds as suggested by ^{31}P{^{1}H} NMR spectroscopy. Unfortunately, none of the reaction products can be effectively purified and fully characterized. We tentatively assign one of these compounds as the expected [^{i}PrNP]$_2$MCl$_2$ on the basis of the ^{31}P{^{1}H} NMR spectroscopic data (M = Zr, 13.15 ppm; M = Hf, 10.61 ppm) comparable to those of the corresponding [MeNP]$_2$MCl$_2$ (vide infra).

Yellow crystals of [^{i}PrNP]ZrCl$_3$(THF) suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C. Crystallographic details are summarized in Table 1. As illustrated in Figure 2, this compound is a six-coordinate species with the zirconium center being surrounded by one [^{i}PrNP]$^-$, one THF, and three chloride ligands. The geometry at zirconium is best described as a distorted octahedron in which the three chloride ligands are virtually in a meridional coordination mode. The coordinated THF molecule is approximately trans to the amido nitrogen donor with the O−Zr−N angle of 154.5°.[26] Surprisingly, the zirconium atom is severely displaced from the mean N−phenylene−P plane by 0.9533 Å,[26] although all bond distances in this molecule are well within the expected values. The Zr−P distance of 2.775 Å (average)[26] is comparable to those found in the trialkylphosphine complexes of zirconium such as ZrCl$_2$[η^2-N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$ (2.7982 Å average)[27] and [(^{i}PrN-*o*-C$_6$H$_4$)$_2$O]Zr(η^2-CH$_2$CMe$_2$)(PMe$_3$)$_2$ (2.7965 Å average).[28] The deviation of zirconium from the N−phenylene−P plane is thus due likely to either the relatively large zirconium size with respect to the rigid amido phosphine ligand or the intramolecularly steric repulsion arising from the bulky [^{i}PrNP]$^-$ substituents. As a result, the bite angle of the amido phosphine ligand of 71.95° (average)[26] in [^{i}PrNP]ZrCl$_3$(THF) is significantly smaller than those of other metal derivatives of [^{i}PrNP]$^-$ reported previously, e.g., [^{i}PrNP]NiCl(PMe$_3$) (85.21(9)°)[19] and [^{i}PrNP]ZnEt (85.04(12)°),[23] and the closely related ZrCl$_2$[η^2-N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$ (77.465° average).[27] Nevertheless, the amido nitrogen donor remains planar, as indicated by the sum of the bond angles of 360°.

Interestingly, the reactions of [MeNP]Li(THF)$_2$[19] with a stoichiometric amount of MCl$_4$(THF)$_2$ (M = Zr, Hf) in toluene at −35 °C produced a mixture of products. The ^{31}P{^{1}H} NMR spectroscopic data of the reaction aliquots are consistent with the concomitant generation of [MeNP]MCl$_3$(THF) (M = Zr, 1.70 ppm; M = Hf, 3.90 ppm) and the bis-ligated [MeNP]$_2$MCl$_2$. This result is in contrast to that observed from [^{i}PrNP]$^-$ due to the smaller size of the [MeNP]$^-$ ligand than for former. Consistently, treatment of MCl$_4$(THF)$_2$ (M = Zr, Hf) with 2 equiv of [MeNP]Li(THF)$_2$ under similar conditions afforded the corresponding [MeNP]$_2$MCl$_2$ quantitatively. The phosphorus donors in [MeNP]$_2$ZrCl$_2$ and [MeNP]$_2$HfCl$_2$ appear as a singlet resonance in the ^{31}P{^{1}H} NMR spectroscopy at 12.28 and 10.46 ppm, respectively, indicating an intramolecular symmetry for the two [MeNP]$^-$ ligands on the NMR time scale. The ^{1}H and ^{13}C{^{1}H} NMR spectra of [MeNP]$_2$ZrCl$_2$ and [MeNP]$_2$HfCl$_2$

---

(22) Only four structures of triarylphosphine complexes of group 4 metals are available from Cambridge Structure Database; see: Cotton, F. A.; Kibala, P. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 270. Willoughby, C. A.; Duff, R. R., Jr.; Davis, W. M.; Buchwald, S. L. *Organometallics* **1996**, *15*, 472. Hu, W. Q.; Sun, X. L.; Wang, C.; Gao, Y.; Tang, Y.; Shi, L. P.; Xia, W.; Sun, J.; Dai, H. L.; Li, X. Q.; Yao, X. L.; Wang, X. R. *Organometallics* **2004**, *23*, 1684. Priya, S.; Balakrishna, M. S.; Mague, J. T. *Chem. Lett.* **2004**, *33*, 308.

