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Dioxobenzene dianions — unusual ligands in methylnickel compounds*

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Abstract

Novel square planar methylnickel compounds with benzene–dioxo ligands (O---O)[NiMe(PMe$_3$)]$_2$ (O---O = benzene-1,2-dioxo (**1**); benzene-1,2-dioxo-4-methyl (**2**); benzene-1,2-dioxo-3-methoxo (**3**)) were prepared from [NiMe(OMe)(PMe$_3$)]$_2$ and the corresponding 1,2-dihydroxobenzene. In the presence of trimethylphosphine dinuclear complexes (O---O)Ni$_2$Me$_2$(PMe$_3$)$_3$, **1a–3a**, and **4** (O---O = naphthaline-2,3-dioxo) were obtained, while (−I) substituents gave rise to the formation of ligand-rich ionic species [NiMe(PMe$_3$)$_4$]$^+$[(O---O)NiMe(PMe$_3$)]$^-$ (O---O) = benzene-1,2-dioxo-4-nitro (**5**); benzene-1,2-dioxo-3-formyl (**6**); benzene-1,2-dioxo-4-formyl (**7**). All three types of compounds were unexpected. Compound **3a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.784(4)$, $b = 9.095(2)$, $c = 16.796(4)$ Å, $\alpha = 96.83(2)$, $\beta = 101.99(3)$, $\gamma = 102.85(3)°$, $V = 1260.5(2)$ Å^3, $Z = 2$. Final discrepancy indices are $R = 0.0398$ and $R_w = 0.0439$. The molecule **3a** contains two square planar nickel centres with their coordination planes at right angles. The point of connection is provided by a trigonal planar oxygen atom (Ni1–O1 = 1.919(5), Ni2–O1 = 1.966(4), O1–C3(sp^2) = 1.356(6) Å). In a similar synthesis resorcinols gave dinuclear complexes (O---O)[NiMe(PMe$_3$)$_2$]$_2$ (O---O = benzene-1,3-dioxo (**8a**); benzene-1,3-dioxo-5-methoxo (**9a**); benzene-1,3-dioxo-2-nitro (**10a**) as expected for two phenolic functions.

Introduction

Hydroquinones are formed in a direct Reppe synthesis from acetylene, carbon monoxide and water in a homogeneous system with metal carbonyls of Fe, Ru, Co or Rh as catalysts [1]. Characteristic colour tests for phenol and enol functions long recognized in organic chemistry are due to Fe–O complexes of these groups with Fe^{3+} ions. No organometallic compounds with dioxobenzene dianions have been described. The first nickel(II) complex with pyrocatechol was published in 1982 by Andrä and Fleischer [2]. Our investigations of alkoxo- and phenoxo-bridged methylnickel compounds [3] have lead us to synthesize the first organonickel complexes with dioxobenzene dianions. A rich coordination chemistry and some unexpected reactions are the subject matter of this report.

Experimental

All air-sensitive and volatile material was handled under argon and new compounds were characterized by spectroscopic techniques given in the preceding papers [3].

μ-(Benzene-1,2-dioxo)-bis[methyl(trimethylphosphine)nickel] (1)

850 mg of [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ [4] (2.35 mmol) in 30 ml of ether were combined with 260 mg of 1,2-dihydroxobenzene (2.35 mmol) in 30 ml of ether. After 24 h stirring at 20 °C a light brown solid was separated by filtration. From the deep brown solution at 0 °C 340 mg of dark brown crystals were obtained (35% yield), m.p. 95–97 °C (decomp.).

Anal. Calc. for C$_{14}$H$_{28}$Ni$_2$O$_2$P$_2$ (407.7): C, 41.24; H, 6.92. Found: C, 41.20; H, 6.84%.

^{1}H NMR (300 MHz, (CD$_3$)$_2$CO, 295 K, Me$_4$Si external reference, $\delta 0$): δ(NiCH_3) −0.87 (d, 3H, ^3J(PH) 6.6 Hz) and −0.57 (d, 3H, ^3J(PH) 4.6 Hz); δ(PCH_3) 1.20 (d, 9H, ^2J(PH) 9.1 Hz) and 1.33 (d, 9H, ^2J(PH) 10.0 Hz); δ(CH) 4.97 (t, 1H, ^3J(HH) 6.5 Hz), 5.05 (t, 1H, ^3J(HH) 6.5 Hz), 6.04 (d, 1H, ^3J(HH)

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6.5 Hz) and 6.19 (d, 1H, ^{3}J(HH) 6.5 Hz). ^{31}P{H} NMR (121.5 MHz, 295 K, $(CD_3)_2CO$, H_3PO_4 external reference, δ0): δ −3.80 (s) and −4.00 (s).

