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Article

Synthesis, Coordination Chemistry, and Catalysis of the First 1,2-Bis(diphenylphosphino)-1,2-diphenylhydrazine, $Ph_2PN(Ph)N(Ph)PPh_2$[†]

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The reaction of chlorodiphenylphosphine with dilithiohydrazobenzene gave 1,2-bis(diphenylphosphino)-1,2-diphenylhydrazine, $[PPh_2N(Ph)N(Ph)PPh_2]$ (**1**). Treatment of **1** with $NiCl_2(DME)$, $PdCl_2(PhCN)_2$, and $PtCl_2(COD)$ resulted in the formation of complexes of the type *cis*-$[MCl_2\{Ph_2PN(Ph)N(Ph)PPh_2\}]$ (M = Ni (**3**), Pd (**4**), Pt (**5**)). The molecular structures of the starting ligand **1** and the complexes **3**, **4**, and **5** have been determined by X-ray diffraction. The ligand **1** and its Ni(II) complex **3** were evaluated for their catalytic activity in the oligo-/polymerization of ethylene using methylaluminoxane (MAO) and triethylaluminium (TEA) as cocatalyst.

Introduction

Phosphines are one of the most important classes of ligands in chemistry in both the industrial and academic spheres.[1] The synthesis of new chelating bis(phosphines) and the development of metal complexes based on them is an important area in the field of transition metal catalysis.[2] Alkane-diyl-bridged bis(phosphines), e.g., dppe as a prominent representative, found numerous catalytic applications due to the appropriate bite angle provided by the ethane-diyl backbone, which supports the formation of stable five-membered chelate rings.[3] This gave a powerful impetus to extend the scope of transition metal catalysis by preparing novel bis-phosphino ligands with spacing between the phosphorus(III) centers similar to that in dppe. Katti[4] and Woollins[5] recently reported the dinitrogen-bridged diphosphines $R_2PN(R')N(R')PR_2$ ($R' = Me, Et$) and bis(dihalophosphino)hydrazines, $X_2PN(R')N(R')PX_2$ ($R' = Me, Et$), which have similar chain length compared to dppe. It is noteworthy to mention that even though the first publication on the synthesis of bis(phosphino)-substituted alkylhydrazines appeared four decades ago,[6] only very few reports are found in the literature.[7,8] Surprisingly, the catalytic potential of this ligand system has not been discussed, except by Bollmann, Wasserscheid, et al., who described the use of $[PPh_2N(Me)N(Me)PPh_2]$ in ethylene tetramerization,[9] giving 58.8% C_8 (98.4% 1-C_8) and 25.2% C_6 (69.6% 1-C_6) along with 8% of polyethylene. In the same reaction carbon-bridged diphenylphosphinoethane (dppe) furnished 39.2% C_8 (96.6% 1-C_8) and 19.7% C_6 (38.2% 1-C_6) along with 35% of polyethylene.[9] The substituents at the bridging carbon atom show a great influence on the selectivity and productivity of the reaction. The use of systems of the type $(R^1)(R^2)P(R^5)CHCH(R^6)P(R^3)(R^4)$ (R^5 and R^6 are hydrocarbyl and substituted hydrocarbyl and not hydrogen) yields different selectivities depending on the substituents. By varying the R^5 and R^6 groups up to 72.9% of 1-C_8 can be obtained while reducing the amount of polyethylene to as low as 1.7%.[10] To our delight, very recently D. F. Wass et al. reported the efficient utilization of $[PR_2N(Me)N(Me)PR_2]$ ($R = o\text{-}MeC_6H_4, o\text{-}OMeC_6H_4$) ligands in the selective trimerization of isoprene to form terpenes. Notably, dppe and dppm (bis(diphenylphosphino)methane) were found to be inactive in this reaction.[11]

In this regard, it is interesting to evaluate the influence of other substituents attached to the N atom $[PPh_2N(R)N(R)PPh_2]$ in ethylene oligo- and polymerization reactions.

[†] This work is dedicated to Professor Dirk Walther on the occasion of his 70th birthday.

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(1) (a) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. *1*, p 2. (b) Noyori, R. *Asymmetric Catalysis In Organic Synthesis*; John Wiley & Sons, Inc.: New York, 1994. (c) Parshall, G. W; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; John Wiley & Sons, Inc.: New York, 1992; Chapter 8. (d) Kagan, H. B. Asymmetric Synthesis Using Organometallic Catalysts. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. *8*, Chapter 53.

(2) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992. (b) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983.

(3) Tao, X.; Huang, J.; Yao, H.; Qian, Y. *J. Mol. Catal A: Chem.* **2002**, *186*, 53–56. (b) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741–2769.

(4) Reddy, V. S.; Katti, K. V. *Inorg. Chem.* **1994**, *33*, 2695–2696. (b) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *Chem. Ber.* **1994**, *127*, 1355–1357. (c) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *Inorg. Chem.* **1995**, *34*, 5483–5488.

(5) Slawin, A. M. Z.; Wainwright, M.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, 513–519.

(6) Spangenberg, S. F.; Sisler, H. H. *Inorg. Chem.* **1969**, *8*, 1004–1006.

(7) Havlicek, M. D.; Gilje, J. W. *Inorg. Chem.* **1972**, *11*, 1624–1628.

(8) Nöth, H.; Ullmann, R. *Chem. Ber.* **1976**, *109*, 1942–1963.

(9) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712–14713.

