Structural Characterization and a New One-Pot Synthesis of *trans*-Chloro(phenyl)bis(triphenylphosphane)nickel(II)

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trans-[NiCl(Ph)(PPh_3)$_2$], the organometallic precursor for a new class of neutral polymerization catalysts, has been synthesized via a new synthetic route. The previously used alkylaluminum compounds are replaced by zinc dust for the reduction of the nickel(II) salt in the presence of triphenylphosphane forming the intermediate Ni(PPh_3)$_4$. In a one-pot reaction, chlorobenzene then adds oxidatively to the intermediate to form the title compound, which was structurally characterized, in high yields. Its geometry is compared to known structures of the higher homologues of group 10. All complexes adopt a distorted square-planar geometry, but the parent structure shows significantly shorter metal-ligand bond lengths than its Pd and Pt congeners, as expected. Density functional theory calculations (B3LYP/6–31G*) on the full structure are in very good agreement with the solid-state structure.

Introduction

In the almost 50 years since the discovery of transition metal catalysis for olefin polymerization by Ziegler and Natta[1–3] a lot of research activities have been directed towards molecular homogeneous catalytic systems. As a result of this research the zirconocenes and other early transition metal catalysts were found to be extremely active in ethylene polymerization after activation by methylalumoxane (MAO),[4,5] but proved quite sensitive to the presence of air, moisture and polar groups.

Over the past years several new, highly active polymerization catalysts of late transition metals have been developed.[6–8] Compared to catalysts containing early transition metals they exhibit a greater tolerance towards functional groups, which is useful for the copolymerization with polar monomers. They also provide the possibility of making polymers with novel branching structures and thereby new materials with unknown properties.

Recently a new class of neutral polymerization nickel(II) catalysts based on salicylaldimine or anilinotropone ligands has been introduced, which are highly active in the polymerization of olefins (Scheme 1).[9–12] Some of them no longer need to be activated, either by MAO or by other phosphane-binding complexes, and show comparable polymerization activities to early transition metal catalysts. They are even capable of forming polymers in aqueous solutions[13] and produce linear to moderately branched polyethylene.

R = H, *t*Bu, Ph, 9-phenanthroline, 9-anthracene

Scheme 1. Neutral nickel(II) polymerization catalysts

The key intermediate and organometallic precursor for the synthesis of this type of catalysts is *trans*-[NiCl(Ph)(PPh_3)$_2$], which has been mentioned frequently in recent patents.[14–18] Herein we report a new one-pot synthesis of this complex with improved overall yield from readily available and inexpensive reagents. The crystal structure was determined for the first time and is compared to its higher group 10 homologues Pd and Pt, as well as to the results of a DFT calculation for the gas-phase structure.

Results and Discussion

Generally, the divalent complexes [MCl(Ph)(PPh_3)$_2$] (M = Ni, Pd, Pt) result from the oxidative addition of chlorobenzene to the corresponding zerovalent tetraphosphane complex. Accordingly, the title compound can be synthesized by addition of chlorobenzene to Ni(PPh_3)$_4$.[19] A previously published synthesis prepared the latter by reduction of Ni(acac)$_2$ with alkylaluminum compounds.[20] The disad-

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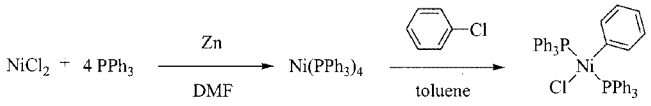
vantage of this reaction is the moderate yield of 55% for the preparation of $Ni(PPh_3)_4$ and the sensitivity of the alkylaluminum compounds.

Another method would be the replacement of weaker ligands, as in the addition of triphenylphosphane to $Ni(COD)_2$, which requires the synthesis of the Ni^0 precursor, usually also carried out by reduction of $Ni(acac)_2$ with trimethylaluminum.[21]

We were able to combine these steps into a one-pot synthesis starting from readily available and inexpensive reagents. The first step is the reduction of $NiCl_2$ by one equivalent of zinc dust in DMF in the presence of triphenylphosphane (Scheme 2), which results in the formation of the brick-red, air sensitive $Ni(PPh_3)_4$.



