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Methylnickel compounds containing 2-phosphinylethanolato ligands – Syntheses, properties, and ethene coupling reactions

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Dedicated to Professor H. Schmidbaur.

Abstract

Combining dimethylphosphinylethanols HO(R¹R²)CCH₂PMe₂ (1: R¹ = R² = C₆H₅; **2**: R¹ = R² = 4-OMe-C₆H₄; **5**: R¹ = R² = 4-OMe-C₆H₄) with methyl(methoxo)(trimethylphosphine)nickel gave mononuclear methyl(trimethylphosphine)nickel(chelate) compounds 7–9. Ligand **6** (R¹ = Me, R² = 4-OMe-C₆H₅) afforded a dinuclear methylnickel compound **14**. By reacting (TMEDA)lithium-dimethylphosphinylmethanide with ketones O==C(R¹R²), the dimethylphosphinylethanols HO(R¹R²)CCH₂PMe₂ (**3**: R¹R² = 9-fluorenyl; **4**: R¹ = H, R² = C₆H₅) were synthesized as prechelate ligands. Under otherwise similar conditions, the fluorenyl substituted anion in **3** gave rise to a mononuclear complex **10** which was found to act as a source of trimethylphosphine forming dinuclear **11** and at the same time to act as an acceptor of trimethylphosphine forming pentacoordinate **10** · PMe₃. Ni(COD)(PMe₃)₂ was used as a scavenger of PMe₃ in converting **8** or **9** to the dinuclear methylnickel compounds **12** and **13**, respectively. Modifying the P,O chelating unit of a methyl nickel compound by introducing 2-phosphinylethanolato ligands leads to novel single-component catalysts for ethene oligomerization showing moderate reactivity and thermal stability. © 2005 Published by Elsevier B.V.

Keywords: (2-Phosphinyl)ethanolates; Methylnickel compounds; Solution dynamics; Ethene coupling reactions

1. Introduction

Among the late transition-metal compounds with bidentate (P,O) ligands effecting the oligomerization of ethene, complexes of nickel have been extensively studied [1]. In catalytically active compounds of nickel(II), these monoanionic ligands form five- or six-membered metallocycles. When equipped with alkyl or hydride nickel functions, the molecular complexes are regarded as models for the active species in olefin coupling reactions [2–6].

* Corresponding author. *E-mail address:* hfklein@ac.chemie.tu-darmstadt.de (H.-F. Klein). In order to shed more light on the mechanism of the C,Ccoupling reaction, we set out to isolate and characterize some catalyst precursors containing a non-conjugated backbone of a P,O-metallacycle and showing increased bond flexibility. In this contribution, we describe some novel (2-dimethylphosphinylethanolato)methylnickel complexes with supporting trimethylphosphine and some dinuclear methylnickel complexes containing Obridging 2-dialkylphosphinylethanolato ligands without an auxiliary phosphine ligand. The molecular structure of the latter complex is presented and the catalytic properties in C,C-coupling reactions of ethene under moderate conditions are discussed.

2. Experimental

2.1. General procedures and materials

All air-sensitive and volatile materials were handled by standard vacuum techniques and kept under argon. The chemicals (Merck/Schuchardt) were used as purchased, but liquids were degassed in vacuo by a freeze-thaw procedure. Literature methods were followed in the preparation of LiCH₂PMe₂ [16], LiCH₂P- $Me_2 \cdot TMEDA$ [7], [NiMe(OMe)PMe_3]₂ [11], and Ni(COD)(PMe₃)₂ [17]. Microanalyses were carried out by Kolbe, Microanalytical Laboratory, Mülheim/Ruhr, FRG. Melting points or decomposition temperatures were determined in sealed glass capillaries on a Büchi Model 510 apparatus and are uncorrected. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr windows, were recorded on a Bruker Model FRA 106 spectrophotometer. NMR spectra (300 and 75 MHz for ¹H and ¹³C, respectively) were recorded with Bruker ARX-300, ³¹P NMR spectra (81 MHz) with a Bruker AM-200 instrument. ¹³C and ³¹P resonances were obtained with broad-band proton decoupling.

2.2. Procedures

2.2.1. Synthesis of 2-dimethylphosphinyl-1,1diphenylethanol (1)

Upon a sample of 2.65 g of LiCH₂PMe₂ · TMEDA (13.5 mmol) at -78 °C, 60 ml of pentane was condensed in vacuo, and 2.45 g of benzophenone (13.5 mmol) in 50 ml of pentane was added rapidly under stirring. The blue solution was stirred for 1 h and was then taken to dryness in vacuo. The residue was dissolved in 50 ml of THF containing 3 ml of water and kept stirring overnight. The volatiles were removed in vacuo and the residue was extracted with diethyl ether affording colorless crystals of 1 (2.58 g, 74%), m.p. 84–85 °C.

Anal. Calc. for $C_{16}H_{19}OP$ (258.2): C, 74.43; H, 7.36; P, 12.01. Found: C, 75.23; H, 7.10; P, 11.76%.

IR (Nujol mull, 4000–1700 cm⁻¹): 3451 m v(OH). ¹H NMR (200 MHz, THF- d_8 , 298 K): δ 0.84 (d, 6H, ²J(PH) = 3.6 Hz, PCH₃), 2.42 (d, 2H, ²J(PH) = 2.6 Hz, PCH₂), 4.71 (s, 1H, OH), 7.08–7.26 (m, 6H, 3-H, 4-H), 7.43–7.52 (m, 4H, 2-H). ¹³C NMR (75 MHz, THF- d_8 , 298 K): δ 15.9 (d, ¹J(PC) = 14.3 Hz, PCH₃), 49.2 (d, ¹J(PC) = 16.3 Hz, PCH₂), 77.8 (d, ²J(PC) = 10.6 Hz, COH), 126.9 (4-C), 128.3 (3-C), 128.6 (2-C), 149.9 (1-C). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ – 54.0 (s).

