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Four-membered and five-membered metallocycles of methylnickel compounds*

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Abstract

Square planar methylnickel phenoxides *trans*-NiMe(OR)(PMe$_3$)$_2$ (R = 3-NO$_2$–C$_6$H$_4$ (**1a**), 4-NO$_2$–C$_6$H$_4$ (**2a**), 4-CHO–C$_6$H$_4$ (**3a**), C$_6$F$_5$ (**4a**), 4-C$_6$H$_5$N$_2$–C$_6$H$_4$ (**5a**)) were prepared from [NiMe(OMe)(PMe$_3$)]$_2$ and the corresponding phenol in the presence of trimethylphosphine. Without the phosphine only one of the dinuclear methylnickel phenoxides [NiMe(OR)(PMe$_3$)]$_2$ (R = C$_6$F$_5$, **4**) could be obtained, while triphenylsilanol gave *cis*/*trans*-[NiMe(OSiPh$_3$)(PMe$_3$)]$_2$ (**6**) or *cis*-Ni$_2$Me$_2$(OMe)(OSiPh$_3$)(PMe$_3$)$_2$ (**7**) that do not add trimethylphosphine. 2-Hydroxopyridine forms both types of complex, **8a** and **8**, without utilizing its N-donor functions. Five-membered O,N-chelate rings are exclusively formed by 2-hydroxomethylpyridine and pyridine-2-carboxylic acids giving NiOXC$_5$H$_4$N(Me)(PMe$_3$) (X = CH$_2$ (**9**), CO (**10**)) and dinuclear Ni$_2$Me$_2$(PMe$_3$)$_3$(NC$_5$H$_3$-2,3-COO-N:O:O) (**11**). Triethylphosphine complexes *trans*-NiMe(X)(PEt$_3$)$_2$ (X = Cl (**12**), Br (**13**)) and [NiMe(OR)(PEt$_3$)]$_2$ (R = CH$_3$ (**14**), H (**15**), C$_6$H$_5$ (**16**)) are also described as related to chelate complexes NiMe(quinoline-8-oxo-N:O)(PEt$_3$) (**17**) and *trans*-[NiMe(PEt$_3$)]$_2$C$_2$O$_4$ (**18**).

Introduction

Continuing our search for new coordination modes of methyl(trimethylphosphine)nickel moieties with O,N-donor ligands [1, 2] we have investigated the role of pyridinecarboxylic acids and other oxo-pyridines of different geometries and ligating properties in order to learn which configuration of O and N donors will lead to μ-oxo bridged dinuclear compounds and which will give chelate rings of mononuclear methylnickel compounds as with 8-hydroxoquinoline [2]. Some triethylphosphine complexes of this type are also described.

Experimental

All air-sensitive and volatile material was handled under argon and new compounds were characterized by spectroscopic techniques as described earlier [1, 2].

Preparations

(3-Nitrophenolato)-methyl-bis(trimethylphosphine)nickel (1a)

Upon 690 mg of [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ [3] (1.91 mmol) and 531 mg of 3-nitrophenol (3.82 mmol) at −70 °C were condensed *in vacuo* 0.5 ml of trimethylphosphine (4.8 mmol) and 60 ml of ether. The mixture was warmed up to 20 °C and filtered. The orange solution at −30 °C gave orange crystals that were isolated by decantation, washed with refluxing ether, and dried *in vacuo* at 20 °C: 850 mg (61% yield), m.p. 110–112 °C, decomp. > 125 °C.

Anal. Calc. for C$_{13}$H$_{25}$NNiO$_3$P$_2$ (364.0): C, 42.90; H, 6.92; N, 3.85. Found: C, 42.68; H, 7.00, N, 3.90%.

^{1}H NMR (60 MHz, (CD$_3$)$_2$CO, 308 K, Me$_4$Si external reference, δ0): δ(NiCH_3) −1.02 (s, 3H), δ(PCH_3) 1.17 (s, 18H), δ(CH) 7.47 (m, 4H). IR (nujol, cm^{-1}): 1477 s, ν_{as}NO$_2$; 1345 s, 1328 s, ν_sNO$_2$.

(4-Nitrophenolato)-methyl-bis(trimethylphosphine)nickel (2a)

In a similar procedure starting from 470 mg of [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ (1.30 mmol) and 361 mg of

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4-nitrophenol (2.60 mmol) in 50 ml of ether 830 mg of orange–brown needles were obtained (88% yield), decomp. >90 °C.

Anal. Calc. for $C_{13}H_{25}NNiO_3P_2$ (364.0): C, 42.90; H, 6.92; N, 3.85. Found: C, 42.65; H, 6.98; Ni 3.92%.