Scheme 2. Synthesis of *trans*-chloro(phenyl)bis(triphenylphosphane)nickel(II)

After removal of DMF and addition of toluene, chlorobenzene was added to the resulting solution. In a previous study of coupling of aryl chlorides, it was reported that an excess amount of zinc in the first reaction step or higher temperatures lead to the decomposition of the oxidative addition product, forming biphenyl and nickel(II) chloride.[22] To suppress this side reaction we changed the solvent to toluene and used only one equivalent of zinc for the reduction of $NiCl_2$ at a reaction temperature of 0 °C for the oxidative addition. We obtained the yellow complex *trans*-$[NiCl(Ph)(PPh_3)_2]$ in good yield (72%). This is much better than the overall yield which can be reached via the two-step synthesis, where the first reaction step (reduction of a Ni^{II} precursor) proceeds with yields of about 60% and the second reaction step (oxidative addition) with about 71%.[19]

Table 1. Selected bond lengths (Å) and angles (°) for the structure of the nickel complex in comparison to the higher homologues and the results of a DFT calculation at the B3LYP/6−31G(d) level

	Pt[27]	Pd[23]	Ni	DFT (Ni)
M−Cl	2.459(1)	2.407(1)	2.2201(6)	2.28
M−C71	2.021(4)	2.016(3)	1.887(2)	1.87
M−P1	2.302(1)	2.316(1)	2.2232(5)	2.25
M−P2	2.295(1)	2.324(1)	2.2151(5)	2.24
P1−M−P2	176.19(6)	177.55(2)	169.29(2)	173.5
C1−M−C71	179.0(2)	179.81(8)	173.07(6)	167.2
P1−M−Cl	87.54(5)	89.75(2)	92.35(2)	90.7
P2−M−Cl	88.83(5)	88.57(2)	88.09(2)	88.2
P1−M−C71	92.38(14)	90.29(7)	88.73(5)	90.7
P2−M−C71	91.23(14)	91.38(7)	92.11(5)	91.7
C72−C71−C76	117.7(5)	117.8(3)	117.4(2)	116.8
Ni−C72	–	–	2.824(2)	2.81
Ni−C76	–	–	2.900(2)	2.93

Yellow crystals of the title compound were obtained by slowly adding hexane to a saturated solution of the complex in toluene. Surprisingly, the X-ray structure was not known up to now even though the X-ray structures of the higher congeners were determined some years ago. The molecular structure is shown in Figure 1. Important bond lengths and angles are given in Table 1, together with the corresponding values for *trans*-$[PdCl(Ph)(PPh_3)_2]$,[23,24] *trans*-$[PtCl(Ph)(PPh_3)_2]$[25−27] and data from a B3LYP/6−31G(d) calculation of the nickel complex.

All the structures show a slightly distorted square-planar geometry, where the two triphenylphosphane ligands, the phenyl group and the chloro ligand bind to the metal center

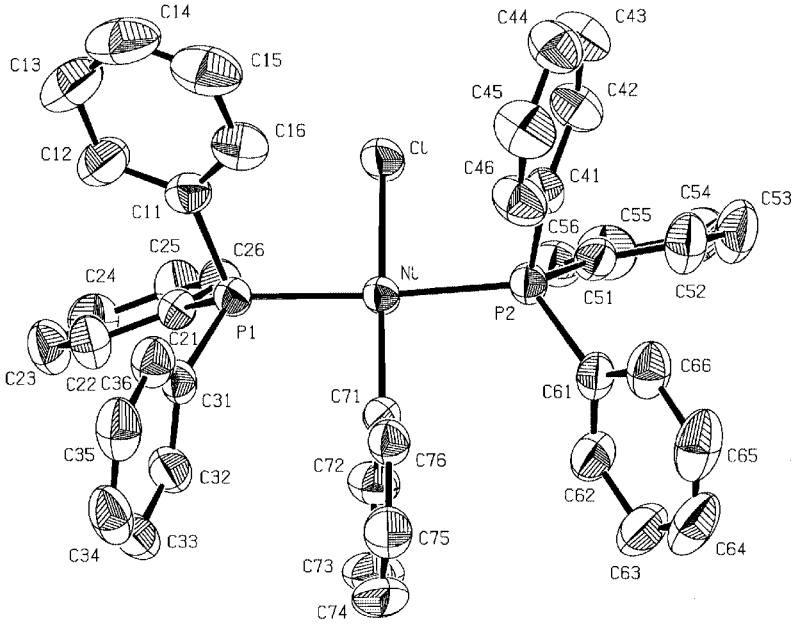


Figure 1. ORTEP representation of *trans*-chloro(phenyl)bis(triphenylphosphane)nickel(II) in the solid state; thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity

in a trans fashion. The trans position of the chloro and phenyl ligands of the nickel compound was already predicted by Hidai et al., based on the frequency of the Ni−Cl stretching vibration in the IR spectra.[19] The nickel-phosphorus distances are 2.2232(5) Å and 2.2151(5) Å, while the nickel-carbon and nickel-chlorine bond lengths are 1.887(2) and 2.2201(6), respectively. The decrease of the metal-ligand bond lengths compared to the higher homologues is within the expected range. The differences between the palladium and platinum structures are small due to relativistic orbital contraction. In all complexes the two metal-phosphorus bonds are slightly asymmetric. The distortion of the square-planar geometry around the metal center can be seen from the P−M−P and C_{71}−M−Cl angles. The largest distortion from the optimum value (180°) is seen in the nickel structure [169.29(2) and 173.07(6)], and the least distortion in the palladium complex [177.55(2) and 179.81(8)°]. The changes in the angles correspond nicely to the changes in the bond lengths and show the steric interaction between all the ligands. In all structures the steric demand of the chlorine atom forces both triphenylphosphane ligands into an almost eclipsed conformation.[23] This conformation seems to be stabilized by π-π interactions between two phenyl rings of the phosphane ligands and the phenyl ring attached to the metal center, which are in a stacked alignment.

The value for the ipso angle around C_{71} (Figure 1) depends on the electronic nature of the substituent: electron-donating groups lead to a decrease of the ipso angle, while electron-deficient groups lead to an increase.[23] In our case the value of the C_{72}−C_{71}−C_{76} angle decreases, even though nickel is more electron donating than palladium. This trend is also apparent from the ^{13}C NMR spectrum, where the signal of the ipso-C atom is observed at a chemical shift of δ = 148.9 ppm compared to δ = 154.0 ppm in the Pd case, indicating a lower deshielding by the metal center.[23,28] The decrease of the ipso angle can be explained by the stronger interaction of the trans chloro ligand, which can be seen in the shorter bond length. This compensates the higher electronegativity of the nickel center.

The density functional theory calculations at the double-ζ level 6−31G(d) show the quality of the electronic structure methods. Even larger transition metal complexes can nowadays be calculated with reasonable effort within acceptable time. All bond lengths are in excellent agreement with the results of the solid-state X-ray structure and show that even metal complexes with two triphenylphosphane ligands and a total of 81 atoms can be treated.

Conclusion

An important precursor for the new class of neutral polymerization catalysts could be synthesized via a new one-pot synthesis with significantly improved yields. The complex *trans*-chloro(phenyl)bis(triphenylphosphane)nickel(II) was structurally characterized by a solid-state single crystal X-ray structure determination. Density functional theory calculations on the complex show that nowadays even first-row transition metals with large ligands can be calculated and that the results are in good agreement with the solid-state structure.

Experimental Section

General Remarks: All manipulations were carried out under Argon using standard Schlenk techniques. Solvents and chlorobenzene were dried and degassed prior to use. NMR spectra were acquired with a JEOL JNM GX 400 spectrometer. Anhydrous nickel(II) chloride and zinc dust were purchased from Merck; triphenylphosphane was purchased from Aldrich. All reagents were used without further purification.