(10) (a) Han, T. K.; Chae, S. S.; Kang, S. O.; Wee, K. R.; Kim, S. K. WO 2009/022770. (b) Han, T. K.; OK, M. A.; Chae, S. S.; Kang, S. O.; Jung, J. H. WO 2008/088178.

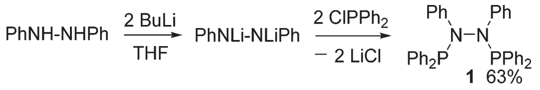
(11) Bowen, L. E.; Charernsuk, M.; Hey, T. W.; McMullin, C. L.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2010**, DOI: 10.1039/b913302j.

Also, to the best of our knowledge, ligands of the type $R_2PN(R')N(R')PR_2$ ($R' =$ aryl) are not yet known.

In this paper we report for the first time the synthesis and characterization of the arylhydrazine derivative, namely, 1,2-bis(diphenylphosphino)-1,2-diphenylhydrazine. The coordination chemistry of this new phosphanyl hydrazine with Ni(II), Pd(II), and Pt(II) precursors is also described through X-ray structural analysis. The influence of this ligand and its Ni(II) complex in the oligo- and polymerization of ethylene was investigated.

Results and Discussion

Synthesis of Bis(phosphanyl)hydrazine [$PPh_2N(Ph)N(Ph)PPh_2$], 1. 1,2-Bis(diphenylphosphino)-1,2-diphenylhydrazine (**1**; PNNP) was synthesized from well-known commercially available hydrazobenzene. The dilithium derivative of hydrazobenzene was prepared in situ by the reaction with 2 equiv of *n*-butyllithium in THF at −78 °C. Subsequently, chlorodiphenylphosphine was treated with the in situ formed dilithiated hydrazobenzene at 0 °C to afford the desired PNNP ligand [eq 1] in good isolated yield. The addition of $ClPPh_2$ to the THF solution of the dilithiated hydrazine also furnished **1**, as seen by ^{31}P NMR. However, this way lead to essential quantities of byproducts.[12] Also, working in low polar solvents like diethyl ether or pentane increased the formation of byproducts, which mainly consist of $Ph_2P\text{-}PPh_2$ ($^{31}P\{^1H\}$ NMR: −14.5 ppm). As mentioned earlier, previous studies have described the preparation of related methyl/ethyl derivative [$PPh_2N(R)N(R)PPh_2$] either by treating $Cl_2PN(R)N(R)PCl_2$ with PhMgCl[4,5] or by condensation reaction of *N*,*N*′-dimethylhydrazine and PPh_2Cl at −196 °C.[6]



$$\text{PhNH-NHPh} \xrightarrow[\text{THF}]{\text{2 BuLi}} \text{PhNLi-NLiPh} \xrightarrow[-\text{ 2 LiCl}]{\text{2 ClPPh}_2} \text{Ph}_2\text{P(Ph)N-N(Ph)PPh}_2 \quad \mathbf{1}\ 63\% \qquad (1)$$

Colorless crystals of **1**, suitable for X-ray crystal structure analysis, were obtained by addition of absolute ethanol to a saturated dichloromethane solution of **1** followed by storing the resulting solution at +4 °C. The ligand **1** is not prone to alcoholysis at room temperature and found to be fairly stable towards oxygen in the solid state. The ^{31}P NMR chemical shift was found to be at +64.6 ppm and is in agreement with the values reported for [$PPh_2N(Et)N(Et)PPh_2$] (64.2 ppm) and [$PPh_2N(Me)N(Me)PPh_2$] (62.5 ppm).

Selected bond distances and angles are given in Table 1. The molecular structure of the ligand is shown in Figure 1. The P−N−N−P chain is constrained to the *cis* configuration. The two nitrogen atoms are in a planar environment with the angles adding to 359.8° around N1 and N2. The P−N and N−N distances are in the usual range, comparable to related diphenylphosphino-1,2-diarylhydrazines.[12]

Our attempts to prepare **1** in another way, using Et_3N as dehydrochlorinating agent, were not successful. In toluene hydrazobenzene did not react with $ClPPh_2$ in the presence of Et_3N. However, we obtained diphenylphosphino-1,2-diphenylhydrazine (**2**) in DCM as well as in DMF at room temperature in the presence of Et_3N (eq 2).[12] Using harsher conditions, i.e., heating the DMF solution at 80 °C to incorporate bis-substitution, led to decomposition by forming unidentified products. Nevertheless, **2** can be converted to **1** in moderate yield by lithiation using BuLi, followed by addition of the in situ formed lithiated solution to $ClPPh_2$ at 0 °C.

Table 1. Selected Bond Lengths (Å) and Angles (deg)