^{1}H NMR (60 MHz, $(CD_3)_2CO$, 308 K, Me_4Si external reference, δ0): δ(NiCH_3) −0.99 (s, 3H), δ(PCH_3) 1.16 (s, 18H), δ(*CH-2,6*) 6.95 (d, 2H, ^3J(HH) 9.2 Hz), δ(*CH-3,5*) 8.03 (d, 2H, ^3J(HH) 9.2 Hz). IR (nujol, cm^{-1}): 1468 s, $\nu_{as}NO_2$; 1313 vs, 1300 vs, ν_sNO_2.

(4-Formylphenolato)-methyl-bis(trimethylphosphine)nickel (3a)

In a similar procedure starting from 450 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.24 mmol) and 304 mg of 4-hydroxobenzaldehyde (2.48 mmol) in 50 ml of ether 720 mg of orange–brown needles were obtained (84% yield), m.p. 91–93 °C, decomp. >107 °C.

Anal. Calc. for $C_{14}H_{26}NiO_2P_2$ (347.0): C, 48.46; H, 7.55. Found: C, 48.37; H, 7.65%.

^{1}H NMR (60 MHz, $(CD_3)_2CO$, 308 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.05 (s, 3H), δ(PCH_3) 1.19 (s, 18H), δ(*CH-2,6*) 7.01 (d, 2H, ^3J(HH) 8.4 Hz), δ(*CH-3,5*) 7.59 (d, 2H, ^3J(HH) 8.4 Hz), δ(C*HO*) 9.67 (s, 1H). IR (nujol, cm^{-1}): 2730 m, 2682 w, νC*HO*; 1658 s, 1650 s, νCO.

Di-μ(pentafluorophenolato)-bis[methyl(trimethylphosphine)-nickel] (4)

To 330 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (0.91 mmol) in 40 ml of toluene at −70 °C were added dropwise 335 mg of pentafluorophenol (1.82 mmol) in 10 ml of toluene. The mixture was allowed to warm up and evaporated to dryness. The red–brown residue was extracted with 100 ml of ether over a glass-sinter disc. Crystallization at −30 °C gave 460 mg of red–brown crystals (76% yield), m.p. 96–98 °C (decomp.).

Anal. Calc. for $C_{20}H_{24}F_{10}Ni_2O_2P_2$ (665.8): C, 36.08; H, 3.58. Found: C, 35.60; H, 4.10%.

^{1}H NMR (300 MHz, toluene-d_8, 233 K, Me_4Si external reference, δ0) *cis* (35%): δ(NiCH_3) −0.63 (d, 6H, ^3J(PH) 6.0 Hz), δ(PCH_3) 0.87 (d, 18H, ^2J(PH) 11.5 Hz). *trans* (65%): δ(NiCH_3) −0.80 (d, 6H, ^3J(PH) 6.0 Hz), δ(PCH_3) 0.59 (d, 18H, ^2J(PH) 11.5 Hz). IR (nujol, cm^{-1}): 1641 m, 1620 m, 1568 m, νC=C; 1507 vs, 1498 vs, 1489 vs, νC−F; 1156 s, 1149 s, δ_sNiCH$_3$; 1015 vs, 999 vs, 981 vs, δC–F.

Methylpentafluorophenolato-bis(trimethylphosphine)nickel (4a)

Upon 300 mg of **4** (0.45 mmol) in 40 ml of THF at −70 °C was condensed *in vacuo* 1.0 ml of trimethylphosphine (9.6 mmol). The bright red solution was evaporated to dryness and the residue was extracted with 20 ml of ether. Crystallization at −30 °C gave 140 mg of yellow–brown crystals (38% yield), m.p. 72–73 °C, decomp. >86 °C.

Anal. Calc. for $C_{13}H_{21}F_5NiOP_2$ (409.0): C, 38.18; H, 5.18. Found: C, 37.69; H, 5.30%.

^{1}H NMR (60 MHz, toluene-d_8, 308 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.05 (s, 3H), δ(PCH_3) 0.77 (s, 18H). ^{19}F NMR (56.4 MHz, toluene-d_8, 308 K, CCl_3F external reference, δ0): δ(F) 170.0 m. IR (nujol, cm^{-1}): 1643 m, 1613 w, νC=C; 1511 vs, 1500 vs, νC–F; 1170 m, δ_sNiCH$_3$; 1010 vs, 980 vs, δC–F.

(Azobenzene-4-oxo)-methyl-bis(trimethylphosphine)nickel (5a)

Upon 480 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.33 mmol) and 526 mg of 4-hydroxoazobenzene (2.66 mmol) at −70 °C were condensed *in vacuo* 0.4 ml of trimethylphosphine and 200 ml of ether. After 3 h at 20 °C the solution was filtered, cooled to −30 °C to give 890 mg of red cubes (79% yield), decomp. >78 °C.