(23) Liang, L.-C.; Lee, W.-Y.; Hung, C.-H. *Inorg. Chem.* **2003**, *42*, 5471.

(24) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(25) Liang, L.-C.; Huang, M.-H.; Hung, C.-H. *Inorg. Chem.* **2004**, *43*, 2166. Lee, W.-Y.; Liang, L.-C. *Dalton Trans.* **2005**, 1952.

(26) This corresponds to the average value calculated from the two independent molecules found in the asymmetric unit cell of [^{i}PrNP]ZrCl$_3$(THF).

(27) Fryzuk, M. D.; Williams, H. D.; Rettig, S. J. *Inorg. Chem.* **1983**, *22*, 863.

(28) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822.

Table 1. Crystallographic Data for [^{i}PrNP]ZrCl$_3$(THF), [MeNP]$_2$ZrCl$_2$, and [MeNP]$_2$HfCl$_2$

param	{[^{i}PrNP]ZrCl$_3$(THF)}$_2$(THF)	{[MeNP]$_2$ZrCl$_2$}THF	[MeNP]$_2$HfCl$_2$
formula	$C_{72}H_{86}Cl_6N_2O_3P_2Zr_2$	$C_{56}H_{54}Cl_2N_2OP_2Zr$	$C_{52}H_{46}Cl_2N_2P_2Hf$
fw	1484.51	995.07	1010.24
D_{calc} (g cm^{-3})	1.298	1.368	1.512
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	11.1870(4)	13.8730(4)	14.9060(2)
b (Å)	17.3430(7)	18.9470(6)	18.9720(4)
c (Å)	20.1670(8)	18.4460(7)	16.3230(3)
α (deg)	97.629(2)	90	90
β (deg)	97.176(2)	94.8800(10)	105.9330(10)
γ (deg)	98.1730(10)	90	90
V (Å^3)	3797.2(3)	4831.0(3)	4438.75(14)
Z	2	4	4
T (K)	100(2)	100(2)	100(2)
diffractometer	Kappa CCD	Kappa CCD	Kappa CCD
radiatn, l (Å)	Mo Ka, 0.710 73	Mo Ka, 0.710 73	Mo Ka, 0.710 73
2q$_{max}$ (deg)	50.22	50.10	50.02
tot. reflcns	37 959	29 174	19 512
indepndt reflcns	12 513	8457	3914
R$_{int}$	0.0998	0.0867	0.0794
abs coeff (mm^{-1})	0.571	0.447	2.581
data/restraints/params	12 513/0/744	8457/0/578	3914/0/267
goodness of fit	1.052	1.169	1.237
final R indices [$I > 2s(I)$]	R1 = 0.0922 wR2 = 0.2570	R1 = 0.0761 wR2 = 0.1701	R1 = 0.0247 wR2 = 0.0704
R indices (all data)	R1 = 0.1716 wR2 = 0.3161	R1 = 0.1267 wR2 = 0.2132	R1 = 0.0304 wR2 = 0.0904

reveal a singlet resonance for the *o*-methyl substituents, a phenomenon that may be ascribed to a rapid rotation about the N−Ar bonds. In principle, four possible stereoisomers (and their corresponding enantiomers) can be deduced for the solution structures of these 6-coordinate species on the basis of the NMR investigation, assuming that both molecules contain an octahedral core. Figure 3 illustrates the possible structures; however, it is relatively inconclusive to distinguish one from another with the NMR data alone. We thus chose to examine their solid-state structures by X-ray crystallography.