μ-(Benzene-1,2-dioxo)-dimethyl-tris(trimethylphosphine)dinickel (1a)

(a) In the synthesis given above the red–brown mother liquor was reduced to 30 ml *in vacuo* and crystallized at 0 °C to give 400 mg of orange leaflets (35% yield).

(b) 920 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.54 mmol) and 280 mg of 1,2-dihydroxobenzene (2.54 mmol) in 70 ml of ether containing 0.3 ml trimethylphosphine (2.88 mmol) were stirred for 2 h at 20 °C. The red–brown solution was filtered and crystallized at −30 °C to afford 980 mg of orange leaflets (80% yield), m.p. 110–112 °C (decomp.).

Anal. Calc. for $C_{17}H_{37}Ni_2O_2P_3$ (483.8): C, 42.20; H, 7.71. Found: C, 41.18; H, 7.21%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): δ(NiC*H*$_3$) −1.05 (t, 3H, ^{3}J(PH) 10.4 Hz) and −0.17 (d, 3H, ^{3}J(PH) 5.7 Hz); δ(PC*H*$_3$) 1.23 (d, 9H, ^{2}J(PH) 10.0 Hz) and 1.28 (t′, 18H, $|^{2}J(\mathrm{PH})+{}^{4}J(\mathrm{PH})|$ 3.0 Hz); δ(C*H*) 6.17 (m, 3H) and 7.83 (m, 1H). ^{31}P{^{1}H} NMR (121.5 MHz, $(CD_3)_2CO$, 295 K, H_3PO_4 external reference, δ0): δ −3.22 (s) and −15.34 (s).

μ-(Benzene-1,2-dioxo-4-methyl)-bis[methyl(trimethylphosphine)nickel] (2)

1000 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.76 mmol) and 350 mg of 1,2-dihydroxo-4-methylbenzene (2.76 mmol) in 50 ml of ether were stirred for 24 h at 20 °C. An orange–brown precipitate was initially formed and dissolved by further reaction. Some dark solid was filtered off and the solution was evaporated to dryness *in vacuo*. The residue was dissolved in 30 ml of ether and crystallized at −30 °C to give 430 mg of violet–brown crystals (37%), m.p. 76–78 °C (decomp.).

Anal. Calc. for $C_{16}H_{30}Ni_2O_2P_2$ (421.8): C, 42.72; H, 7.17. Found: C, 44.60; H, 7.58%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): Isomer **A** (56%): δ(NiC*H*$_3$) −0.88 (d, 3H, ^{3}J(PH) 6.3 Hz) and −0.65 (d, 3H, ^{3}J(PH) 5.2 Hz); δ(PC*H*$_3$) 1.19 (d, 9H, ^{2}J(PH) 9.9 Hz) and 1.37 (d, 9H, ^{2}J(PH) 10.0 Hz); δ(CC*H*$_3$) 1.80 (s, 3H); δ(C*H*) 4.79 (dd, ^{1}H, ^{3}J(HH) 7.0 Hz, ^{4}J(HH) 1.0 Hz), 6.07 (d, 1H, ^{4}J(HH) 1.0 Hz) and 6.08 (d, 1H, ^{3}J(HH) 7.0 Hz). Isomer **B** (44%): δ(NiC*H*$_3$) −0.89 (d, 3H, ^{3}J(PH) 6.3 Hz) and −0.65 (d, 3H, ^{3}J(PH) 5.2 Hz); δ(PC*H*$_3$) 1.18 (d, 9H, ^{2}J(PH) 9.9 Hz) and 1.38 (d, 9H, ^{2}J(PH) 10.0 Hz); δ(CC*H*$_3$) 1.82 (s, 3H); δ(C*H*) 4.84 (dd, 1H, ^{3}J(HH) 7.0 Hz. ^{4}J(HH) 1.0 Hz), 5.94 (d, 1H, ^{4}J(HH) 1.0 Hz) and 5.95 (d, 1H, ^{3}J(HH) 7.0 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $(CD_3)_2CO$, 295 K, H_3PO_4 external reference, δ0): δ −3.94 (s) and −6.08 (s).