Anal. Calc. for $C_{19}H_{30}N_2NiOP_2$ (423.1): C, 53.94; H, 7.15; N, 6.62. Found: C, 53.82; H, 7.17; N, 6.59%.

^{1}H NMR (60 MHz, $(CD_3)_2CO$, 308 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.01 (s, 3H), δ(PCH_3) 1.19 (s, 18H), δ(C*H*) 7.46 (m, 9H).

Di-μ(triphenylsiloxo)-bis[methyl(trimethylphosphine)nickel] (6)

480 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.33 mmol) and 735 mg of triphenylsilanol (2.66 mmol) in 50 ml of ether were kept stirring for 2 h at 20 °C. After filtration the dark brown solution was concentrated to 15 ml. With 50 ml of pentane 810 mg of brown solid were precipitated (71% yield), decomp. >85 °C.

Anal. Calc. for $C_{44}H_{54}Ni_2O_2P_2Si_2$ (852.6): C, 61.99; H, 6.38. Found: C, 61.40; H, 6.35%.

^{1}H NMR (60 MHz, toluene-d_8, 308 K, Me_4Si external reference, δ0) *cis*(53%): δ(NiCH_3) −0.43 (d, 6H, ^3J(PH) 6.0 Hz), δ(PCH_3) 0.63 (d, 18H, ^2J(PH) 9.8 Hz). *trans* (47%): δ(NiCH_3) −0.63 (d, 6H, ^2J(PH) 6.0 Hz), δ(PCH_3) 0.71 (d, 18H, ^2J(PH) 9.8 Hz). *cis* and *trans*: δ(C*H*) 7.52 (m, 30H).

μ-Methoxo-μ(triphenylsiloxo)-bis[cis-methyl(trimethylphosphine)-nickel] (7)

In a similar procedure starting from 560 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.55 mmol) and 430 mg of triphenylsilanol (1.55 mmol) in 50 ml of ether 800 mg of orange–brown crystals were obtained (89% yield), decomp. >101 °C.

Anal. Calc. for $C_{27}H_{42}Ni_2O_2P_2Si$ (578.0): C, 56.11; H, 7.32. Found: C, 55.84; H, 7.24%.

^{1}H NMR (60 MHz, CD_3OD, 308 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.37 (d, 6H, ^3J(PH) 5.8 Hz), δ(PCH_3) 1.11 (d, 18H, ^2J(PH) 9.8 Hz), δ(OCH_3) 3.35 (s, 3H), δ(CH) 6.56 (m, 15H). IR (nujol, cm^{-1}): 2775 s, ν_sOCH_3; 1152 m, δ_sNiCH_3.

Di-μ(pyridine-2-oxo)-bis[methyl(trimethylphosphine)nickel] (8)

340 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (0.94 mmol) and 180 mg of 2-hydroxopyridine (1.88 mmol) in 40 ml of ether were kept for 2 h at 20 °C. The red–brown solution was filtered, cooled to −30 °C to give 350 mg of red–brown crystals (76% yield), m.p. 119–121 °C (decomp.).

Anal. Calc. for $C_{18}H_{32}N_2Ni_2O_2P_2$ (487.8): C, 44.32; H, 6.61, N, 5.74. Found: C, 44.30; H, 6.64; N, 5.74%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0) *cis* (57%): δ(NiCH_3) −0.19 (d, 6H, ^3J(PH) 6.5 Hz), δ(PCH_3) 1.05 (d, 18H, ^2J(PH) 11.0 Hz). *trans* (43%): δ(NiCH_3) −0.53 (d, 6H, ^3J(PH) 6.1 Hz), δ(PCH_3) 1.12 (d, 18H, ^2J(PH) 10.0 Hz). *cis* and *trans*: δ(CH) 7.04 (m, 16H).

Methyl(pyridine-2-oxo)-bis(trimethylphosphine)nickel (8a)

To 200 mg of **8** (0.41 mmol) in 40 ml of ether was added 0.2 ml of trimethylphosphine (1.92 mmol). Filtration and crystallization at −30 °C gave 230 mg of dark yellow crystals (88% yield), m.p. 90–92 °C, decomp. >127 °C.