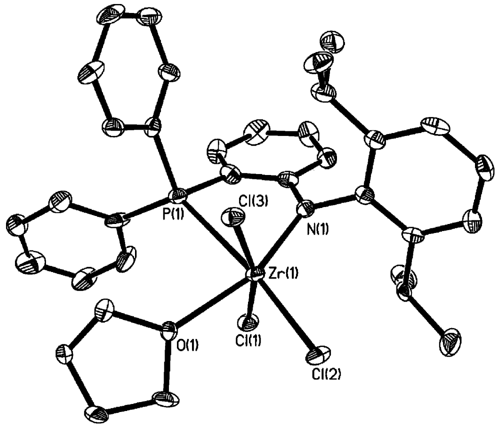

Figure 2. Molecular structure of [^{i}PrNP]ZrCl$_3$(THF) with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains two independent [^{i}PrNP]ZrCl$_3$(THF) molecules and one unbound THF; only one [^{i}PrNP]ZrCl$_3$(THF) is presented for clarity. Selected bond distances (Å) and angles (deg): Zr(1)−N(1) 2.085(7), Zr(1)−O(1) 2.260(6), Zr(1)−Cl(3) 2.425(2), Zr(1)−Cl(2) 2.427(2), Zr(1)−Cl(1) 2.454(2), Zr(1)−P(1) 2.786(3), Zr(2)−N(2) 2.095(8), Zr(2)−O(2) 2.274(6), Zr(2)−Cl(5) 2.413(3), Zr(2)−Cl(6) 2.426(3), Zr(2)−Cl(4) 2.446(2), Zr(2)−P(2) 2.764(2); N(1)−Zr(1)−O(1) 155.6(3), N(1)−Zr(1)−Cl(3) 98.7(2), O(1)−Zr(1)−Cl(3) 86.79(17), N(1)−Zr(1)−Cl(2) 114.4(2), O(1)−Zr(1)−Cl(2) 88.79(17), Cl(3)−Zr(1)−Cl(2) 92.70(8), N(1)−Zr(1)−Cl(1) 87.6(2), O(1)−Zr(1)−Cl(1) 82.18(17), Cl(3)−Zr(1)−Cl(1) 165.21(9), Cl(2)−Zr(1)−Cl(1) 96.87(8), N(1)−Zr(1)−P(1) 72.0(2), O(1)−Zr(1)−P(1) 84.73(16), Cl(3)−Zr(1)−P(1) 86.84(8), Cl(2)−Zr(1)−P(1) 173.52(8), Cl(1)−Zr(1)−P(1) 82.37(8), N(2)−Zr(2)−O(2) 153.4(3), N(2)−Zr(2)−Cl(5) 116.6(2), O(2)−Zr(2)−Cl(5) 89.11(18), N(2)−Zr(2)−Cl(6) 97.6(2), O(2)−Zr(2)−Cl(6) 87.36(17), Cl(5)−Zr(2)−Cl(6) 92.30(9), N(2)−Zr(2)−Cl(4) 87.9(2), O(2)−Zr(2)−Cl(4) 82.72(17), Cl(5)−Zr(2)−Cl(4) 95.28(9), Cl(6)−Zr(2)−Cl(4) 167.40(9), N(2)−Zr(2)−P(2) 71.9(2), O(2)−Zr(2)−P(2) 82.36(17), Cl(5)−Zr(2)−P(2) 171.45(9), Cl(6)−Zr(2)−P(2) 86.82(8), Cl(4)−Zr(2)−P(2) 84.19(8).

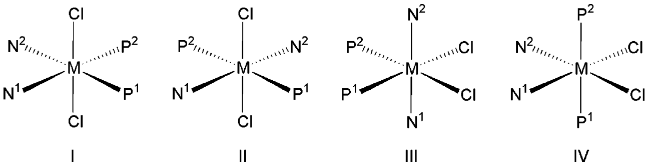

Figure 3. Possible stereoisomers for [NP]$_2$MCl$_2$, where N^{x}P^x (x = 1, 2) represents the chelating amido−phosphine ligands.