μ-(Benzene-1,2-dioxo-4-methyl)-dimethyl-tris(trimethylphosphine)dinickel (2a)

In a procedure similar to the synthesis of **1a** an orange oil was obtained (40% raw yield).

μ-(Benzene-1,2-dioxo-3-methoxo)-bis[methyl(trimethylphosphine)nickel] (3)

1050 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.90 mmol) and 406 mg of 1,2-hydroxo-3-methoxobenzene (2.90 mmol) in 50 ml of ether were stirred 1 h at 20 °C. A red–brown solid was separated by filtration and the solution was slowly cooled to −30 °C. The dark brown crystals were combined with the first solid to give 500 mg (39% yield), m.p. 98–100 °C (decomp.).

Anal. Calc. for $C_{15}H_{30}Ni_2O_3P_2$ (437.8): C, 41.16; H, 6.91. Found: C, 42.01; H, 7.15%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): Isomer **A** (47%): δ(NiC*H*$_3$) −0.87 (d, 3H, ^{3}J(PH) 6.9 Hz) and −0.55 (d, 3H, ^{3}J(PH) 5.0 Hz); δ(OC*H*$_3$) 3.80 (s, 3H); δ(C*H*) 4.77 (m, 1H), 5.07 (m, 1H) and 5.98 (m, 1H). Isomer **B** (53%): δ(NiC*H*$_3$) −0.82 (d, 3H, ^{3}J(PH) 6.3 Hz) and −0.56 (d, 3H, ^{3}J(PH) 5.0 Hz); δ(OC*H*$_3$) 3.84 (s, 3H); δ(C*H*) 4.82 (m, 1H), 5.05 (m, 1H) and 5.83 (m, 1H).

μ-(Benzene-1,2-dioxo-3-methoxo)-dimethyl-tris(trimethylphosphine)dinickel (3a)

(a) In the synthesis of **3** the red–brown mother liquor was reduced to 40 ml and kept at −30 °C to give 590 mg of brown crystals (40% yield).

(b) 830 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.29 mmol) and 321 mg of 1,2-dihydroxo-3-methoxobenzene (2.29 mmol) in 40 ml of ether containing 0.3 ml trimethylphosphine (2.88 mmol) were kept for 2 h at 20 °C. The volatiles were removed *in vacuo* and the brown residue was extracted with 40 ml of fresh ether over a glass-sinter disc. Crystallization at −30 °C gave 900 mg of brown crystals (76% yield), m.p. 100–102 °C (decomp.).

Anal. Calc. for $C_{18}H_{39}Ni_2O_3P_3$ (513.9): C, 42.07; H, 7.65. Found: C, 40.04; H, 7.41%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): Isomer **A** (35%): δ(NiC*H*$_3$ −1.22 (t, 3H, ^{3}J(PH) 10.5 Hz) and 0.01 (d, 3H, ^{3}J(PH) 5.8 Hz); δ(OC*H*$_3$) 4.05 (s, 3H). Isomer **B** (65%): δ(NiC*H*$_3$) −1.06 (t, 3H, ^{3}J(PH) 10.5 Hz) and −0.18 (d, 3H, ^{3}J(PH) 5.8 Hz); δ(OC*H*$_3$) 3.66 (s, 3H). Isomer **A** and **B**: δ(PC*H*$_3$) 1.25 (m, 27H); δ(C*H*) 6.76 (m, 3H).

μ-(Naphthalene-2,3-dioxo)-dimethyl-tris(trimethylphosphine)dinickel (4a)

On to 420 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.16 mmol) and 186 mg of 2,3-dihydroxonaphthalene (1.16 mmol) at −70 °C were condensed *in vacuo* 50 ml of THF and 0.15 ml of trimethylphosphine (1.44 mmol). After stirring for 3 h at 20 °C the volatiles were removed *in vacuo* and the brown residue was extracted with 80 ml of acetone. From this solution at −50 °C 480 mg of dark yellow crystals were obtained (78% yield), m.p. 138–140 °C (decomp.).