Anal. Calc. for $C_{12}H_{25}NNiOP_2$ (320.0): C, 45.04; H, 7.87; N, 4.38. Found: C, 45.08; H, 7.92; N, 4.37%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): δ(NiCH_3) −0.94 (s, 3H), δ(PCH_3) 1.06 (s, 18H), δ(*CH-3*) 5.87 (dd, 1H, ^2J(HH) 7.7 Hz, ^3J(HH) 1.3 Hz), δ(*CH-5*) 5.93 (td, 1H, ^2J(HH) 5.9 Hz, ^3J(HH) 1.3 Hz), δ(*CH-4*) 6.98 (ddd, ^2J(HH) 7.7 and 5.9 Hz, ^3J(HH) 1.6 Hz), δ(*CH-6*) 7.35 (dd, 1H, ^2J(HH) 5.9 Hz, ^3J(HH) 1.6 Hz).

Methyl(pyridine-2-methanolato-N:O)-(trimethylphosphine)nickel (9)

640 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.77 mmol) and 386 mg of 2-(hydroxomethyl)pyridine (3.54 mmol) in 80 ml of ether were kept for 2 h at 20 °C. The volatiles were removed *in vacuo* and the oily residue was extracted with 200 ml of pentane. This solution at −30 °C gave an oil that crystallized within 8 days to give 570 mg of brown leaflets (62% yield).

Anal. Calc. for $C_{10}H_{18}NNiOP$ (257.9): C, 46.56; H, 7.03; N, 5.43. Found: C, 46.46; H, 6.99; N, 5.18%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.09 (s, 3H), δ(PCH_3) 1.24 (d, 9H, ^2J(PH) 10.0 Hz), δ(CH_2) 4.86 (s, 2H), δ(CH) 7.72 (m, 4H).

Methyl(pyridine-2-carboxylato-N:O)-(trimethylphosphine)nickel (10)

560 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.55 mmol) and 381 mg of pyridine-2-carboxylic acid (3.10 mmol) in 80 ml of THF were kept for 1 h at 20 °C. The volatiles were removed *in vacuo* and the residue was extracted with 400 ml of ether. Cooling the solution to −30 °C afforded 730 mg of orange–brown needles (87% yield), decomp. >124 °C.

Anal. Calc. for $C_{10}H_{16}NNiO_2P$ (271.9): C, 44.17; H, 5.93; N, 5.15. Found: C, 43.77; H, 5.83; N, 4.96%.

^{1}H NMR (300 MHz, THF-d_8, 233 K, Me_4Si external reference, δ0): δ(NiCH_3) −0.70 (d, 3H, ^3J(PH) 5.6 Hz), δ(PCH_3) 1.31 (d, 9H, ^2J(PH) 10.5 Hz), δ(CH) 8.02 (m, 4H). IR (nujol, cm^{-1}): 1655 vs, ν_{as}OCO; 1352 vs, ν_sOCO.

Dimethyl(pyridine-2,3-dicarboxylato-N:O:O)-tris(trimethylphosphine)dinickel (11)

To 480 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.33 mmol) and 222 mg of pyridine-2,3-dicarboxylic acid (1.33 mmol) in 80 ml of THF at −70 °C was added 0.3 ml of trimethylphosphine (2.88 mmol). After 1 h at 20 °C the volatiles were removed *in vacuo* and the residue was extracted with 500 ml of ether. Cooling the solution to −30 °C afforded 680 mg of yellow needles (95% yield), decomp. >109 °C.

Anal. Calc. for $C_{18}H_{36}NNi_2O_4P_3$ (540.8): C, 39.38; H, 67.1; N, 25.9. Found: C, 39.26; H, 6.60; N, 2.37%.

^{1}H NMR (300 MHz, THF-d_8, 295 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.10 (s, 3H), −0.81 (s, 3H), δ(PCH_3) 1.25 (s, 27H), δ(CH) 7.69 (m, 3H). IR (nujol, cm^{-1}): 1670 vs, 1619 vs, ν_{as}OCO; 1379 vs, 1335 vs, ν_sOCO.

Chloromethyl-bis(triethylphosphine)nickel (12)

To 2500 mg of $NiCl_2(PEt_3)_2$ [4] (6.83 mmol) in 100 ml of THF at −70 °C were added 9.8 ml of 1.4 M CH_3Li in ether (13.66 mmol). After stirring for 1 h at −40 °C the mixture was slowly brought to −20 °C and 2.5 ml of methanol were added through a pipette. After 1 h stirring the volatiles were removed *in vacuo*. Extraction with 60 ml of pentane and cooling to −30 °C gave 1200 mg of yellow needles (51% yield) decomp. >71 °C.

Anal. Calc. for $C_{13}H_{33}ClNiP_2$ (345.5): C, 45.19; H, 9.62. Found: C, 45.08; H, 9.65%.

^{1}H NMR (300 MHz, toluene-d_8, 295 K, Me_4Si external reference, δ0): δ(NiCH_3) −0.68 (t, 3H, ^3J(PH) 9.7 Hz), δ(PCH_2) 1.42 (m, 12H), δ(PCCH_3) 1.11 (quintet, 18H, ^3J(PH) ≈ ^5J(PH) ≈ ^3J(HH) 7.5 Hz).