Single crystals of [MeNP]$_2$ZrCl$_2$ and [MeNP]$_2$HfCl$_2$ suitable for X-ray diffraction analysis were grown by layering diethyl ether on a concentrated THF solution at −35 °C. As depicted in Figures 4 and 5, both structures correspond to the stereoisomer I in which the two chloride ligands are virtually trans to each other whereas the two phosphorus donors (and the two nitrogen donors) are cis. A similar phenomenon was also reported for the closely related ZrCl$_2$[η^2-N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$.[27] Although [MeNP]$_2$ZrCl$_2$ and [MeNP]$_2$HfCl$_2$ are isostructural, the space group of the former, which cocrystallizes with 1 equiv of unbound THF molecule, is $P2_1/c$ while that of the latter, without incorporating any solvent, is $C2/c$. Similar to those found in [^{i}PrNP]ZrCl$_3$(THF), all bond distances in [MeNP]$_2$ZrCl$_2$ and [MeNP]$_2$HfCl$_2$ are well comparable to the expected values and the metal center is significantly displaced from the corresponding mean N−phenylene−P planes by 0.8243 and 0.7542 Å for Zr and 0.7104 and 0.7104 Å for Hf. The average bite angle of the amido−phosphine ligands of 71.48° in [MeNP]$_2$ZrCl$_2$ and 72.88° in [MeNP]$_2$HfCl$_2$ is similar to that found in

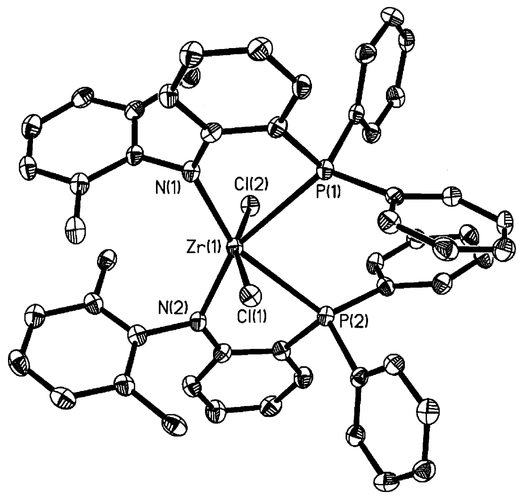

Figure 4. Molecular structure of $[MeNP]_2ZrCl_2$ with thermal ellipsoids drawn at the 35% probability level. One unbound THF molecule found in the asymmetric unit cell is omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)−N(1) 2.132(5), Zr(1)−N(2) 2.140(5), Zr(1)−Cl(2) 2.4497(16), Zr(1)−Cl(1) 2.4507(15), Zr(1)−P(1) 2.7993(16), Zr(1)−P(2) 2.8017(18); N(1)−Zr(1)−N(2) 130.14(19), N(1)−Zr(1)−Cl(2) 97.22(13), N(2)−Zr(1)−Cl(2) 88.50(14), N(1)−Zr(1)−Cl(1) 90.78(13), N(2)−Zr(1)−Cl(1) 97.38(14), Cl(2)−Zr(1)−Cl(1) 163.48(6), N(1)−Zr(1)−P(1) 71.41(13), N(2)−Zr(1)−P(1) 158.45(14), Cl(2)−Zr(1)−P(1) 88.85(5), Cl(1)−Zr(1)−P(1) 80.00(5), N(1)−Zr(1)−P(2) 158.16(13), N(2)−Zr(1)−P(2) 71.55(14), Cl(2)−Zr(1)−P(2) 79.02(5), Cl(1)−Zr(1)−P(2) 88.18(5), P(1)−Zr(1)−P(2) 86.94(5).