2.2.2. Synthesis of 2-dimethylphosphinyl-1,1di(4-methoxyphenyl)ethanol (2)

To a sample of 0.85 g of LiCH₂PMe₂ (10.4 mmol) in 50 ml of THF at -78 °C, 2.58 g of 4,4'-dimethoxybenzo-

phenone (10.6 mmol) was added under stirring to give a blue solution. After 1 h, 8 ml of water was added and the mixture was stirred at 20 °C for 14 h. The volatiles were removed in vacuo, and the yellow residue was extracted with 70 ml of diethyl ether. Crystallization at -25 °C afforded colorless crystals of **2** (2.34 g, 71%), m.p. 103–104 °C.

Anal. Calc. for C₁₈H₂₃O₃P (318.4): C, 67.91; H, 7.28; P, 9.73. Found: C, 68.03; H, 7.19; P, 9.82%.

IR (Nujol mull, 4000–1700 cm⁻¹): 3291m v(OH). ¹H NMR (200 MHz, THF- d_8 , 298 K): δ 0.83 (d, 6H, ²J(PH) = 3.6 Hz, PCH₃), 2.36 (d, 2H, ²J(PH) = 2.6 Hz, PCH₂), 3.71 (s, 3H, OCH₃), 4.71 (d, 1H, ⁴J(PH) = 7 Hz, OH), 6.72–6.79 (m, 4H, 3,5-H), 7.28– 7.35 (m, 4H, 2,6-H). ¹³C NMR (75 MHz, THF- d_8 , 298 K): δ 13.9 (d, ¹J(PC) = 10.6 Hz, PCH₃), 48.8 (d, ¹J(PC) = 31.8 Hz, PCH₂), 55.1 (s, OCH₃), 75.4 (d, ²J(PC) = 10.0 Hz, COH), 111.4 (4-C), 126.4 (2-C), 129.9 (3-C), 157.4 (1-C). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ –54.9 (s).

2.2.3. Synthesis of (9-dimethylphosphinyl)methylenfluorenol (3)

To a sample of 1.00 g of LiCH₂PMe₂ · TMEDA (12.2 mmol) in 30 ml of THF at -20 °C, 2.20 g of 9-fluorenone (12.2 mmol) was added rapidly under stirring in 40 ml of THF. The mixture was allowed to warm up and at 20 °C formed a solution with a green fluorescence. After quenching with 15 ml of water and stirring for 14 h, the volatiles were removed in vacuo and the yellow residue was dried at 40 °C in vacuo for 2 h. Extraction with 30 ml of toluene and crystallization at 4 °C afforded colorless crystals of 3 (1.93 g, 62%), m.p. 103–104 °C.

Anal. Calc. for C₁₆H₁₉OP (258.2): C, 75.02; H, 6.64; P, 12.09. Found: C, 75.36; H, 6.75; P, 11.87%.

IR (Nujol mull, 4000–1700 cm⁻¹): 3298m v(OH). ¹H NMR (200 MHz, THF- d_8 , 298 K): δ 0.84 (d, 6H, ²*J*(PH) = 3.3 Hz, PCH₃), 2.09 (d, 2H, ²*J*(PH) = 2.7 Hz, PCH₂), 4.73 (s, 1H, OH), 7.23–7.79 (m, 4H, 3,4-H), 7.58–7.68 (m, 4H, 2,5-H). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ –54.4 (s).

2.2.4. Synthesis of 2-dimethylphosphinyl-1-phenylethanol(4)

To a sample of 1.05 g of benzaldehyde (9.9 mmol) in 20 ml of pentane at 20 °C, 1.95 g of LiCH₂PMe₂ · TME-DA (9.9 mmol) was added dropwise in 40 ml of pentane. After quenching with 4 ml of water, the volatiles were removed in vacuo and the white residue was dried at 40 °C in vacuo for 1 h. Extraction with pentane and crystallization at 4 °C afforded a colorless oil of **4**. Crude yield 1.67 g (99%).

IR (Nujol mull, 4000–1700 cm⁻¹): 3361m v(OH). ¹H NMR (300 MHz, THF- d_8 , 298 K): δ 0.83 (d, 6H, ²J(PH) = 3.0 Hz, PCH₃), 1.02 (d, 2H, ²J(PH) = 2.8 Hz, PCH₂), 5.36 (s, br, 1H, OH), 7.13–7.37 (m, 5H, C₆H₅). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ – 55.0 (s).

2.2.5. Synthesis of 2-dimethylphosphinyl-1,1di(4-N,N'-dimethylaminophenyl)ethanol (5)

To a sample of 2.07 g of LiCH₂PMe₂ (10.5 mmol) in 50 ml of diethyl ether at -78 °C, 2.82 g of 4,4'-bis(dimethylamino)benzophenone (10.5 mmol) was added under stirring to give a blue solution which rapidly turned colorless. After 1 h, 3 ml of water was added and the mixture was stirred at 20 °C for 14 h. The volatiles were removed in vacuo and the yellow residue was extracted with 70 ml of diethyl ether. Crystallization at -25 °C afforded colorless crystals of **5**. (3.00 g, 83%) m.p. 112–114 °C.

Anal. Calc. for $C_{20}H_{29}ON_2P$ (344.4): C, 69.74; H, 8.49; N, 8.13; P, 8.99. Found: C, 70.06; H, 8.19; N, 8.59; P, 9.50%.

IR (Nujol mull, 4000–1700 cm⁻¹): 3298m ν (OH). ¹H NMR (200 MHz, THF- d_8 , 298 K): δ 0.80 (s, 6H, PCH₃), 2.31 (s, 2H, PCH₂), 2.86 (s, 12H, NCH₃), 4.15 (s, 1H, OH), 6.54–6.68 (m, 4H, 3,5-H), 7.19–7.25 (m, 4 H, 2,6-H). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ –55.0 (s).

2.2.6. Synthesis of 2-dimethylphosphinyl-1-methyl-1-(4-methoxyphenyl)ethanol (6)

To a sample of 1.49 g of (4-methoxy)acetophenone (9.9 mmol) in 20 ml of pentane at 20 °C, 1.95 g of LiCH₂PMe₂ · TMEDA (9.9 mmol) was added dropwise in 40 ml of pentane. After 2 h, 8 ml of water was added and the mixture was stirred at 20 °C for 2 h. The volatiles were removed in vacuo at 40 °C and the white residue was extracted with 70 ml of pentane to give 1.95 g of a colorless oil (crude yield 99%). Distillation at 131–133 °C/0.3 mbar afforded a colorless viscous liquid of **2**. Yield 1.78 g (85%).