Bromomethyl-bis(triethylphosphine)nickel (13)

To 2200 mg of $NiBr_2(PEt_3)_2$ [4] (4.84 mmol) in 60 ml of THF at −70 °C were added 6.9 ml of 1.4 M CH_3Li in ether (9.68 mmol). Workup as for **12** gave 1400 mg of dark yellow crystals (74% yield), decomp. >56 °C.

Anal. Calc. for $C_{13}H_{33}BrNiP_2$ (389.9): C, 40.04; H, 8.53; Ni, 15.05. Found: C, 39.69; H, 8.16; Ni 15.15%.

^1H NMR (300 MHz, toluene-d_8, 295 K, Me_4Si external reference. δ0): $\delta(NiCH_3)$ −0.63 (t, 3H, $^3J(PH)$ 9.5 Hz), $\delta(PCH_2)$ 1.46 (m, 12H), $\delta(PCCH_3)$ 1.08 (quintet, 18H, $^3J(PH) \approx {}^5J(PH) \approx {}^3J(HH)$ 7.5 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, toluene-d_8, 295 K Me_4Si external reference, δ0): $\delta(NiCH_3)$ −15.5 (t, $^2J(PC)$ 26.0 Hz), $\delta(PCCH_3)$ 8.59 (s), $\delta(PCH_2)$ 15.02 (t, $^1J(PC)$ 11.8 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8, 298 K, H_3PO_4 external reference, δ0): δ 13.23 (s).

Di-μ(methoxo)-bis[cis-methyl(triethylphosphine)nickel] (14)

1800 mg of **13** (4.62 mmol) and 540 mg of $NaOCH_3$ (10 mmol) in 50 ml of pentane were kept stirring for 20 h at 20 °C. The orange–brown solution was filtered and brought to 15 ml *in vacuo*. Cooling to −70 °C gave 780 mg of dark brown prisms (76% yield), m.p. 45–47 °C (decomp.).

Anal. Calc. for $C_{16}H_{42}Ni_2O_2P_2$ (445.9): C, 43.10; H, 9.49. Found: C, 43.01; H, 9.62%.

^1H NMR (60 MHz, toluene-d_8, 308 K, Me_4Si external reference, δ0): $\delta(NiCH_3)$ −0.89 (d, 6H, $^3J(PH)$ 5.6 Hz), $\delta(PC_2H_5)$ 1.28 (m, 30H), $\delta(OCH_3)$ 3.20 (t, 3H, $^4J(PH)$ 2.0 Hz), 3.57 (s, 3H). $^{13}C\{^1H\}$ NMR (75.5 MHz, toluene-d_8, 295 K, Me_4Si external reference, δ0): $\delta(NiCH_3)$ −17.01 (d, $^2J(PC)$ 39.24 Hz); $\delta(PCCH_3)$ 8.29 (s), $\delta(PCH_2)$ 14.13 (d, $^1J(PC)$ 24.9 Hz), $\delta(OCH_3)$ 50.77 (s), 52.63 (s). IR (nujol, cm^{-1}): 2799 s, 2788 s, $\nu_s OCH_3$.

Di-μ(hydroxo)-bis[methyl(triethylphosphine)nickel] (15)

To 780 mg of **14** (1.75 mmol) in 50 ml of pentane at 5 °C was added 1.0 ml of oxygen-free water (excess). After stirring for 1 h the mixture was evacuated to dryness. Extraction with 20 ml of pentane and cooling to −70 °C gave 530 mg of dark yellow crystals (72% yield), decomp. >30 °C (slow).

Anal. Calc. for $C_{14}H_{38}Ni_2O_2P_2$ (417.8): C, 40.25; H, 9.17. Found: C, 39.68; H, 9.35%.

^1H NMR (300 MHz, toluene-d_8, 295 K. Me_4Si external reference, δ0) *cis* (35%): $\delta(OH)$ −6.37 (s, 1H), −2.44 (s, 1H), $\delta(NiCH_3)$ −1.05 (s, 6H). *trans* (65%): $\delta(OH)$ −4.25 (s, 2H), $\delta(NiCH_3)$ −1.16 (s, 6H). *cis* and *trans*: $\delta(PC_2H_5)$ 1.05 (m, 30H). IR (nujol, cm^{-1}) 3638 m, νOH; 805 s(broad) $\delta_1 OH$; 491 m(broad), $\delta_2 OH$; 431 m, 420 m, νNi_2O_2.