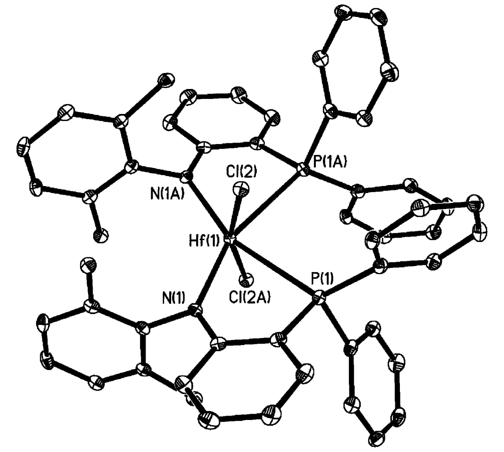

Figure 5. Molecular structure of $[MeNP]_2HfCl_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Hf(1)−N(1) 2.127(3), Hf(1)−N(1A) 2.127(3), Hf(1)−Cl(2A) 2.4170(9), Hf(1)−Cl(2) 2.4170(9), Hf(1)−P(1A) 2.7736(9), Hf(1)−P(1) 2.7736(9); N(1)−Hf(1)−N(1A) 126.52(16), N(1)−Hf(1)−Cl(2A) 95.67(8), N(1A)−Hf(1)−Cl(2A) 91.70(8), N(1)−Hf(1)−Cl(2) 91.70(8), N(1A)−Hf(1)−Cl(2) 95.67(8), Cl(2A)−Hf(1)−Cl(2) 163.58(5), N(1)−Hf(1)−P(1A) 160.40(8), N(1A)−Hf(1)−P(1A) 72.88(8), Cl(2A)−Hf(1)−P(1A) 79.52(3), Cl(2)−Hf(1)−P(1A) 88.64(3), N(1)−Hf(1)−P(1) 72.88(8), N(1A)−Hf(1)−P(1) 160.40(8), Cl(2A)−Hf(1)−P(1) 88.64(3), Cl(2)−Hf(1)−P(1) 79.52(3), P(1A)−Hf(1)−P(1) 87.94(4).

$[^iPrNP]ZrCl_3(THF)$. Interestingly, the two N−phenylene−P planes in $[MeNP]_2MCl_2$ are nearly parallel to each other as evidenced by the dihedral angle of 8.5 and 11.0° for M = Zr and Hf, respectively, leading to a stairlike conformation for the $[Me\text{-}NP]_2M$ moiety. Nevertheless, the metal center lies perfectly on the square plane defined by the four donor atoms of the two amido phosphine ligands (deviation of 0.0167 Å for Zr and 0 Å for Hf). With cis amido donors bearing the *o*-dialkylphenyl substituent, the N−M−N angle of 130.14(19)° for M = Zr and 126.52(16)° for M = Hf is thus considerably larger than the corresponding P−M−P of 86.94(5) and 87.94(4)°, respectively.

Conclusions

In summary, we have prepared a series of diarylamido−phosphine complexes of zirconium and hafnium and established their structural characterization by means of solution NMR spectroscopy and X-ray crystallography. These compounds represent the rarely encountered triarylphosphine complexes of group 4 metals. Studies involving the reduction chemistry of these molecules will be the subjects of further reports.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J), in hertz. ^1H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. Attempts to obtain satisfactory analysis were hampered due to extreme air- and moisture-sensitivity of these molecules.

Materials. Compounds $[^iPrNP]Li(THF)_2$,[23] $[MeNP]Li(THF)_2$,[19] and $MCl_4(THF)_2$ (M = Zr, Hf)[24] were prepared according to the procedures reported previously. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Data for compounds $[^iPrNP]ZrCl_3(THF)$, $[MeNP]_2ZrCl_2$, and $[MeNP]_2HfCl_2$ were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using WinGX crystallographic software package. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The crystals of $[^iPrNP]ZrCl_3(THF)$ and $[MeNP]_2ZrCl_2$ were of poor quality but sufficient to establish the identity of these molecules.