Anal. Calc. for $\mathrm{C_{21}H_{39}Ni_2O_2P_3}$ (533.9): C, 47.25; H, 7.36. Found: C, 46.66; H, 7.26%.

^{1}H NMR (300 MHz, 295 K, $\mathrm{Me_4Si}$ external reference, $\delta 0$): $\delta(\mathrm{NiC}H_3)$ −0.96 (t, 3H, $^3J(\mathrm{PH})$ 10.4 Hz) and −0.18 (d, 3H, $^3J(\mathrm{PH})$ 5.4 Hz); $\delta(\mathrm{PC}H_3)$ 1.29 (t′, 18H, $|^2J(\mathrm{PH})+{}^4J(\mathrm{PH})|$ 3.5 Hz) and 1.23 (d, 9H, $^2J(\mathrm{PH})$ 10.4 Hz); $\delta(\mathrm{C}H)$ 7.22 (m, 6H).

[Methyl-tetrakis(trimethylphosphine)nickel(II)]-[methyl(benzene-1,2-dioxo-4-nitro-O:O)-(trimethylphosphine)nickelate(II)] (5)

On to 720 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.99 mmol) and 308 mg of 1,2-dihydroxo-4-nitrobenzene (1.99 mmol) at −70 °C were condensed *in vacuo* 80 ml of ether and 1.0 ml of trimethylphosphine (excess). The mixture was warmed up under stirring and kept for 1 h at 20 °C. Filtration and cooling to −30 °C gave 870 mg of dark red leaflets (64% yield), m.p. 93–95 °C (decomp.).

Anal. Calc. for $\mathrm{C_{23}H_{54}NNiO_4P_5}$ (681.0): C, 40.57; H, 7.99; N, 2.66. Found: C, 39.32; H, 7.70; N, 1.95%.

^{1}H NMR (300 MHz, $\mathrm{(CD_3)_2CO}$, 193 K, $\mathrm{Me_4Si}$ external reference, $\delta 0$): Cation: $\delta(\mathrm{NiC}H_3)$ −0.18 (quartet, 3H, $^3J(\mathrm{P_{eq}H})$ 12.0 Hz, $^3(\mathrm{P_{ax}H}) < 1$ Hz); $\delta(\mathrm{P_{eq}C}H_3)$ 1.35 (s, 27H); $\delta(\mathrm{P_{ax}C}H_3)$ 1.54 (d, 9H, $^2J(\mathrm{PH})$ 7.5 Hz). Anion isomer **A** (55%): $\delta(\mathrm{NiC}H_3)$ -0.94 (d, 3H, $^3J(\mathrm{PH})$ 7.8 Hz); $\delta(\mathrm{PC}H_3)$ 1.13 (d, 9H, $^2J(\mathrm{PH})$ 9.3 Hz). Anion isomer **B** (45%): $\delta(\mathrm{NiC}H_3)$ −0.97 (d, 3H, $^3J(\mathrm{PH})$ 7.4 Hz); $\delta(\mathrm{PC}H_3)$ 1.13 (d, 9H, $^2J(\mathrm{PH})$ 7.8 Hz). Anion (both isomers): $\delta(\mathrm{C}H)$ 6.64 (m, 3H). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz $\mathrm{(CD_3)_2CO}$, 193 K, $\mathrm{H_3PO_4}$ external reference, $\delta 0$): Cation: $\delta(\mathrm{P_{eq}})$ −22.50 (d, $^2J(\mathrm{PP})$ 51.6 Hz); $\delta(\mathrm{P_{ax}})$ 2.11 (quartet, $^2J(\mathrm{PP})$ 51.6 Hz). Anion: $\delta(\mathrm{P})$ −22.50 (s) and −2.28 (s).

[Methyl-tetrakis(trimethylphosphine)nickel(II)]-[methyl(benzene-1,2-dioxo-3-formyl-O:O)-(trimethylphosphine)nickelate(II)] (6)

On to 510 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.41 mmol) and 194 mg of 1,2-dihydroxo-3-formylbenzene (1.41 mmol) at −70 °C were condensed *in vacuo* 50 ml of ether and 1.0 ml of trimethylphosphine (excess). After stirring the mixture for 1 h at 20 °C the volatiles were removed *in vacuo* and the oily residue was extracted with 40 ml of ether. At −30 °C an orange oil was deposited that crystallized after four days: 690 mg orange crystals (75% yield), m.p. 85–87 °C (decomp.).