	1	3	4	5
N1−P1	1.7259(13)	1.7164(13)	1.7180(14)	1.720(2)
N2−P2	1.721(2)	1.7194(13)	1.7155(14)	1.712(2)
N1−N2	1.428(2)	1.429(2)	1.430(2)	1.431(3)
Cl1−M		2.1916(4)	2.3384(4)	2.3431(6)
Cl2−M		2.1838(4)	2.3478(4)	2.3525(6)
P1−M		2.1265(4)	2.1979(4)	2.1926(6)
P2−M		2.1115(4)	2.2134(4)	2.1995(6)
N1−N2−P2	112.39(11)	108.54(9)	117.52(10)	117.83(15)
C19−N2−P2	130.75(12)	123.02(10)	128.19(11)	127.9(2)
C19−N2−N1	116.68(15)	115.60(11)	114.27(12)	114.3(2)
N2−N1−P1	112.08(10)	116.36(9)	109.58(10)	109.69(14)
C13−N1−P1	132.20(12)	128.99(10)	122.53(10)	122.4(2)
C13−N1−N2	115.53(13)	114.63(12)	116.01(12)	116.0(2)
Cl2−M−Cl1		95.21(2)	93.16(2)	90.12(2)
P1−M−Cl1		88.42(2)	92.270(15)	93.57(2)
P1−M−Cl2		174.17(2)	174.03(2)	175.91(2)
P2−M−Cl2		90.14(2)	89.91(2)	90.81(2)
P2−M−Cl1		173.96(2)	175.11(2)	177.04(3)
P2−M−P1		86.03(2)	84.505(15)	85.41(2)
N1−P1−M		108.09(4)	108.55(5)	107.72(7)
N2−P2−M		109.60(4)	107.30(5)	106.78(7)
C7−P1−M		109.58(5)	112.06(6)	113.24(8)
C1−P1−M		115.13(6)	115.51(6)	115.61(8)
C25−P2−M		111.54(5)	114.57(6)	114.79(10)
C31−P2−M		116.58(5)	108.78(6)	109.34(9)

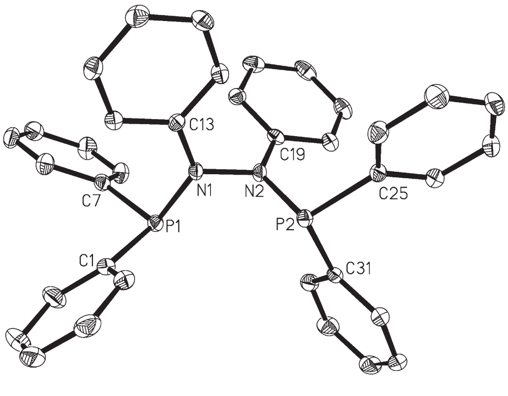


Figure 1. Molecular structure of $Ph_2PN(Ph)N(Ph)PPh_2$ (**1**). Thermal ellipsoids are drawn at the 30% probability level. The H atoms are omitted for clarity.

$$\text{PhNH-NHPh} + \text{ClPPh}_2 + \text{Et}_3\text{N} \xrightarrow{\text{CH}_2\text{Cl}_2} \underset{\mathbf{2}\ 50\%}{\text{Ph}_2\text{P-NPh-NHPh}} \xrightarrow[\substack{\text{2. ClPPh}_2\\ -\text{ LiCl}}]{\substack{\text{1. BuLi}\\ \text{THF}}} \mathbf{1}\ 43\% \qquad (2)$$

Coordination Chemistry of [$PPh_2N(Ph)N(Ph)PPh_2$]. Reaction of the ligand **1** with group 10 metals, namely, $NiCl_2(DME)$, $PdCl_2(PhCN)_2$, and $PtCl_2(COD)$, in a 1:1 molar ratio at room temperature in dichloromethane resulted in the formation of mononuclear, square-planar complexes *cis*-[$NiCl_2\{Ph_2PN(Ph)N(Ph)PPh_2\}$] (**3**), *cis* -[$PdCl_2\{Ph_2PN(Ph)N(Ph)PPh_2\}$] (**4**), and *cis*-[$PtCl_2\{Ph_2PN(Ph)N(Ph)PPh_2\}$] (**5**) (eq 3) in excellent yields. The $^{31}P\{^1H\}$ NMR spectra of **3**, **4**, and **5** show singlets at δ 117.14, 126.07, and 96.34 ppm,

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[12] Fedotova, Y. V.; Kornev, A. N.; Sushev, V. V.; Kursky, Y. A.; Mushtina, T. G.; Makarenko, N. P.; Fukin, G. K.; Abakumov, G. A.; Zakharov, L. N.; Rheingold, A. L. *J. Organomet. Chem.* **2004**, *689*, 3060–3074.

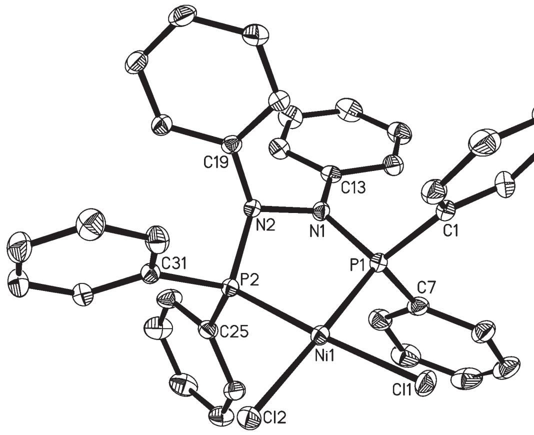
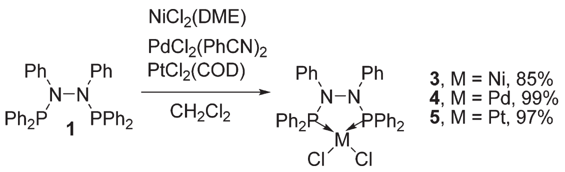


Figure 2. Molecular structure of [NiCl$_2${Ph$_2$PN(Ph)N(Ph)-PPh$_2$-*P,P*}] (**3**). Thermal ellipsoids are drawn at the 30% probability level. The H atoms are omitted for clarity.