Synthesis of $[^iPrNP]ZrCl_3(THF)$. Solid $ZrCl_4(THF)_2$ (200 mg, 0.53 mmol) was suspended in toluene (2 mL) and cooled to −35 °C. To this was added a toluene solution (4 mL) of $[^iPrNP]Li(THF)_2$ (311 mg, 0.53 mmol) at −35 °C dropwise. After being stirred at room temperature for 2 h, the reaction mixture was filtered through a pad of Celite followed by evaporation to dryness under reduced pressure. The solid thus obtained was recrystallized from diethyl ether at −35 °C to afford the product as yellow crystals suitable for X-ray diffraction analysis. Yield: 270 mg (72%). ^1H NMR (C_6D_6, 500 MHz): δ 7.74 (t, 4, Ar), 7.31 (s, 3, Ar), 7.07 (m, 7, Ar), 6.93 (t, 1, Ar), 6.59 (t, 1, Ar), 6.21 (dd, 1, Ar), 4.12 (m, 4, OCH_2CH_2), 3.76 (septet, 2, $CHMe_2$), 1.55 (d, 6, $CHMe_2$), 1.11 (m, 4, OCH_2CH_2), 1.02 (d, 6, $CHMe_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 1.95. $^{31}P\{^1H\}$ NMR (toluene, 80.952 MHz): δ 1.95. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 160.78 (d, $J_{CP} = 25.1$, C), 151.19 (s, C), 135.36 (s, C), 134.95 (s, CH), 134.58 (d, J_{CP} = 11.1, CH), 132.64 (s, CH), 131.90 (d, J_{CP} = 28.4, C), 130.81 (s, CH), 130.37 (s, CH), 129.06 (d, J_{CP} = 9.2, CH), 126.29 (s, CH), 122.20 (d, J_{CP} = 5.0, CH), 120.78 (d, J_{CP} = 34.3, C), 117.98 (d, J_{CP} = 8.8, CH), 76.88 (br s, O*C*H$_2$CH$_2$), 29.27 (s, *C*HMe$_2$), 27.42 (s, CH*Me*$_2$), 25.62 (s, OCH$_2$*C*H$_2$), 24.46 (s, CH*Me*$_2$). Anal. Calcd for $C_{34}H_{39}Cl_3NOPZr$: C, 57.82; H, 5.57; N, 1.98. Found: C, 55.18; H, 6.24; N, 1.49.

Synthesis of [^{i}PrNP]HfCl$_3$(THF). Solid HfCl$_4$(THF)$_2$ (100 mg, 0.22 mmol) was suspended in toluene (1 mL) and cooled to −35 °C. To this was added a toluene solution (2 mL) of [^{i}PrNP]Li(THF)$_2$ (126 mg, 0.22 mmol) at −35 °C dropwise. After being stirred at room temperature for 1 h, the reaction mixture was filtered through a pad of Celite followed by evaporation to dryness under reduced pressure. The solid thus obtained was recrystallized from diethyl ether at −35 °C to afford the product as yellow crystals. Yield: 105 mg (62%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.73 (t, 4, Ar), 7.33 (m, 3, Ar), 7.06 (m, 7, Ar), 6.94 (t, 1, Ar), 6.55 (t, 1, Ar), 6.27 (dd, 1, Ar), 4.20 (m, 4, OC*H*$_2$CH$_2$), 3.83 (septet, 2, C*H*Me$_2$), 1.56 (d, 6, CH*Me*$_2$), 1.06 (d, 6, CH*Me*$_2$), 0.99 (m, 4, OCH$_2$C*H*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202.31 MHz): δ 4.09. ^{31}P{^{1}H} NMR (toluene, 80.952 MHz): δ 4.00. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz): δ 161.66 (d, J_{CP} = 23.4, C), 149.95 (s, C), 138.89 (s, C), 134.94 (s, CH), 134.65 (d, J_{CP} = 10.6, CH), 132.86 (s, CH), 131.82 (d, J_{CP} = 31.2, C), 130.86 (s, CH), 129.29 (s, CH), 129.06 (d, J_{CP} = 9.1, CH), 126.10 (s, CH), 121.44 (d, J_{CP} = 5.5, CH), 119.99 (d, J_{CP} = 8.7, C), 119.23 (d, J_{CP} = 7.8, CH), 77.25 (s, O*C*H$_2$CH$_2$), 29.10 (s, *C*HMe$_2$), 27.37 (s, CH*Me*$_2$), 25.53 (s, OCH$_2$*C*H$_2$), 24.59 (s, CH*Me*$_2$). Anal. Calcd for $C_{34}H_{39}Cl_3HfNOP$: C, 51.46; H, 4.95; N, 1.77. Found: C, 50.45; H, 5.06; N, 1.66.