IR (Nujol mull, 4000–1700 cm⁻¹): 3361m v(OH). ¹H NMR (200 MHz, acetone- d_6 , 298 K): δ 0.79 (d, 3H, ²*J*(PH) = 2.9 Hz, PCH₃), 0.82 (d, 3H, ²*J*(PH) = 3.1 Hz, PCH₃), 1.63 (s, 3H, CH₃), 1.95 (d, 2H, ²*J*(PH) = 2.9 Hz, PCH₂), 3.75 (s, 3H, OCH₃), 4.21 (s, br, 1H, OH), 6.82–6.87 (m, 2H, 3,5-*H*), 7.39–7.44 (m, 2H, 2,6-*H*). ³¹P NMR (81 MHz, acetone- d_6 , 298 K): δ –54.0 (s).

2.2.7. Synthesis of (2-dimethylphosphinyl-1,1diphenylethanolato)-[O,P]-methyl-(trimethylphosphine)nickel (7)

A brown solution of 0.44 g of $[NiMe(OMe)PMe_3]_2$ (1.5 mmol) in 30 ml of THF at -78 °C when combined with 0.88 g of 1 (3.0 mmol) under stirring turned rapidly to yellow. The mixture was warmed to 20 °C and evaporated to give an orange oil, which was recrystallized from pentane at 4 °C to give bunches of light brown needles of 7 (0.67 g, 55%), m.p. 90–92 °C (dec.). Anal. Calc. for $C_{20}H_{30}NiOP_2$ (407.1): C, 59.01; H, 7.43; P, 15.22. Found: C, 60.15; H, 7.12; P, 15.05%.

¹H NMR (200 MHz, THF- d_8 , 298 K): δ –1.22 (s, 3 H, NiCH₃), 0.97 (s, br, 6H, PCH₃), 1.37 (s, br, 9H, PCH₃), 2.57 (s, br, 2H, PCH₂), 6.98–7.16 (m, 6H, 3,4,5-H), 7.65–7.69 (m, 4H, 2,6-H). ¹³C NMR (75 MHz, THF- d_8 , 298 K): δ 9.4 (d, ¹J(PC) = 20.8 Hz, PCH₃), 10.6 (d, ¹J(PC) = 18.9 Hz, PCH₂), 47.2 (d, ¹J(PC) = 29.3 Hz, PCH₃), 83.6 (CO), 123.7 (4-C), 125.5 (2-C), 125.7 (3-C), 154.3 (1-C). ³¹P NMR (81 MHz, THF- d_8 , 233 K): δ –7.0 (m, 0.95 P, trans-PMe₃), 3.0 (d, 0.05 P, ²J(PP) = 18 Hz, cis-PMe₃), 15.0 (d, 0.05 P, ²J(PP) = 18 Hz, cis-PMe₂), 22.0 (m, 0.95 P, trans-PMe₂); 193 K: δ –5.0 (d, 0.97 P, ²J(PP) = 338 Hz, trans-PMe₃), 4.0 (d, 0.03 P, ²J(PP) = 19 Hz, cis-PMe₃), 17.0 (d, 0.03 P, ²J(PP) = 19 Hz, cis-PMe₂), 23.0 (d, 0.97 P, ²J(PP) = 338 Hz, trans-PMe₂).

2.2.8. Synthesis of [2-dimethylphosphinyl-1,1di(4-methoxyphenyl)ethanolato]-[O,P]methyl(trimethylphosphine)nickel (8)

A brown solution of 0.41 g of $[NiMe(OMe)PMe_3]_2$ (1.1 mmol) in 30 ml of THF when combined with 0.72 g of 2 (2.3 mmol) under stirring at 20 °C attained a lighter color. The volatiles were evaporated to give a yellow residue which was recrystallized from pentane at 4 °C to afford as a first fraction colorless crystals of unreacted 2 (IR), which were removed by decantation. From the mother liquor, a second fraction of light brown crystals of **8** was obtained (0.73 g, 69%), m.p. 99–101 °C (dec.).

Anal. Calc. for $C_{22}H_{34}NiO_3P_2$ (467.1): C, 56.57; H, 7.33; P, 13.26. Found: C, 56.55; H, 7.33; P, 13.29%.

¹H NMR (200 MHz, THF- d_8 , 298 K): δ –1.25 (s, 3 H, NiC H_3), 0.97 (s, 6H, PC H_3), 1.34 (s, 9H, PC H_3), 2.50 (s, 2H, PC H_2), 3.67 (s, 3H, OC H_3), 6.64 (m, 4H, 3,5-H), 7.53 (m, 4H, 2,6-H). ¹³C NMR (75 MHz, THF- d_8 , 298 K): δ 11.3 (d, ¹J(PC) = 21.5 Hz, PC H_3), 12.6 (d, ¹J(PC) = 18.0 Hz, PC H_2), 48.8 (d, ¹J(PC) = 31.8 Hz, PC H_3), 55.1 (OC H_3), 112.9 (CO), 128.1 (4-C), 128.4 (2-C), 147.5 (3-C), 158.3 (1-C). ³¹P NMR (81 MHz, THF- d_8) 233 K: δ –5.0 (m, 0.96 P, trans-PMe₃), 3.0 (d, 0.04 P, ² $J_{P,P}$ = 18 Hz, cis-PMe₃), 16.0 (d, 0.04 P, ² $J_{P,P}$ = 18 Hz, cis-PMe₂), 2.0 (m, 0.96 P, trans-PMe₃), 4.0 (d, 0.04 P, ²J(PP) = 20 Hz, cis-PMe₃), 16.0 (d, 0.04 P, ²J(PP) = 20 Hz, cis-PMe₂), 22.0 (d, 0.96 P, ²J(PP) = 339 Hz, trans-PMe₂).