Anal. Calc. for $\mathrm{C_{24}H_{55}Ni_2O_3P_5}$ (664.0): C, 43.41; H, 8.35. Found: C, 42.97; H, 8.50%.

^{1}H NMR (300 MHz, $\mathrm{(CD_3)_2CO}$, 213 K, $\mathrm{Me_4Si}$ external reference, $\delta 0$): Cation: $\delta(\mathrm{NiC}H_3)$ 0.16 (quintet, 3H, $^3J(\mathrm{PH})$ 9.1 Hz); $\delta(\mathrm{PC}H_3)$ 1.40 (s, 36 H). Anion isomer **A** (35%): $\delta(\mathrm{NiC}H_3)$ −0.96 (d, 3H, $^3J(\mathrm{PH})$ 6.9 Hz); $\delta(\mathrm{PC}H_3)$ 1.14 (d, 9H, $^2J(\mathrm{PH})$ 9.5 Hz); $\delta(\mathrm{C}H\mathrm{O})$ 10.40 (s, 1H). Anion isomer **B** (65%): $\delta(\mathrm{NiC}H_3)$ −0.95 (d, 3H, $^3J(\mathrm{PH})$ 6.9 Hz); $\delta(\mathrm{PC}H_3)$ 1.16 (d, 9H, $^2J(\mathrm{PH})$ 9.5 Hz); $\delta(\mathrm{C}H\mathrm{O})$ 10.20 (s, 1H). Anion (both isomers): $\delta(\mathrm{C}H)$ 6.14 (m, 3H). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{(CD_3)_2CO}$, 193 K, $\mathrm{H_3PO_4}$ external reference, $\delta 0$): Cation: $\delta(\mathrm{P_{eq}})$ −22.05 (d, $^2J(\mathrm{PP})$ 51.6 Hz); $\delta(\mathrm{P_{ax}})$ 2.56 (quartet, $^2J(\mathrm{PP})$ 51.6 Hz). Anion: δ −1.88 (s) and −1.75 (s).

[Methyl-tetrakis(trimethylphosphine)nickel(II)] [methyl(benzene-1,2-dioxo-4-formyl-O:O)-(trimethylphosphine)nickelate(II)] (7)

On to 570 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.58 mmol) and 218 mg of 1,2-dihydroxo-4-formylbenzene (1.58 mmol) at −70 °C were condensed *in vacuo* 100 ml of ether and 1.0 ml of trimethylphosphine (excess). After stirring for 3 h at 20 °C the orange–brown solution was filtered and cooled to −30 °C to give 770 mg of red crystals (74% yield), m.p. 93–95 °C (decomp.).

Anal. Calc. for $\mathrm{C_{24}H_{55}Ni_2O_3P_5}$ (664.0): C, 43.41; H, 8.35. Found: C, 42.80; H, 8.70%.

^{1}H NMR (300 MHz, $\mathrm{(CD_3)_2CO}$, 193 K, $\mathrm{Me_4Si}$ external reference, $\delta 0$): Cation: $\delta(\mathrm{NiC}H_3)$ −0.19 (quartet, 3H, $^3J(\mathrm{PH})$ 12.2 Hz); $\delta(\mathrm{PC}H_3)$ 1.33 (s, 27H) and 1.50 (s, 9H). Anion isomer **A** (54%): $\delta(\mathrm{NiC}H_3)$ −1.00 (d, 3H, $^3J(\mathrm{PH})$ 7.4 Hz); $\delta(\mathrm{C}H\mathrm{O})$ 9.25 (s, 1H). Anion isomer **B** (46%): $\delta(\mathrm{NiC}H_3)$ −0.97 (d, 3H, $^3J(\mathrm{PH})$ 7.6 Hz); $\delta(\mathrm{PC}H_3)$ 1.09 (d, 9H, $^2J(\mathrm{PH})$ 9.7 Hz); $\delta(\mathrm{C}H\mathrm{O})$ 9.24 (s, 1H). Anion (both isomers): $\delta(\mathrm{C}H)$ 6.37 (m, 3H). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{(CD_3)_2CO}$, 193 K, $\mathrm{H_3PO_4}$ external reference, $\delta 0$): Cation: $\delta(\mathrm{P_{eq}})$ −22.12 (d, $^2J(\mathrm{PP})$ 52.6 Hz); $\delta(\mathrm{P_{ax}})$ 2.55 (quartet, $^2J(\mathrm{PP})$ 52.6 Hz). Anion: δ −2.14 (s) and −1.89 (s).