***trans*-Chloro(phenyl)bis(triphenylphosphane)nickel(II):** In a Schlenk flask, anhydrous nickel(II) chloride (1.30 g, 10 mmol), zinc dust (0.66 g, 10 mmol) and triphenylphosphane (11.02 g, 42 mmol) were suspended in DMF (100 mL). The reaction mixture was heated to 50 °C for 2 h and stirred at room temp. for another 15 h after the formation of a brick-red precipitate. The solvent was then evaporated and toluene (200 mL) was added. After adding chlorobenzene (3.10 mL, 25 mmol) the solution was stirred for 3 h at 0 °C. The color changed to a deep brown. After filtration the solution was concentrated to about 70 mL and hexane (100 mL) was added. A yellow solid precipitated which was isolated by filtration, washed twice with hexane (50 mL) and dried for 24 h under high vacuum (5.01 g, 72%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 6.15 (br. s, 2 H, *m*-H of Ni-Ph), 6.24 (br. s, 1 H, *p*-H of Ni-Ph), 6.75 (br. s, 2 H, *o*-H of Ni-Ph), 7.28 (br. s, 12 H, *m*-H of PPh_3), 7.37 (br. s, 6 H, *p*-H of PPh_3), 7.57 (br. s, 12 H, *o*-H of PPh_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ = 120.7 (s, *m*-C of Ph), 126.4 (s, *p*-C of Ni-Ph), 127.7 (t, $J_{C,P}$ = 5.0 Hz, *m*-C of PPh_3), 129.5 (s, *p*-C of PPh_3), 131.8 (t, $J_{C,P}$ = 21.9 Hz, *i*-C of PPh_3), 134.5 (t, $J_{C,P}$ = 5.8 Hz, *o*-C of PPh_3), 137.4 (t, $J_{C,P}$ = 4.2 Hz, *o*-C of Ni-Ph), 148.9 (s, i-C of Ni-Ph) ppm.[29] ^{31}P NMR (161.8 MHz, CD_2Cl_2, 25 °C): δ = 21.6. $C_{42}H_{35}ClNiP_2$ (695.78): calcd. C 72.50, H 5.07; found C 71.88, H 5.04.

Computational Details: The density functional/Hartree−Fock hybrid model Becke3LYP,[30−33] as implemented in Gaussian 98,[34] was used together with the double-ζ basis set 6−31G(d). The geometry was fully optimized.

X-ray Crystallographic Study: Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 2. Crystals suitable for an X-ray structure determination were obtained from toluene/hexane. Preliminary examination and data collection were carried out on a kappa-CCD device (Nonius) at the window of a rotating anode (NONIUS FR591; 50 kV; 60 mA; 3.0 kW) and graphite monochromated Mo-K_α radiation (λ = 0.71073 Å).[35] The unit-cell parameters were obtained by full-matrix least-squares refinement of 6718 reflections. Data collection was performed at 293 K with an exposure time of 20 s per frame (7 sets; 980 frames; phi and omega scans; 1.0° scan-width). A total of 74222 reflections were integrated. Raw data were corrected for Lorentz and polarization effects. If necessary, corrections for absorption and decay effects were applied during the scaling procedure.[36] After merging, a sum of 6378 independent reflections remained, and were used for all calculations. The structure was solved by a combination of direct methods[37] and difference-

Fourier syntheses.[38] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the final difference-Fourier maps and refined with isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_0^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at a maximum shift/err of less than 0.001. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography*. All other calculations (including ORTEP graphics) were done with the program PLATON.[39]

CCDC-195346 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data for *trans*-chloro(phenyl)bis(triphenylphosphane)nickel(II)

Chem. formula	$C_{42}H_{35}ClNiP_2$
Mol. wt.	695.78
Color/shape	Yellow/needle
Cryst size (mm)	0.46 × 0.25 × 0.25
Cryst syst	Monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	15.7865(1)
b (Å)	11.9167(1)
c (Å)	20.0396(1)
β (deg)	112.2954(3)
V (Å^3)	3488.07(4)
Z	4
T (K)	293
$\rho_{calcd.}$ (g cm^{-3})	1.325
μ (mm^{-1})	0.754
F_{000}	1448
Θ range (deg)	1.39−25.34
Data collected (h,k,l)	±19, ±14, ±24
No. of reflns collected	74222
No. of indep reflns/R_{int}	6378 (all)/0.041
No. of obsd reflns [$I > 2\sigma(I)$]	5367 (obsd)
No. of params refined	555
R1 (obsd/all)	0.0296/0.0396
wR2 (obsd/all)	0.0737/0.0783
GOF (obsd/all)	1.039/1.039
Max/min $\Delta\rho$ (e·Å^{-3})	+0.28/−0.22

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