2.2.9. Synthesis of [2-dimethylphosphinyl-1,1-

di(4-*N*,*N*-*dimethylaminophenyl*)*ethanolato*]-[*O*,*P*]*methyl*(*trimethylphosphine*)*nickel* (**9**)

Upon samples of 0.51 g of $[NiMe(OMe)PMe_3]_2$ (1.3 mmol) and 0.81 g of 5 (2.6 mmol), respectively, 30 ml of THF was condensed in vacuo. After warming to 20 °C, the mixture was stirred for 1 h. The volatiles were

then evaporated and the yellow residue was extracted with pentane at 50 °C. Crystallization from pentane at 20 °C gave yellow microcrystals of **9** (0.56 g, 44%), m.p. 140–143 °C (dec.).

Anal. Calc. for C₂₄H₄₀N₂NiOP₂ (492.2): C, 58.56; H, 8.18; N, 5.69; P, 12.59. Found: C 60.79; H, 7.73; N, 5.85; P, 13.05%.

¹H NMR (200 MHz, THF- d_8 , 298 K): δ –1.27 (s, br, 3H, NiC H_3), 0.92 (s, br, 6H, PC H_3), 1.33 (s, 9H, PC H_3), 2.47 (s, 2H, PC H_2), 2.81 (s, 12H, NC H_3), 6.51–6.55 (m, 4H, 3,5-H), 7.41–7.45 (m, 4H, 2,6-H). ³¹P NMR (81 MHz, THF- d_8) 233 K: δ –15.0 (s, 0.06 P, PMe₃), -6.0 (m, 0.94 P, *trans-P*Me₃), 2.0 (d, 0.03 P, ²J(PP) = 223 Hz, *cis-P*Me₂), 22.0 (m, 0.94 P, *trans-P*Me₂); 193 K: δ –14.0 (s, 0.17 P), -5.0 (d, 0.97 P, ²J(PP) = 342 Hz, *trans-P*Me₃), 4.0 (m, 0.03 P, *cis-P*Me₃), 17.0 (m, 0.03 P, *cis-P*Me₂), 23.0 (d, 0.97 P, ²J(PP) = 342 Hz, *trans-P*Me₂), 23.0 (d, 0.97 P, ²J(PP) = 342 Hz, *trans-P*Me₂), 23.0 (d, 0.97 P, ²J(PP) = 342 Hz, *trans-P*Me₂).

2.2.10. Synthesis of [9-dimethylphosphinylmethylen-9fluorenolato]-[O,P]-methyl(trimethylphosphine)nickel (11)

A brown solution of 0.33 g of $[NiMe(OMe)PMe_3]_2$ (0.9 mmol) in 50 ml of THF at 20 °C was combined with 0.58 g of **3** (2.3 mmol) and stirred for 3 h. The mixture was evaporated to afford a yellow solid which was washed with pentane and recrystallized from toluene to give yellow microcrystals of **7** (0.55 g, 76%), m.p. 82–84 °C (dec.).

Anal. Calc. for C₂₀H₂₈NiOP₂ (405.1): C, 59.32; H, 6.92; P, 15.30. Found: C, 58.29; H, 6.65; P, 15.68%.

¹H NMR (300 MHz, THF- d_8 , 298 K): δ -2.44 (d, 0.57H, ${}^{3}J(PH) = 5.1$ Hz, NiCH₃), -1.16 (d, 3H, ${}^{3}J(PH) = 7.1$ Hz, NiCH₃), 0.85 (d, 9H, ${}^{2}J(PH) = 5.0$ Hz, PCH₃), 1.27 (d, 6H, ${}^{2}J(PH) = 6.5$ Hz, PCH₃), 1.93 (d, 2H, ${}^{2}J(PH) = 7.8$ Hz, PCH₂), 6.96–7.03 (m, 4H, 3,4,5,6-H), 7.27-7.38 (m, 2H, 2,7-H), 7.86-7.89 (m, 2H, 1,8-*H*). ¹³C NMR (75 MHz, THF- d_8 , 298 K): δ 24.6 (s, NiCH₃), 12.1 (d, ${}^{1}J(PC) = 16.2$ Hz, PCH₃), $(d, {}^{1}J(PC) = 22.1$ P*C*H₃), 13.2 Hz, 48.0 (d, $^{1}J(PC) = 25.4$ Hz, PCH₂), 91.5 (CO), 120.8 (5-C), 123.9 (2-C), 127.4 (3-C), 157.2 (4-C). ³¹P NMR (81 MHz, THF- d_8 , 193 K): $\delta -11.0$ (s, PMe₃), 20 (s, PMe₂).

2.2.11. Synthesis of trans-bis {µ-(2-dimethylphosphinyl-1,1-diphenylethanolato[O,P])methylnickel} (12)

Samples of 0.4 g of 7 (1.20 mmol) and 0.20 g of Ni(COD)(PMe₃)₂ (2.86 mmol) were combined in 60 ml of diethyl ether at 20 °C to give a yellow solution, which after 2 h attained a brown color. The volatiles were removed in vacuo, and the brown residue was dried in vacuo at 20 °C for 1 h and washed with pentane. The solid was then dissolved in THF, the orange solution was filtered and kept at 4 °C to yield orange prisms of 7 (0.21 g, 53%), m.p. 196–197 °C.

Anal. Calc. for $C_{17}H_{21}NiOP$ (331.1): C, 61.69; H, 6.39; P, 9.36. Found: C, 61.52; H, 6.40; P, 8.55%.

¹H NMR (200 MHz, THF- d_8 , 298 K): δ –2.27 (d, 3 H, ³*J*(PH) = 5.0 Hz, NiCH₃), 0.68 (d, 6H, ²*J*(PH) = 10.4 Hz, PCH₃), 2.33 (d, 2H, ²*J*(PH) = 9.7 Hz, PCH₂), 7.08–7.21 (m, 2H, 4-*H*), 7.31–7.49 (m, 3,5-*H*), 8.27–8.31 (m, 4H, 2,6-*H*). ¹³C{¹H} NMR (75 MHz, THF- d_8 , 298 K): δ –21.5 (d, ¹*J*(PC) = 43.9 Hz, NiCH₃), 11.6 (d, ¹*J*(PC) = 30.6 Hz, PCH₃), 52.5 (d, ¹*J*(PC) = 26.7 Hz, PCH₂), 81.7 (C–O), 126.6 (4-C), 127.4 (2-C), 129.3 (3-C), 149.4 (1-C). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ 20.0 (s, PCH₃).