Di-μ(phenolato)-bis[methyl(triethylphosphine)nickel] (16)

To 500 mg of **14** (1.13 mmol) in 80 ml of pentane at −20 °C were added 210 mg of phenol (2.26 mmol). After stirring for 1 h a light brown solid was separated by filtration. Cooling the filtrate to −30 °C gave 300 mg of dark brown crystals (46% yield), m.p. 85–87 °C (decomp.).

Anal. Calc. for $C_{26}H_{46}Ni_2O_2P_2$ (570.0): C, 54.79; H, 8.13. Found: C, 55.21; H, 8.44%.

^1H NMR (60 MHz, $(CD_3)_2CO$, 308 K, Me_4Si external reference, δ0) *cis* (77%): $\delta(NiCH_3)$ −1.33 (d, 6H, $^3J(PH)$ 5.8 Hz). *trans* (23%): $\delta(NiCH_3)$ −1.79 (d, 6H, $^3J(PH)$ 5.8 Hz). *cis* and *trans*: $\delta(PC_2H_5)$ 1.27 (m, 30H), $\delta(CH)$ 7.14 (m, 10H).

Methyl-(quinoline-8-oxo-N:O)-(triethylphosphine)nickel (17)

450 mg of **14** (1.01 mmol) and 290 mg of 8-hydroxoquinoline (2.0 mmol) in 50 ml of pentane were kept stirring for 1 h at −20 °C. Filtration and evaporation of the volatiles left a dark red oil, containing less than 5% impurities (NMR): 620 mg (92% raw yield). $C_{16}H_{24}NNiOP$ (336.1).

^1H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): $\delta(NiCH_3)$ −0.68 (s, 3H), $\delta(PCCH_3)$ 1.25 (m, 9H), $\delta(PCH_2)$ 1.63 (m, 6H), $\delta(CH)$ 7.45 (m, 6H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): $\delta(NiCH_3)$ −15.52 (s), $\delta(PCCH_3)$ 8.75 (s), $\delta(PCH_2)$ 15.31 (s), $\delta(CH)$ 108.88 −169.15 (9 s).

μ(Oxalato-O:O:O:O)-bis[trans-methyl(triethylphosphine)nickel] (18)

625 mg of **14** (1.40 mmol) and 175 mg of oxalic acid dihydrate (1.40 mmol) in 80 ml of pentane were kept stirring for 24 h at 20 °C. The mixture was evaporated to dryness and the residue was extracted with 60 ml of toluene. At −30 °C 560 mg of dark brown crystals were obtained (85% yield), m.p. 113–115 °C (decomp.).

Anal. Calc. for $C_{16}H_{36}Ni_2O_4P_2$ (471.8): C, 40.73; H, 7.69. Found: C, 41.40; H, 7.80%.

^1H NMR (60 MHz, toluene-d_8, 308 K, Me_4Si external reference, δ0): $\delta(NiCH_3)$ −0.47 (d, 6H, $^3J(PH)$ 4.5 Hz), $\delta(PC_2H_5)$ 0.97 (m, 30 H). IR (nujol, cm^{-1}): 1648 vs (broad), $\nu_{as}OCO$; 1348 s, $\nu_s OCO$.

Results and discussion

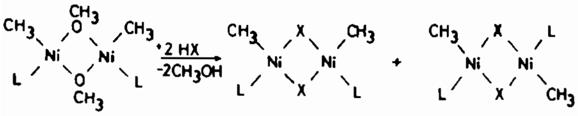
Dinuclear methylnickel compounds with equal or different alkoxo bridges ($X,X' = OCH_3, OC_2H_5$) exclusively attain a *cis* configuration **A** [3], while methyl(trimethylphosphine)nickel phenoxides (X= X'=C_6H_5O, 4-CH_3–C_6H_4O) reversibly dimerize giving equilibria of **A** and **B**. Since for X=X'=Cl only **B** is found [5] more acidic phenols were expected to give a series of phenoxo-bridged complexes with dominating **B**.

A(*cis*) B(*trans*)
L=PMe_3

Reacting substituted phenols of lower pK_a than the parent C_6H_5OH (pK_a=10.0) with methyl(trimethylphosphine)nickel methoxide according to eqn. (1) unexpectedly led to decomposition in most cases (Table 1).

With pentafluorophenol **4** is smoothly formed without decomposition. In toluene **4** shows almost the same **A**/**B** ratio as reported for the parent phenoxo compound [3]. Likewise two triphenylsiloxo bridges and two trimethylsiloxo bridges cause dominant **A**. No isomer **B** was detected in the mixed triphenylsiloxo–methoxo compound **7**.

In order to establish which stereoisomer is present the IR bands of **7** arising from characteristic OCH_3 vibrations are compared with those of other A-type methoxo compounds (Table 2). Clearly the methoxo bridge in **7** is located opposite both $NiCH_3$ groups.