respectively, with $J\{^{195}\text{Pt}-^{31}\text{P}\}$ of 3992 Hz for **5**, comparable to the values previously reported for [PtCl$_2${Ph$_2$PN(Et)-N(Et)PPh$_2$}] (^{31}P: 100.4 ppm, $J\{^{195}\text{Pt}-^{31}\text{P}\}$: 4055 Hz).[5] An upfield shift of approximately 6 and 4 ppm in the values of ^{31}P NMR for **4** and **5** was observed compared to related [MCl$_2${Ph$_2$PN(Et)N(Et)PPh$_2$}] (M = Pd, Pt).[5]



(3)

Slow diffusion of pentane into a chloroform solution of **3**, **4**, and **5** led to the formation of yellow crystals of **3** and **4** as well as colorless crystals of **5**, suitable for X-ray diffraction. The crystals contain CHCl$_3$ as lattice solvent. Selected bond distances and angles are given in Table 1, and a view of their molecular structure is shown in Figures 2, 3, and 4.

As mentioned above, all the complexes possess square-planar geometry around the metal center, and this is consistent with the diamagnetism of the Ni complex **3**. The five-membered chelate ring (MP$_2$N$_2$) displays a classic open-envelope conformation. Similar to other five-membered PNNPM metallacycles, one of the two nitrogen atoms is deviated from the five-membered-ring plane by 0.50, 0.51, and 0.52 Å respectively for **3**, **4**, and **5**.[13] In the case of complex **5** the M–P, P–N, and M–Cl bond lengths are similar to the values previously reported for single bonds in the related *cis*-[PtCl$_2${*o*-C$_6$H$_4$OCH$_3$)$_2$PN(Me)N(Me)P(*o*-C$_6$H$_4$OCH$_3$)$_2$}]. These data reveal that, in comparison to the spectroscopic differences highlighted above, these complexes of PNNP (*N*-aryl) structurally do not differ in any substantial way from those of related PNNPM (*N*-alkyl) metallacycles in that the metal–ligand bond lengths, bond lengths within the five-membered ring chelates, and angles at the metal center are comparable.

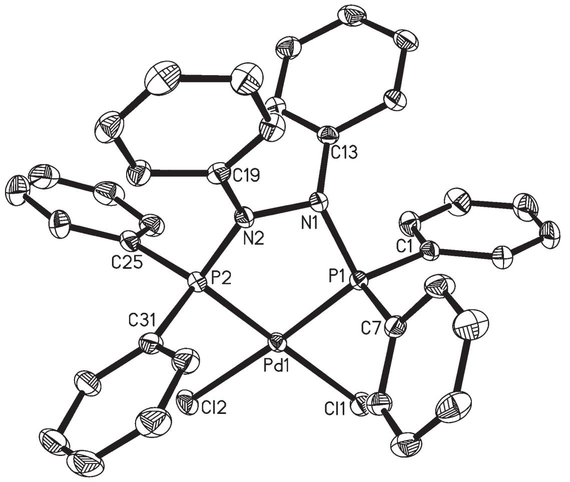


Figure 3. Molecular structure of [PdCl$_2${Ph$_2$PN(Ph)N(Ph)-PPh$_2$-*P,P*}] (**4**). Thermal ellipsoids are drawn at the 30% probability level. The H atoms are omitted for clarity.

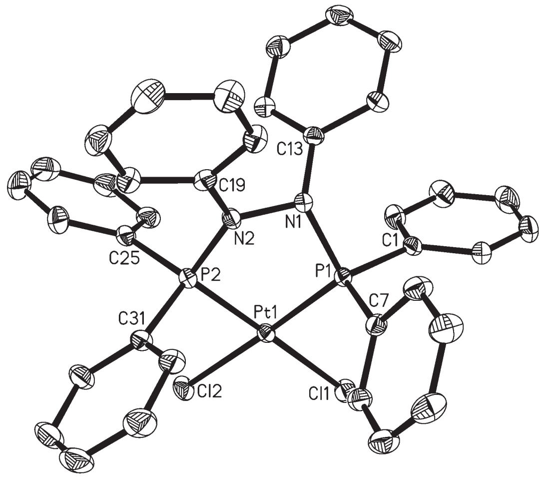
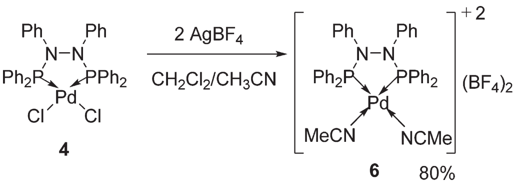


Figure 4. Molecular structure of [PtCl$_2${Ph$_2$PN(Ph)N(Ph)-PPh$_2$-*P,P*}] (**5**). Thermal ellipsoids are drawn at the 30% probability level. The H atoms are omitted for clarity.

The dicationic complex [Pd(NCMe)$_2${Ph$_2$PN(Ph)N(Ph)-PPh$_2$}](BF$_4$)$_2$ (**6**) was prepared by chloride abstraction from **4** with AgBF$_4$ (eq 4). Its ^{31}P{^{1}H} NMR spectrum contains a singlet at δ 123.25 ppm.



(4)

The structure of compound **6** was confirmed by X-ray crystallography. Unfortunately, the crystals contained solvent molecules, which could not be modeled. Furthermore both anions are disordered. The molecular structure of the cation and the crystal data are given in the Supporting Information.