2.2.12. Synthesis of trans-bis {μ-(2-dimethylphosphinyl-1,1-di(4-methoxyphenyl)ethanolato-[O,P]) methylnickel} (13)

Method (a): A solution of 0.24 g of **8** (0.50 mmol) in 30 ml of cyclopentene was held at 20 °C for 2 h. The solution was filtered and and kept at 4 °C to afford yellow crystals of **13** suitable for X-ray diffraction. Yield 0.10 g (51%). Method (b): 0.17 g of **8** (0.36 mmol) and 0.12 g of Ni(COD)(PMe₃)₂ (0.37 mmol) were combined in 30 ml of diethyl ether at 20 °C to give a yellow solution which after 2 h was filtered and kept at 4 °C to yield a yellow solid of **13** (0.90 g, 64%), m.p. 193– 195 °C.

Anal. Calc. for C₁₉H₂₅NiO₃P (391.1): C, 58.35; H, 6.44; Ni, 15.01. Found: C, 58.35; H, 6.40; Ni, 14.88%.

¹H NMR (200 MHz, THF- d_8 , 298 K): δ –2.25 (d, 3H, ³*J*(PH) = 5.0 Hz, NiCH₃), 0.69 (d, 6H, ²*J*(PH) = 10.4 Hz, PCH₃), 2.27 (d, 2H, ²*J*(PH) = 9.7 Hz, PCH₂), 3.80 (s, 6H, OCH₃), 6.88–6.93 (m, 4H, 3,5-*H*), 8.14–8.19 (m, 4H, 2,6-*H*). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ 19.0 (s, PCH₃).

2.2.13. Synthesis of trans-bis {μ-(2-dimethylphosphinyl-1methyl-1-(4-methoxyphenyl)ethanolato)-[O,P]methylnickel} (14)

Upon 0.57 g of [NiMe(OMe)PMe₃]₂ (1.6 mmol) and 0.63 g of **6** (3.2 mmol), 60 ml of THF was condensed in vacuo. After warming to 20 °C, the mixture was stirred for 2 h. The volatiles were then evaporated and the yellow residue was extracted with pentane at 50 °C. From pentane at -30 °C an orange oil was obtained, which was dissolved in diethyl ether to give at -30 °C yellow microcrystals of **14** (0.69 g, 62%), m.p. 189–193 °C.

Anal Calc. for C₁₃H₂₅NiO₄P (335.0): C, 46.61; H, 7.52; P 9.25. Found: C, 47.39; H, 6.57; P, 9.36%.

¹H NMR (200 MHz, THF- d_8 , 298 K): δ –1.74 (d, 3 H, ³J(PH) = 5.4 Hz, NiCH₃), –1.69 (d, 3H, ³J(PH) = 5.2 Hz, NiCH₃), 0.59 (d, 3H, ²J(PH) = 10.4 Hz, PCH₃), 0.68 (d, 3H, ²J(PH) = 10.8 Hz, PCH₃), 1.09 (d, 3H, ²J(PH) = 8.3 Hz, PCH₃), 1.10 (d, 3H, ²J(PH) = 7.9 Hz, PCH₃), 1.48 (s, 3H, CCH₃), 1.62 (s, 3H, CCH₃), 1.78–1.93 (m, 4H, PCH₂), 3.78 (s, 3 H, OCH₃), 3.82 (s, 3H, OCH₃), 6.87–7.01 (m, 4H, 3,5-*H*), 8.24–8.45 (m, 4H, 2,6-*H*). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ 20.0 (s, *P*Me₂), 20.1 (s, *P*Me₂).

2.2.14. Synthesis of (2-isopropyl(phenyl)phosphinyl)-4,6-di-tert-butylphenolato(methyl)nickel (15)

Upon 0.46 g of [NiMe(OMe)PMe₃]₂ (1.3 mmol) and 0.90 g of (2-isopropyl(phenyl)phosphinyl)-4,6-di-*tert*butylphenol (2.54 mmol), 60 ml of THF was condensed in vacuo. After warming to 20 °C, the mixture turned orange and was stirred for 12 h. The volatiles were then evaporated and the yellow residue was extracted with pentane at 50 °C. From pentane at -30 °C yellow microcrystals were obtained. The mother liquor was evaporated to dryness to give a yellow solid, which was identical with the first fraction (IR). Combined yield 0.94 g of **15** (69%), m.p. 88–90 °C.

Anal. Calc. for C₂₇H₄₄NiOP₂ (505.3): C, 64.18; H, 8.77; P, 12.26. Found: C, 63.64; H, 8.55; P, 12.56%.

¹H NMR (200 MHz, THF- d_8 , 298 K): δ -0.93 (d, 3 H, ${}^{3}J(PH) = 1.8$ Hz, NiCH₃), 0.98–1.24 (m, 12H, CCH₃), 1.30–1.45 (m, 21H, CCH₃, PCH₃), 2.61–2.72 (m, 1H, CH), 6.90-6.95 (m, 1H, 3-H), 7.13 (d, 1H, ${}^{3}J(PH) = 2.4$ Hz, 5-H), 7.38–7.40 (m, 3H, 9,10-H), 7.59–7.68 (m, 2H, 8-H). ${}^{13}C$ NMR (75 MHz, THF- d_8 , 298 K): δ -22.2 (m, NiCH₃), 10.8 (d, ¹J(PC) = 22.2 Hz, PCH₃), 16.0 (s, CH₃), 17.6 (s, CH₃), 24,2 (d, $^{1}J(PC) = 37.2$ Hz, PCMe), 27.8, 30.3 (all CCH₃), 32.6, 33.8 (all CMe₃), 113.6 (2-C), 124.9 (5-C), 125.2 (3-C), $127.2 \text{ (d, }^{2}J(\text{PC}) = 9.0 \text{ Hz}, 8-C), 128.1 \text{ (10-C)}, 131.2 \text{ (d, }$ ${}^{3}J(PC) = 9.0$ Hz, 7-C), 131.9 (6-C), 133.1 (4-C), 135.6 $(d, {}^{3}J(PC) = 9.0 \text{ Hz}, 9-C), 174.3 (d, {}^{2}J(PC) = 23.4 \text{ Hz},$ 1-C). ³¹P NMR (81 MHz, THF- d_8 , 298 K): δ -8.0 $(d_{trans}^{2}J(PP) = 310 \text{ Hz}, PMe_{3}), 0.3 (d_{trans}^{2}J(PP) = 24$ Hz, PMe_3), 40.0 (d, $_{trans}^2 J(PP) = 308$ Hz, PPh), 40.5 $(d, cis^2 J(PP) = 24 \text{ Hz}, PPh).$