A **B**

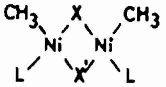
(1)

TABLE 1. Dinuclear methylnickel complexes

HX	% in toluene solution	
	A	**B**
3-NO_2–C_6H_4OH (**1**)	[b]	
4-NO_2–C_6H_4OH (**2**)	[b]	
4-CHO–C_6H_4OH (**3**)	[b]	
C_6F_5OH (**4**)	35	65
C_6H_5OH[a]	34	66
4-$C_6H_5N_2$–C_6H_4OH (**5**)	[b]	
$(C_6H_5)_3SiOH$ (**6**)	53	47
$(CH_3)_3SiOH$[a]	68	32
$(C_6H_5)_3SiOH$, CH_3OH (**7**)[c]	100	0
C_5H_4N-2-OH (**8**)[d]	57	43

[a] Ref. 3. [b] Decomposition at −20 °C giving Ni and NiL_4. [c] In CD_3OD, see text. [d] In $(CD_3)_2CO$.

TABLE 2. IR data and configuration of methoxo bridges

	ν_sCH (cm^{-1})	νC–O (cm^{-1})
X=OCH_3	2798	1094
X'=OCH_3	2777	1032[a]
X=OCH_3	2799	1108[b]
X'=F		
X=$N(CH_3)_2$	[c]	–
X'=OCH_3	2775	1041
X=$Si(C_6H_5)_3$ (**7**)		
X'=OCH_3	2775	1047

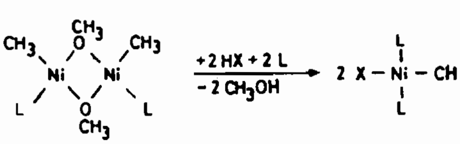
[a] Ref. 3. [b] Ref. 5. [c] Two bands.

TABLE 3. Mononuclear methylnickel complexes

HX	Complex
3-NO_2-C_6H_4OH	**1a**
4-NO_2-C_6H_4OH	**2a**
4-CHO-C_6H_4OH	**3a**
C_6F_5OH	**4a**
4-$C_6H_5N_2$-C_6H_4OH	**5a**
$(C_6H_5)_3SiOH$	[a]
$(C_6H_5)_3SiOH$, CH_3OH	[a]
C_5H_4N-2-OH	**8a**

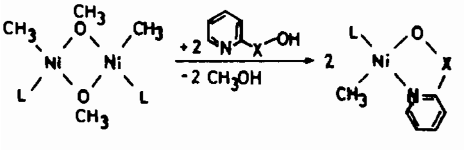
[a] No uptake of ligand by **6** or **7**.

Two pyridine-2-oxo bridges in **8** give rise to **A** and **B** isomers apparently disregarding the N donors. Decomposition (Table 1) is avoided by adding for each metal one equivalent of trimethylphosphine in a synthesis according to eqn. (2).



(2)

Table 3 demonstrates that nitro, azo and aldehyde functions are compatible with $NiCH_3$ groups and with trimethylphosphine ligands but not with coordinatively unsaturated nickel in the unstable intermediates **1**–**3** and **5**. Siloxo and alkoxo bridged **6** and **7** at 20 °C in the presence of trimethylphosphine show fast exchange of ligands (singlets for $NiCH_3$ and PCH_3 proton resonances) but do not give a stable mononuclear complex. While **8a** utilizes added P-donor ligands rather than its N-donor function, that would give a four-membered chelate ring, 2-(hydroxomethyl)pyridine and pyridine-2-carboxylic

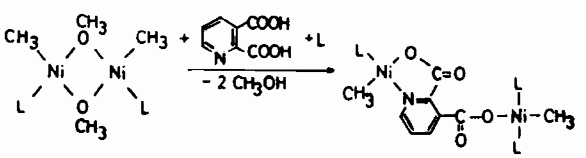


9: $X=CH_2$
10: $X=CO$

(3)

acid according to eqn. (3) form stable five-membered rings that are not cleaved by phosphine ligands.

Isomers where O and N donors have changed their positions are not detected. The same feature is observed with pyridine-2,3-carboxylic acid, but due to the presence of the 3-carboxylate function addition of one equivalent of phosphine ligand is required in a synthesis according to eqn. (4).



11 (4)

Without additional phosphine an intractable oil is obtained.