Catalytic Oligo- and Polymerization of Ethylene. Ethylene oligomerization and polymerization are important processes to prepare valuable products such as linear α-olefins, wax, and polyethylene from basic feedstock (ethylene). As mentioned in the Introduction, [PPh$_2$N(Me)N(Me)PPh$_2$] was used successfully in ethylene tetramerization by combining

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[13] Eberhardt, L.; Armspach, D.; Matt, D.; Oswald, B.; Toupet, L. *Org. Biomol. Chem.* **2007**, *5*, 3340–3346.

Table 2. Ethylene Oligomerization Using Ligand 1 in Combination with Cr or Ni and Complex 3 as Catalyst Precursors

					product distribution[e,f]									
no.	PE (g)[a]	oligomers (g)[b]	TON[c]	TOF[d]	C4	C5	C6	C7	C8	C9	C10	C11	C12	C14
Cat1	10	8	12830	8700	8.9 (>98)	1.3 (>98)	30.9 (99)	1.3 (>98)	34.5 (99)	1.4 (>98)	19.2 (>98)	0.4 (>98)	2.0 (>98)	0.1 (>98)
Cat2	25	14	27730	18800	5.8 (>98)	1.2 (>98)	34.5 (99)	1.9 (>98)	35.2 (99)	1.6 (>98)	14.5 (>98)	0.8 (>98)	4.1 (>98)	0.6 (>98)
Cat3	0.03	14	10910	7400	69.6		23.8		4.7		1.1			
Cat4	0.05	15	11980	8120	75.9		19.2		3.1		0.9		0.1	
Cat5	0.60	1.5	1710	1160	24.5 (58)		56.3 (67)		19.2 (70)					

[a] Isolated and purified polymer. [b] Amount of liquid oligomers dissolved in toluene. Volatile butenes are not taken into account. [c] TON in mol/mol. [d] TOF in mol/mol h (over a period of 90 min). [e] Mol percentage of combined C*n* products. Deviations from the Schulz−Flory distribution may be due to loss of butene and hexene (to volatile fraction) and the solubility of C10 and C12 in the polymer. [f] In parentheses the percentage of terminal olefins, as percentage of individual C*n* fraction.

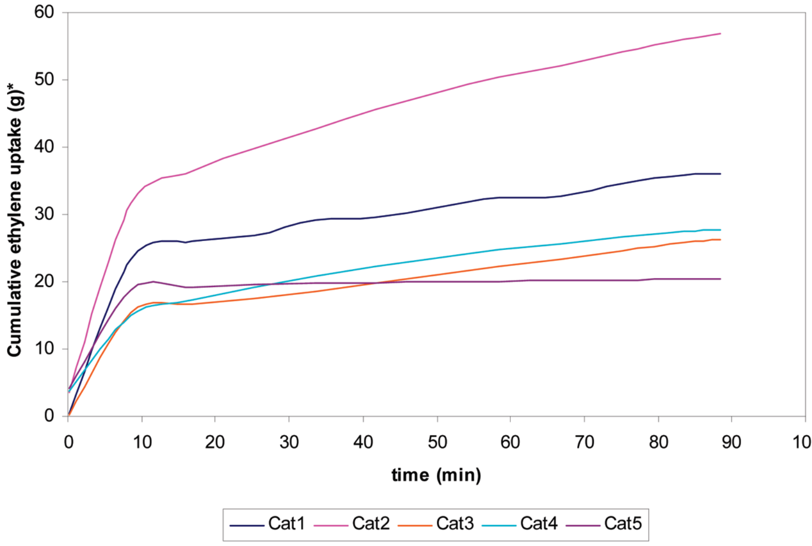

Figure 5. Ethylene uptake−time plots for the oligo-/polymerization of ethylene (*including saturation). Conditions: All reactions were conducted in a 300 mL Parr reactor. Standard reaction conditions: ligand 0.1 mmol, Cr or Ni 0.05 mmol, MAO 300 equiv (Cat1−4), toluene as solvent, total volume 100 mL, *T* 45 °C (for Cr) or 100 °C (for Ni), time 90 min, *P* 30 bar; Cat1 is $Cr(acac)_3$; Cat2 is $CrCl_3 \cdot 3THF$; Cat3 is the preformed complex **3**; Cat4 is $Ni(COD)_2$; Cat5 is $Cr(acac)_3$, TEA (300 equiv).

it with $Cr(acac)_3$ and MAO.[9] Also, various nickel complexes containing chelating ligands such as O−P, O−N, N−N, and N−P have been applied in the oligo- and polymerization of ethylene.[14] We studied the behavior of ligand **1** in ethylene oligomerization by combining it with $Cr(acac)_3$, $CrCl_3 \cdot 3THF$, and $Ni(COD)_2$. The in situ formed complexes were activated with MAO (in one example TEA), and catalytic runs were performed in toluene at 45 or 100 °C for 90 min at 30 bar of ethylene pressure. In addition to this, complex **3** was also tested as catalyst precursor in this reaction. The results of the catalytic studies are summarized in Tables 2 and 3. The ethylene uptake and time plot is shown in Figure 5.

In the presence of chromium catalyst the formation of polyethylene was observed predominantly, besides a small amount of liquid oligomers (Cat1, 2, and 5). When nickel catalysts were used, the major products are lower olefins, and only a trace amount of polyethylene was formed (Cat3 and 4). As seen from Figure 5, the PNNP ligand forms an active catalyst with $CrCl_3 \cdot 3THF$ at 45 °C (Cat2), while with $Cr(acac)_3$ the activity is decreased slightly (Cat1). In the presence of TEA the catalytic reaction is very slow, and only about 2 g of ethylene was consumed over a period of 90 min (Cat5). The catalyst precursor from the Ni complex did not show any activity at 45 °C and requires higher temperature, and therefore the tests were performed at 100 °C (Cat3, 4).