2.2.15. Ethene oligomerization/polymerization tests

Method (a): A 75 ml stainless steel autoclave equipped with magnetic stirring was charged with 0.1 mmol of the nickel complexes 7, 10, 15, or 16 in 12 ml of toluene under argon. Ethene pressure was applied and the reactor was closed. After a time of precatalysis extending from 30 to 40 min the drop of pressure was recorded. Method (b): A 500 ml stainless steel autoclave was charged with 130 ml of toluene under 70 bar of ethene. 0.5 mmol of the nickel complexes 8 or 9 in 5 ml of toluene was added under pressure, which was kept at 70 bar by continuous feeding of ethene until showing no further uptake.

2.2.16. X-ray crystal measurements

Crystal structure analyses: A summary of crystal data and refinement for **13** is given in Table 1. A yellow specimen was sealed under argon in a glass capillary and mounted on a Siemens P4 diffractometer. The data sets

Table 1					
Crystal	data	for	aamnaund	12	

Crystal data for compound 13	
Formula	C ₁₉ H ₂₅ NiO ₃ P
Molecular mass	391.1
Crystal size (mm)	$0.11 \times 0.05 \times 0.04$
Crystal system	monoclinic
Space group	$C2_1/c$ (Nr.15)
a (Å)	1.39600(4)
b (Å)	1.250100(2)
<i>c</i> (Å)	1.631000(3)
β (°)	105.4030(1)
$V(Å^3)$	3.761521(10)
Ζ	8
$D_{\text{calc}} (\text{g cm}^{-3})$	1.039
μ (Mo K α) (mm ⁻¹)	0.812
Temperature (K)	293(2)
Data collection range (°)	$4.3 \leqslant 2\Theta \leqslant 55$
Limiting indices	$-18 \leqslant h \leqslant 18, \ -12 \leqslant k \leqslant 12,$
	$-15 \leqslant l \leqslant 15$
Number of reflections measured	1746
Number of unique data	1746
Parameters	217
Goodness-of-fit on F^2	1.015
$R_1 \ (I \ge 2\sigma(I))$	0.0593
wR_2 (all data)	0.1347

were collected (ω -scan) using graphite-monochromated Mo K α radiation; Lorentz polarization corrections but no absorption corrections were applied. The structure was solved by Patterson and conventional Fourier methods. All non-hydrogen atoms were treated anisotropically, hydrogen atoms were treated with a riding model in idealized positions.

3. Results and discussion

3.1. Synthesis of (2-dimethylphosphinyl)ethanols

A synthetic route as given by Lappert et al. [7] was modified to generate (2-dimethylphosphinyl)ethanols according to Eq. (1)

$$Me_{2}PCH_{2}Li \bigvee_{Me_{2}}^{N} \underbrace{\begin{array}{c} 1. \ O=CR'R^{2} \\ 2. \ H_{2}O \\ Me_{2} \end{array}}_{Me_{2}} R_{Me_{2}}^{1} R_{Me_{2}}^{2} OH$$

$$P_{Me_{2}}$$

$$1 \quad R^{1} = R^{2} = C_{6}H_{5}$$

$$2 \quad R^{1} = R^{2} = 4 - OMe - C_{6}H_{4}$$

$$3 \quad R^{1} + R^{2} = 9 - fluorenyl$$

$$4 \quad R^{1} = H, R^{2} = C_{6}H_{5}$$

$$5 \quad R^{1} = R^{2} = 4 - OMe_{2} - C_{6}H_{4}$$

$$6 \quad R^{1} = Me, R^{2} = 4 - OMe_{2} - C_{6}H_{4}$$

$$(1)$$

The products 1-3 and 5 were isolated as white or yellowish crystals which are air-stable for more than two hours, while **4** and **6** were obtained as colorless oils. All materials are freely soluble in diethyl ether or toluene, and their infrared and NMR spectra contain all features expected from known data [8]. Strong infrared bands between 3291 (**2**) and 3661 cm⁻¹ (**3**) are assigned to v(OH) vibrations, and ³¹P resonances contain a singlet around -54 ppm which is close to the value of trimethylphosphine [9]. Proton resonances of the aniso-chronic PMe₂ groups in **4** and **6** appear as doublets of doublets, and CH₂ groups are split accordingly as expected for a center of chirality at C1. This type of molecule has not yet been investigated as a ligand for late transition metals.

3.2. Methylnickel compounds of (1,1-diaryl-2dimethylphosphinyl)ethanol

After combining the (2-phosphinyl)ethanols 1, 2, and 5 with dimeric methyl(methoxo)(trimethylphosphine)nickel in THF according to Eq. (2), the mixture turned from brown to yellow.



From pentane yellowish brown twinned crystals of 7 and yellow microcrystals of 8 and 9 were obtained, respectively, which under argon decompose above 90 °C and are oxidized in air within less than five minutes. In the infrared spectrum, the region of v(OH)bands is empty and methoxo groups are absent. ¹H and ¹³C NMR spectra are consistent with a squareplanar coordination geometry around nickel effected by methyl and trimethylphosphine groups and a chelating phosphinylethanolato ligand. Further details of solution configurations were revealed in ³¹P NMR measurements.