Since there is very little steric crowding in square planar nickel complexes some examples with triethylphosphine ligands have been synthesized including new methylnickel halides as starting materials. After many failures no simple extension of known procedures [3, 6] appeared feasible. Only under carefully controlled conditions was it possible to obtain the methylnickel halides **12** and **13** according to eqn. (5) in moderate yield.

$$\mathrm{NiX_2(PEt_3)_2} \xrightarrow{\text{(a) LiCH}_3\text{, (b) CH}_3\text{OH}} \mathrm{NiCH_3(X)(PEt_3)_2}$$

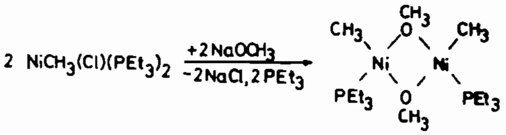
12: $X=Cl$

13: $X=Br$

(5)

Both compounds are better soluble in pentane or ether and less stable thermally than their trimethylphosphine homologues. Iodo(methyl)bis(triethylphosphine)nickel can be obtained from **12** and sodium iodide within 2 h at 0 °C as an oil that decomposes above 0 °C and therefore has not been fully characterized. As evidenced by ^{1}H NMR slow exchange of phosphine ligands producing a $NiCH_3$ triplet at 25 °C immediately shows the expected *trans*-geometry.

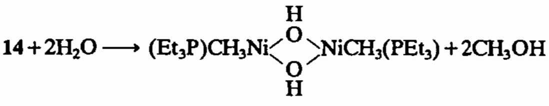
In a smooth synthesis according to eqn. (6) the methoxobridged dinuclear complex **14** is formed in virtual quantitative yield.



14 (6)

Slow decomposition at 0 °C and repeated recrystallization of the dark brown prisms from very little pentane at −30 °C caused considerable loss of product. The crystals decompose at 45 °C under argon and are sensitive to daylight. The IR and NMR spectra clearly indicate a *cis*-configuration of **14**.

Careful hydrolysis under argon transforms **14** to the corresponding hydroxide **15** according to eqn. (7).



$$14 + 2\mathrm{H_2O} \longrightarrow \mathrm{(Et_3P)CH_3Ni}\langle\overset{\mathrm{H}}{\mathrm{O}}\,\underset{\mathrm{H}}{\mathrm{O}}\rangle\mathrm{NiCH_3(PEt_3)} + 2\mathrm{CH_3OH}$$

15

(7)

Synthesis and crystallization are performed in pentane solution, where the trimethylphosphine analogue is insoluble [3]. **15** is sensitive to air and light and is safely stored in the dark at −30 °C. A point of decomposition cannot be exactly determined. In the IR spectrum the ν(OH) band at 3638 cm^{-1} corresponds with 3674 cm^{-1} in the trimethylphosphine compound as do all non-phosphine bands (Table 4). There is no association via hydrogen bridges.

Equilibria involving *cis* and *trans* isomers of **15** give rise to three characteristic ^{1}H NMR signals. The singlet at highest field is due to an OH bridge opposite two phosphine ligands of *cis*-**15** and there is a second signal of equal intensity for the other bridge at lower field. In between the two signals one singlet for both OH bridges of *trans*-**15** is observed. Lowering the temperature to −60 °C causes large upfield shifts; particularly in toluene-d$_8$ temperature shifts of 4 ppm were observed.

TABLE 4. Non-phosphine IR bands of methylnickel hydroxides $[NiCH_3(OH)(PMe_3)]_2$ (I) [3] and $[NiCH_3(OH)(PEt_3)]_2$ (**15**) (II) (cm^{-1})

I	II (15)	Assignment
3674	3638	νOH
1158	1154	$\delta_s NiCH_3$
818	809	$\delta_1 OH$
497	491	$\delta_2 OH$
468	431	νNi_2O_2
440	420	

In the presence of triethylphosphine, solutions of **14** and **15** shine dark red–brown indicating uptake of ligands. Crystallization invariably gives **14** and **15** and no mononuclear compound.

The crystalline bis(phenoxo) bridged complex **16**, generated from **14** and phenol as in eqn. (7), with triethylphosphine appears to give a ligand-rich compound as an oil, that loses phosphine at 0 °C *in vacuo*. In acetone-d_6 **16** displays an isomer ratio *cis*/*trans* = 3.3 as taken from intensities of $NiCH_3$ ^1H NMR signals. Addition of phosphine simplifies the spectrum giving one $NiCH_3$ singlet as expected for a mononuclear species and rapid exchange of ligands. 8-Hydroxoquinoline or oxalic acid with **14** as in eqn. (3) immediately form mononuclear complexes **17** or **18** that are better soluble than their trimethylphosphine analogues [2]. $NiCH_3$ doublets in the presence of triethylphosphine indicate no ligand exchange and stable chelate rings.

In no case have side-reactions, involving protolytic cleavage of $NiCH_3$ functions, been detected. However, if oxygen is admitted Ni–C bonds are rapidly cleaved.

Acknowledgements

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