Table 3. Physical Data of PE

no.	M_{NMR}[a]	α/int (%)	Me/1000C[a]	mp (°C)[b,c]	*d* (g cm^{-3})
Cat1	1400−1600	99/1	16	126	0.929
Cat2	3215−3518	98/2	11	125	0.946

[a] Determined by ^1H NMR integration. [b] Measured by differential scanning calorimetry. [c] Melting peak is given.

As can be seen from Table 2, Cr catalysts (Cat1, 2) gave, apart from polyethylene, a Schulz−Flory distribution of oligomers. The major fraction belongs to C6 and C8 with a selectivity of 99% for 1-C6 and 1-C8. Interestingly, here the formation of *even* as well as *odd* chain length oligomers is observed. In our previous publication, we reported a simplified mechanistic pathway for the formation of odd-numbered linear α-olefins (LAOs) in the presence of the $Ph_2PN(^iPr)PPh_2/CrCl_3 \cdot 3THF/MAO$ system at substoichiometric

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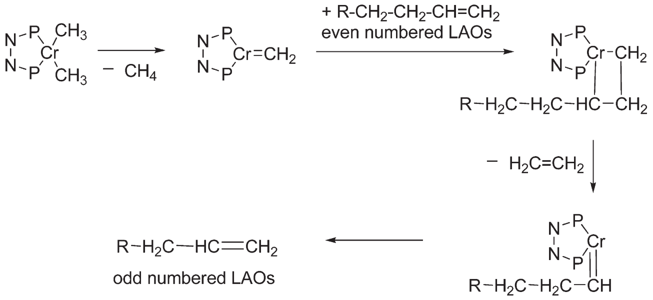
(14) Sun, W. H.; Zhang, D.; Zhang, S.; Jie, S.; Hou, J. *Kinet. Catal.* **2006**, *47* (2), 278–283.

Scheme 1. Possible Mechanistic Pathway for Odd-Numbered LAOs



ligand/Cr ratio.[15] A similar mechanism involving mononuclear Cr complex is expected in the present case. The formation of a methyl compound (PNNP)Cr(Me)$_n$ after the alkylation with MAO and elimination of methane to give chromium carbene "Cr=CH$_2$" groups, followed by the reaction of these carbene groups with the recently formed even-numbered LAOs, leads to the formation of odd-numbered LAOs (Scheme 1). Another plausible explanation for this uncommon behavior is that the active species follows a typical insertion/β-elimination mechanism rather than a simple metallacycle mechanism. Our attempts to synthesize the Cr−PNNP complex, which can give us an insight into the active species in the catalytic process, were not successful. In the case of Ni catalysts, the main products are butenes along with hexenes and a small amount of octenes and higher olefins, each with several isomers (Cat3, 4). In contrast to this, a very high selectivity toward terminal olefins is observed for Cr catalysts (Cat1, 2). The cocatalyst shows an influence not only on the activity but also on selectivity. The use of TEA instead of MAO results in a dramatic decrease in both activity and selectivity (Cat5). The formation of C15 and higher oligomers is not observed in all these attempts under the above-mentioned conditions.

The purified polyethylene obtained from the experiments Cat1 and Cat2 were characterized by ^{1}H NMR (C$_6$D$_5$Br),[16] and the results are included in Table 3. The high selectivity for linear α-olefins ($>98\%$) is observed, and the average molecular weights (M_{NMR}) of the polyethylene depended on the catalyst system used. The data in Table 3 revealed, by changing the catalyst system from Cr(acac)$_3$ to CrCl$_3$·3THF, that the molecular weight of formed polyethylene doubled, while the difference in the selectivity toward α-olefins is negligible.

Conclusions

In conclusion, we have reported the synthesis and characterization of 1,2-bis(diphenylphosphino)-1,2-diphenylhydrazine (**1**) and its square-planar Ni(II) (**3**), Pd(II) (**4**), and Pt(II) (**5**) complexes. The PNNP ligand in combination with Cr(III) or Ni(0) compounds activated by MAO was found to form active catalysts for the oligomerization of ethylene. Whereas chromium-based catalysts resulted in the formation of polyethylene, the nickel catalysts predominantly furnished lower olefins, especially butenes and hexenes.

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques, using predried reagents. The solvents were purified according to conventional procedures and were freshly distilled prior to use. Chemicals were obtained from Aldrich or Strem chemicals. The following spectrometers were used: Mass spectra: AMD 402. NMR spectra: Bruker AV 300 and AV 400. Chemical shifts are given in ppm and are referenced to TMS or the residual nondeuterated solvent as internal standard for ^{1}H and 85% H$_3$PO$_4$ for ^{31}P{^{1}H}. Melting points: sealed capillary, Büchi 535 apparatus (uncorrected). Elemental analyses: Leco CHNS-932 elemental analyzer. Gas chromatography: HP 6890 (Hewlett-Packard) chromatograph using a HP 5 column.