At 297 K a broad signal at 22 ppm is assigned to a coordinated Me₂P group, while at -8 ppm a singlet is observed as typical for coordinated trimethylphosphine under conditions of rapid exchange. At 233 K, these resonances are still broad but are accompanied by two doublets at 16 and 4 ppm (²*J*(P,P) = 16 Hz) containing 5% of total peak intensity. At 193 K the coupling attains 19 Hz, while the intensity of the doublets drops to 3%. 97% of the total intensity is then present in an AB-type pattern of resonances (²*J*(P,P) = 339 Hz) which is characteristic for P nuclei in *trans* positions [10]. The second doublet of doublets was assigned to an isomer contain-

ing the two P nuclei in cis positions. A cis isomer in an equilibrium of configurations in methylnickel P,Ochelates [2a] has been observed for the first time. A similar pattern of resonances at variable temperature was observed with samples of 8 and 9 (see Section 2). The underlying dynamic process appears to be based on a reversible dissociation of trimethylphosphine, which is supported by the known properties of 16-electron methylnickel compounds acting as a source and as an acceptor of trimethylphosphine [11]. A broad singlet at -15 ppm in the 193 K spectrum could be assigned to 18-electron bis(trimethylphosphine)methylnickel an complex. In order to test this possibility, a sample of 7 containing one mole equivalent of trimethylphosphine was measured under the same conditions. In the 233 K spectrum, two ³¹P singlets at 21 and -15 ppm and a third one at 55 ppm of equal intensities were assigned to 7 and free trimethylphosphine, respectively. At 193 K, only two singlets at δ 22 and -14 ppm were observed in a 1:2 ratio as expected for pentacoordinate 7 · PMe₃ still indicating rapid exchange of ligands.

3.3. Methylnickel compounds of (9-dimethylphosphinyl)methylenefluorenol

The observed ligand mobility in compounds 7–9 suggested an attempt at steric fixation of the chelating ligand. Attaching the fluorenyl group to the C1 atom of a 2-phosphinylethanol ties the aromatic substituents together and reduces the steric shielding of the O-donor function. Under conditions of the previous synthesis, (9-dimethylphosphinyl)methylen-fluorenol (3) was combined with methyl(trimethylphosphine)nickel methoxide according to Eq. (2) to afford yellow microcrystals of 10 which under argon decompose above 82 °C. The crystals are only slightly soluble in pentane and moderately soluble in diethyl ether or toluene. The infrared spectrum closely resembles that of 7, while ¹H NMR signals are observed as expected for a chelating monoanionic ligand.

An additional NiMe doublet at -2.4 ppm (apparent intensity 0.57 H) as the only novel feature was assigned to a second species. In the ³¹P NMR spectrum (193 K), a corresponding singlet resonance at δ 20 ppm (apparent intensity 0.18 P) was observed besides the singlet resonances of the rapidly exchanging *trans* isomer of **10** (*cis* isomer below 3% and not detected). Upon addition of one mole equivalent of trimethylphosphine the yellow solution turned orange, and both extra NMR signals disappeared. Evaporation of the solution at -10 °C removed all excess trimethylphosphine with the solvent leaving a solid residue of **10**. The transition from yellow to orange is reminiscent of the pair of dimethylnickel compounds containing either two trimethylphosphine ligands (16 electrons, yellow) or three (18 electrons, orange), suggesting excessive ligand dissociation from orange $10 \cdot PMe_3$.

From the mother liquor of **10**, some dark brown crystals of a by-product (<1%) were collected. The brown compound was reproducibly obtained in high yields when toluene solutions of **10** were slowly evaporated at 60 °C. Eventually, from a deep brown solution dark brown prisms of **11** were grown which upon removal of liquor and drying in vacuo lost their lustrous surface. Elemental analyses were consistent with continuous loss of toluene under these conditions. Solvent-free **11** decomposes under argon above 118 °C turning black but remains unaltered at 20 °C in air for three hours, while solutions in THF, toluene, or acetone under air are oxidatively decomposed within seconds. The extra ¹H doublet and ³¹P singlet resonances in the spectrum of **10** coincide with the peaks of added **11**.

The propensity of methylnickel alkoxides and phenoxides to form $bis(\mu-oxo)$ -bridged dinickel compounds [11] suggests that thermal dissociation of trimethylphosphine from 10 establishes an equilibrium with dinuclear 11 according to Eq. (3). Dinuclear methylnickel complexes containing (2-diphenylphosphinyl)phenolato ligands are believed to take part in equilibria of ligand dissociation [15] but have not been characterized to date.



When toluene solutions of **7** or **8** were evaporated at 60–100 °C, a spontaneous decomposition occurred forming trimethylphosphine oxide among unidentified products. However, addition of Ni(COD)(PMe₃)₂ as a scavenger of trimethylphosphine to a diethyl ether solution of **7** or **8** under milder conditions afforded the desired methylnickel compounds **12** and **13**, respectively (Eq. (4)).



Under argon the orange yellow prisms of 12 (from THF) and the yellow microcrystals of 13 (from ether) melt above 190 °C. Both materials tolerate handling in air at room temperature remaining unaltered for at least three hours. Spectroscopic data are consistent with the presence of a methylnickel group and a chelating (2-diarylphosphinyl)ethanolato ligand. The dinuclear nature of 13 was established by a single-crystal X-ray diffraction analysis.

The molecular structure (Fig. 1) contains two nickel atoms at a non-bonding distance of 293.9(0) pm held in a distorted square planar environment by two bridging O-atoms, a phosphinyl-P atom and a methyl group. The dinuclear complex molecule has a center of inversion based on a transoid arrangement of ligands. The central Ni₂O₂ metallocycle is folded in a cyclobutane-like fashion forming a dihedral angle of 12.86° along the O1–O1* axis. The five-membered chelate ring with a sum of internal angles of 522.57°, including the usual chelate-bite angle P1–Ni1–O1 = 87.62(18)°, shows slight bending. While the bond distances Ni–C1, Ni–O1* and Ni–P1 lie in the expected range, the bond Ni–O1 is notably longer due to the strong *trans*-influence of the methylnickel group.

The action of Ni(COD)(PMe₃)₂ on a (2-isopropyl(phenyl)phosphinyl-phenolato)methylnickel complex [2a] according to Eq. (5) confirms the role of the nickel(0) reagent as a rapid scavenger of trimethylphosphine.