Synthesis [MeNP]$_2$ZrCl$_2$. Solid ZrCl$_4$(THF)$_2$ (200 mg, 0.53 mmol) was suspended in toluene (3 mL) and cooled to −35 °C. To this was added dropwise a prechilled solution of [MeNP]Li(THF)$_2$ (563 mg, 1.06 mmol, 2 equiv) in toluene (5 mL) at −35 °C. The reaction mixture was stirred at room temperature overnight and filtered through a pad of Celite. The toluene filtrate was evaporated to dryness under reduced pressure, affording the product as a yellow solid which was sufficiently pure on the basis of NMR spectroscopy. Yield: 450 mg (92%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.41 (t, 8, Ar), 7.21 (t, 2, Ar), 7.06 (m, 4, Ar), 7.00 (m, 10, Ar), 6.90 (m, 6, Ar), 6.62 (t, 2, Ar), 5.97 (dd, 2, Ar), 1.95 (s, 12, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202.31 MHz): δ 12.28. ^{31}P{^{1}H} NMR (toluene, 80.95 MHz): δ 11.95. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz): δ 160.82 (m, C), 141.36 (s, C), 140.28 (s, C), 136.16 (s, CH), 135.01 (t, J_{CP} = 4.9, CH), 133.70 (s, CH), 131.988 (m, C), 130.75 (s, CH), 130.32 (s, CH), 128.68 (t, J_{CP} = 4.8, CH), 127.91 (s, CH), 120.94 (s, CH), 119.78 (m, C), 115.89 (t, J_{CP} = 5.0, CH), 19.31 (CH$_3$). Anal. Calcd for $C_{52}H_{46}Cl_2N_2P_2Zr$: C, 67.67; H, 5.02; N, 3.03. Found: C, 67.91; H, 5.45; N, 2.71.

Synthesis [MeNP]$_2$HfCl$_2$. Solid HfCl$_4$(THF)$_2$ (172 mg, 0.37 mmol) was suspended in toluene (3 mL) and cooled to −35 °C. To this was added dropwise a prechilled solution of [MeNP]Li(THF)$_2$ (395 mg, 0.74 mmol, 2 equiv) in toluene (5 mL) at −35 °C. The reaction mixture was stirred at room temperature overnight and filtered through a pad of Celite. The toluene filtrate was evaporated to dryness under reduced pressure, affording the product as a yellow solid which was sufficiently pure on the basis of NMR spectroscopy. Yield: 380 mg (100%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.34 (m, 8, Ar), 6.96 (m, 16, Ar), 6.88 (m, 6, Ar), 6.55 (t, 2, Ar), 5.98 (m, 2, Ar), 1.91 (s, 12, Me). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202.31 MHz): δ 10.46. ^{31}P{^{1}H} NMR (toluene, 80.95 MHz): δ 10.56. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz): δ 161.12 (t, J_{CP} = 15.5, C), 141.22 (s, C), 141.14 (s, C), 136.05 (s, CH), 135.11 (s, CH), 133.80 (s, CH), 131.79 (m, C), 130.63 (s, CH), 130.41 (s, CH), 128.50 (s, CH), 127.54 (s, CH), 120.57 (s, CH), 118.92 (m, C), 117.04 (s, CH), 19.22 (CH$_3$). Anal. Calcd for $C_{52}H_{46}Cl_2HfN_2P_2$: C, 61.82; H, 4.59; N, 2.77. Found: C, 60.49; H, 4.80; N, 2.62.

Acknowledgment. We thank the National Science Council of Taiwan for financial support (Grant NSC 93-2113-M-110-016) of this work and Mr. Ting-Shen Kuo at National Taiwan Normal University for solving the X-ray structures of the compounds reported.

Supporting Information Available: X-ray crystallographic data in CIF format for [^{i}PrNP]ZrCl$_3$(THF), [MeNP]$_2$ZrCl$_2$, and [MeNP]$_2$HfCl$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050599+