Ph$_2$PN(Ph)N(Ph)PPh$_2$ (1). Method A. A 2.5 M hexane solution of *n*-BuLi (16.5 mL, 41.25 mmol) was added to a stirred solution of 1,2-diphenylhydrazine (4.0 g, 21.71 mmol) in 40 mL of THF at −78 °C. This reaction mixture was stirred for 3 h while slowly warming to −40 °C. The formed greenish-yellow solution was added slowly via cannula to a stirred solution of ClPPh$_2$ (8.0 mL, 43.42 mmol) cooled with an ice-bath, and stirring was continued overnight at room temperature. THF was removed from the reaction mixture under reduced pressure, and the residue was washed with diethyl ether (3 × 20 mL) and *n*-hexane (2 × 10 mL), followed by drying under vacuum, which resulted in the isolation of a yellow solid. This solid was recrystallized from a mixture of THF/hexane to give pure product as a colorless (or very pale yellow) solid (7.5 g, 63%). Single crystals suitable for X-ray diffraction were obtained from a 1:1 mixture of CH$_2$Cl$_2$/EtOH, mp 131 °C. ^{1}H NMR (THF-d_8): δ 6.58−6.64 (m, 2 H), 6.80−6.89 (m, 8 H), 7.07−7.31 (br m, 12 H), 7.51−7.64 (br m, 8 H). ^{13}C{^{1}H} NMR (THF-d_8): δ 117.61 (s, CH), 120.29 (s, CH), 127.53 (m, CH), 130.75 (m, C$_q$), 135.73 (dd, J = 24.78, 2.55 Hz, C$_q$), 146.51 (t, J = 5.17 Hz, C$_q$). ^{31}P{^{1}H} NMR (THF-d_8): δ 64.64. HRMS (ESI): calcd for [M + H$^+$] (C$_{36}$H$_{31}$N$_2$P$_2$), 553.1957; found, 553.19579. Anal. Calcd for C$_{36}$H$_{30}$N$_2$P$_2$: C, 78.25; H, 5.47; N, 5.07. Found: C, 77.95; H, 5.48; N, 4.85.

Method B. Ph$_2$PN(Ph)NHPh (2). Chlorodiphenylphosphine (1.0 mL, 5.43 mmol) was added to a stirred solution of 1,2-diphenylhydrazine (500 mg, 2.71 mmol) in 10 mL of CH$_2$Cl$_2$. To this reaction mixture was added dropwise Et$_3$N (0.76 mL, 5.43 mmol, diluted in 40 mL of CH$_2$Cl$_2$) over a period of 4 h, and the mixture was stirred at room temperature for a further 12 h. CH$_2$Cl$_2$ was removed from the reaction mixture and the residue extracted with diethyl ether. Removal of the diethyl ether gave a yellow viscous oil. Crystallization from hot hexane gave 500 mg (50%) of a pale yellow crystalline product, whose spectral data agreed with those reported in the literature.[12]

Ph$_2$PN(Ph)N(Ph)PPh$_2$ (1). A 2.5 M hexane solution of *n*-BuLi (0.35 mL, 0.87 mmol) was added to a stirred solution of **2** (338 mg, 0.92 mmol) in 5 mL of THF at −78 °C. This reaction mixture was stirred for 3 h, while slowly warming to −40 °C. The formed greenish-yellow solution was added slowly via cannula to a stirred solution of ClPPh$_2$ (0.17 mL, 0.92 mmol) cooled in an ice-bath, and stirring continued at room temperature overnight. THF was removed from the reaction mixture under reduced pressure, and the residue was washed with diethyl ether (3 × 5 mL) and hexane (2 × 5 mL), followed by drying under vacuum, giving a yellow solid. This solid was recrystallized from a mixture of THF/hexane to give pure product as a colorless (or very pale yellow) solid (218 mg, 43%). Analytical data match with those reported above in method A.

[NiCl$_2${Ph$_2$PN(Ph)N(Ph)PPh$_2$-*P*,*P*}] (3). CH$_2$Cl$_2$ (10 mL) was added to a mixture of solid Ph$_2$PN(Ph)N(Ph)PPh$_2$ (147 mg, 0.266 mmol) and [NiCl$_2$(DME)] (58.5 mg, 0.266 mmol) at room

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(15) For a detailed description of the experimental setup see: Wöhl, A.; Müller, W.; Peulecke, N.; Müller, B. H.; Peitz, S.; Heller, D.; Rosenthal, U. *J. Mol. Catal A: Chem.* **2009**, *297*, 1–8.

(16) For information about the polyethlyne NMR measurement see: Aluri, B. R.; Kindermann, M. K.; Jones, P. G.; Heinicke, J. *Chem.—Eur. J.* **2008**, *14*, 4328−4335, and references therein.

temperature, and the mixture was stirred for 16 h. The solution was filtered, and the volatiles were removed under reduced pressure. The residue was washed with diethyl ether (2 × 10 mL) and pentane (2 × 10 mL) and dried under vacuum to give a yellow solid. This solid was dissolved in $CHCl_3$ and overlayered with pentane to give 154 mg (85%) of colorless crystals of desired product, mp 180 °C (dec). ^1H NMR ($CDCl_3$): δ 6.66−6.69 (m, 4 H), 6.75−6.83 (m, 6 H), 7.34 (t, J = 7.6 Hz, 8 H), 7.47 (t, J = 7.6 Hz, 4 H), 7.94 (m, 8 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 117.14. Anal. Calcd for $C_{36}H_{30}Cl_2N_2NiP_2$: C, 63.38; H, 4.43; N, 4.11. Found: C, 63.30; H, 4.57; N, 4.02.