Fig. 1. Molecular structure of **13** (ORTEP plot without hydrogen atoms). Selected bond lengths (Å) and angles (°): Ni–C1 1.928(9), Ni–P1 2.063(3), Ni–O1 1.953(6), Ni–O1* 1.984(6), Ni–Ni* 2.939, O1–C18 1.436(10), P1–C2 1.852(9), C2–C18 1.540(10); C1–Ni–P1 89.4(3), C1–Ni–O1* 101.0(3), C1–Ni–O1 177.1(3), O1–Ni–O1* 82.0(3), P1–Ni–O1 87.62(18), Ni–O1–Ni* 96.6(2), P1–Ni–O1* 169.5(2), C18–O1–Ni 120.2(5).



However, besides the expected soluble products a dark brown solid resulted which proved insoluble in ether, acetone, or acetonitrile and was not further characterized. Steric hindrance in the vicinity of the phenolato-O donor appears to cause side reactions. In spite of this finding, mixtures of methyl(trimethylphosphine)nickel complexes and Ni(COD)₂ as a scavenger [6b] of trimethylphosphine ligands were tested as catalysts for ethene reactions (see below).

3.4. Methylnickel compounds of (1-aryl-2-dimethylphosphinyl)ethanols

Both dissociation of ligands and access to a vacant coordination site at the nickel atom depend on steric effects in the vicinity of an available site. As seen in the molecular structure of 12, the substituents in the C1-position (C18 in Fig. 1) should have a marked steric influence on the coordination of ligands and the binding of substrates. On replacing one of the aryl substituents by a methyl group, for instance introducing 6 by reaction with methylnickel methoxide according to Eq. (6), all trimethylphosphine was eventually removed with the solvent.



The yellow microcrystals of **14** are air-sensitive although stable under argon up to 189 °C. They are sparingly soluble in pentane and freely so in toluene or THF. Spectral features are those of a dinickel complex, but ¹H, ¹³C, and ³¹P NMR spectra contain twice the number of resonances in equal intensities (see Section 2). This pattern is best explained by the presence of optical isomers in solution. The possible orientations of two 4-MeO-C₆H₄ substituents generate pairs of enantiomers and pairs of diastereoisomers.

A methyl substituent replacing an aryl group at the C1 atom of 2 favors molecular aggregation by bridging alkoxo groups in 14 over coordination of trimethylphosphine. With a hydrogen atom in the C1 position, i.e., using 4 in a reaction according to Eq. (6), the expected fragmentation of the ethanolato ligand [16] proceeds

affording trimethylphosphine oxide among other products.

3.5. Oligomerization of ethene

Complexes 7–10 contain all features required for catalyst activity in C,C-coupling reactions of ethene [1,2]: a methylnickel group in square planar geometry as a model of a growing hydrocarbon chain, a P,O-chelating anion serving as a steering device, and a reversibly dissociating neutral ligand indicating a site for substrate binding. [2-Isopropyl(phenyl)-phosphinyl]phenolato-(methyl)nickel (15) was included for comparison as well as a freely dissociating complex [2-butyl(phenyl)phosphinyl]phenolato(methyl)nickel (16) [12] bearing one or two trimethylphosphine ligands in solution and mixtures of these with Ni(COD)₂ which represent catalyst entities without trimethylphosphine.



In a typical preparative-scale test reaction with the catalysts 7, 10, 15, 16, or $16 + \text{Ni}(\text{COD})_2$, toluene solutions were placed in an autoclave (A) under a given pressure of ethene and kept stirring. Consumption of olefin was followed as the pressure dropped [13]. A technical autoclave (B), in a total volume of 1 dm³ containing toluene, was held at a given temperature under constant pressure by continuous feeding of ethene [14]. Measuring the flow rate gave the rate of ethene conversion in catalytic runs with complexes 8 and 9. Table 2 gives the conditions and turnover numbers (TON). In view of the moderate TON the low-density polyethylene (LDPE) samples were not further characterized.

While no explanation suggests itself for the inactivity of 9 and 10, the low activity of 7 and 8 can be connected with their preference to form dimers as a reservoir of the catalytically active species. In the absence of trimethylphosphine a mononuclear 14-electron species would be

Table 2Test runs for catalytic conversion of ethene

Complex	$T(^{\circ}C)$	p (bar)	Ethene (g)	TON	Product
7	100	50	8.5	294	LDPE
8	70	70	7.6	398	LDPE
9	70	70			
10	80	35			
15	80	35	7.7	257	$C_{4}-C_{24}$
16	80	35	7.7	2220	$C_{4}-C_{14}$
$16 + Ni(COD)_2$	80	42	8.2	1470	LDPE



Scheme 1. Equlibria of dissociation and substrate binding.

expected to be generated in low equilibrium concentration, which however could be rapidly converted by substrate binding (Scheme 1).

Comparing the last two experiments in Table 2 is of particular interest. Dissociation of PMe₃ from the 18electron complex **16**, which must be excessive under the reaction conditions, raises the catalytic activity for ethene oligomerization while in the presence of Ni(COD)₂ as a scavenger of PMe₃ the catalyst activity is turned onto polymerization. This clearly confirms the notion [2a,4b] that coordination of trimethylphosphine suppresses ethene binding at the available coordination sites (\Box), while elimination of 1-olefin from a growing chain in the position of NiMe is enhanced by coordination of trimethylphosphine.

4. Conclusion

Dimethylphosphinylethanols without C–H bonds at the C1-atom are smoothly transformed to stable anionic [P,O]-ligands forming five-membered nickelacycles in square planar geometry. When bearing a Ni–CH₃ function the complexes can act as single-component catalysts in the polymerization of ethene with moderate activity. Supporting trimethylphosphine ligands are dissociated by switching to the bridging [P, μ -O]-coordination mode in dinickel compounds which is most effectively controlled by the steric bulk of the substituents at C1. Dinuclear compounds are likely to form a reservoir for the catalytically active chelate(methyl)nickel species (14 metal-valence electrons) and could give rise to the induction periods observed in the catalysis test runs. Catalytic activity in the oligomerization of ethene can be turned onto polymerization by Ni(COD)₂ acting as scavenger of uncoordinated trimethylphosphine.

5. Supplementary material

Crystallographic data (without structure factors) for the structure reported in this paper have been deposited as supplementary publication with the Cambridge Crystallographic Data Centre. Deposition number is CCDC-151228 for **13**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk).

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