[$PdCl_2$\{$Ph_2PN(Ph)N(Ph)PPh_2$-*P,P*\}] (4). [$PdCl_2(NCPh)_2$] (145 mg, 0.377 mmol) was added to a solution of $Ph_2PN(Ph)N(Ph)PPh_2$ (208 mg, 0.377 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred for 16 h; then the volatiles were removed under reduced pressure. The residue was dissolved in $CHCl_3$ and overlayed with pentane to give 272 mg (99%) of a pure yellow crystalline product, mp 221 °C (melted with decomposition). ^1H NMR ($CDCl_3$): δ 6.76−6.80 (m, 4 H), 6.84−6.88 (m, 6 H), 7.31 (tm, J = 8.0 Hz, 8 H), 7.44 (tm, J = 7.2 Hz, 4 H), 7.79−7.86 (m, 8 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 126.07. HRMS (ESI): m/z calcd for $C_{36}H_{30}Cl_2N_2NaP_2Pd$, 753.01924 $[M + Na]^+$; found, 753.01867. Anal. Calcd for $C_{36}H_{30}Cl_2N_2P_2Pd$ $CHCl_3$: C, 52.33; H, 3.68; N, 3.30. Found: C, 52.23; H, 3.83; N, 3.19.

[$PtCl_2$\{$Ph_2PN(Ph)N(Ph)PPh_2$-*P,P*\}] (5). [$PtCl_2$(COD)] (85 mg, 0.227 mmol) was added to a solution of $Ph_2PN(Ph)N(Ph)PPh_2$ (125 mg, 0.227 mmol) in CH_2Cl_2 (4 mL) at room temperature. The mixture was stirred for 16 h, and then the volatiles were removed under reduced pressure to obtain a white powder. This was washed with hexane to remove the free cyclooctadiene and dried under vacuum to obtain 180 mg of the title complex (97%), mp 250 °C (dec). ^1H NMR ($CDCl_3$): δ 6.76−6.80 (m, 4 H), 6.83−6.86 (m, 6 H), 7.28−7.34 (m, 8 H), 7.42 (td, J = 7.6, 1.3 Hz, 4 H), 7.78−7.85 (m, 8 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 96.34 (s, $^1J_{Pt-P}$ = 3992 Hz). HRMS (ESI): m/z calcd for $C_{36}H_{30}Cl_2N_2NaP_2Pt$, 840.08012 $[M + Na]^+$; found, 840.083. Anal. Calcd for $C_{36}H_{30}Cl_2N_2P_2Pt.CH_2Cl_2$: C, 49.19; H, 3.57; N, 3.10. Found: C, 49.59; H, 3.66; N, 2.77.

[Pd\{$Ph_2PN(Ph)N(Ph)PPh_2$-*P,P*\}$(NCMe)_2$][BF_4]$_2$ (6). The complex [$PdCl_2$\{$Ph_2PN(Ph)N(Ph)PPh_2$-*P,P*\}] (105 mg, 0.144 mmol) was treated with $AgBF_4$ (56 mg, 0.288 mmol) in a 1:1 mixture of CH_2Cl_2/CH_3CN at ambient temperature. The reaction mixture was stirred for 4 h; then the solution was filtered and the volatiles were removed under reduced pressure to leave a yellow crystalline mush. This was recrystallized from a saturated solution of CH_2Cl_2 (105 mg, 80%). ^1H NMR (CD_2Cl_2): δ 2.10 (s, 6 H, CH_3CN), 6.81−6.84 (m, 4 H), 6.99−7.03 (m, 6 H), 7.53 (td, J = 7.3, 3.6 Hz, 8 H), 7.66−7.77 (m, 12 H) (Note: at 2.10 ppm integral ratio is excess). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 123.25. Anal. Calcd for $C_{40}H_{36}B_2F_8N_4P_2Pd$: C, 52.52; H, 3.97; N, 6.13. Found: C, 46.82; H, 3.79; N, 5.35 (no better analyses could be obtained).

Oligo- and Polymerization of Ethylene. The autoclave was heated at 150 °C under vacuum for 2 h and cooled either to 45 °C (Cr catalyst) or to 100 °C (Ni Catalyst) under argon atmosphere. A solution or suspension of ligand and the corresponding metal precursor (according to Figure 5) were stirred together at ambient temperature in toluene (~90.4 mL) for 2 h. To this was added 9.8 mL of MAO in toluene solution (10% w/w), and the resulting solution was transferred into a preheated autoclave (300 mL) under an argon atmosphere. Afterward, the autoclave was pressurized with 30 bar of ethylene by opening the valve of a 2 kg aluminum cylinder. During the run, a constant ethylene pressure of 30 bar was applied, and the temperature was controlled through an internal cooling spiral against the exotherm of the reaction. The weight loss of the ethylene cylinder was recorded and the amount of ethylene consumed was deduced from the weight loss of the ethylene cylinder after saturation.[15] After the run, the autoclave was cooled to below 10 °C. After releasing the excess ethylene from the autoclave, the contents (polymer with solvent and oligomers) were transferred to a flask. Then all the volatiles were flash-distilled at 3−4 mbar/70−80 °C, treated with 1 M hydrochloric acid solution, and submitted for GC analysis. The residual polymer was extracted with a mixture of methanol and concentrated hydrochloric acid (1:1) by stirring overnight at room temperature and was then washed with methanol and dried under vacuum. The melting points of the polymers were measured on a differential scanning calorimeter instrument, model DSC 823^e (Mettler Toledo).

X-ray Structure Analysis of 1, 3, 4, and 5. Data were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97)[17] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).[17] XP (Bruker AXS) was used for graphical representations.

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Supporting Information Available: X-ray details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.