μ-(Benzene-1,3-dioxo)-bis[methyl-bis(trimethylphosphine)nickel]·methanol (8a)

On to 530 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.47 mmol) and 1.61 mg of resorcinol (1.47 mmol) at −70 °C were condensed *in vacuo* 50 ml of ether and 0.5 ml of trimethylphosphine (4.8 mmol). The mixture was warmed up to 20 °C under stirring.

After filtration the red–brown solution was concentrated *in vacuo* to 30 ml and cooled to −50 °C. A total of 650 mg of orange–brown crystals was obtained (79% yield), m.p. 136–138 °C (decomp.).

Anal. Calc. for $C_{20}H_{46}Ni_2O_2P_4$ (559.9): C, 42.90; H, 8.28. Found: C, 42.57; H, 8.43%.

^{1}H NMR (300 MHz, $(CD_3)_2CO$, 295 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.24 (s, 6H); δ(PCH_3) 1.13 (s, 36H); δ(*CH4.6*) 6.11 (dd, 2H, ^3J(HH) 7.8 Hz, ^4J(HH) 2.2 Hz); δ(*CH5*) 6.47 (t, 1H, ^3J(HH) 7.8 Hz); δ(*CH2*) 6.92 (t, 1H, ^4J(HH) 2.2Hz).

μ-(Benzene-1,3-dioxo-5-methoxo)-bis[methylbis(trimethylphosphine)nickel] (9a)

On to 1000 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.76 mmol) and 387 mg of 5-methoxoresorcinol (2.76 mmol) at −70 °C were condensed *in vacuo* 60 ml of ether and 0.6 ml of trimethylphosphine (5.76 mmol). Under stirring the mixture was brought to 20 °C within 1 h. After filtration and cooling to −30 °C, 1460 mg of orange–brown crystals were obtained (85% yield), m.p. 108–110 °C (decomp.).

Anal. Calc. for $C_{22}H_{52}Ni_2O_4P_4$ (622.0): C, 42,48; H, 7.94. Found: C, 42.39; H, 8.14%.

^{1}H NMR (300 MHz, C_6D_6, 295 K, Me_4Si external reference, δ0): δ(NiCH_3) −0.84 (s, 6H); δ(PCH_3) 1.10 (s, 36H); δ(OCH_3) 3.80 (s, 3H); δ(CH_3O*H*) 5.14 (m, 1H); δ(*CH4.6*) 6.66 (s, 2H); δ(*CH2*) 7.14 (s, 1H).

μ-(Benzene-1,3-dioxo-2-nitro)-bis[methylbis(trimethylphosphine)nickel] (10a)

On to 730 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.02 mmol) and 313 mg of 2-nitroresorcinol (2.02 mmol) at −70 °C were condensed *in vacuo* 50 ml of ether and 0.6 ml of trimethylphosphine (5.78 mmol). The mixture was stirred 3 h at −20 °C and changed colour from yellow–brown to light yellow and finally to dark brown. Some solid was filtered off and the solution was kept at −30 °C to give 550 mg of dark brown cubes (45% yield), decomp. >118 °C.

Anal. Calc. for $C_{20}H_{45}NNiO_4P_2$ (604.9): C, 39.71; H, 7.50; N, 2.31. Found: C, 39.44; H, 7.61; N, 2.19%.

^{1}H NMR (60 MHz, $(CD_3)_2CO$, 308 K, Me_4Si external reference, δ0): δ(NiCH_3) −1.18 (s, 6H); δ(PCH_3) 1.13 (s, 36H); δ(C*H*) 6.66 (m, 3H).

X-ray data collection and reduction: complex 3a

TABLE 1. Crystal data and details of data collection and structure refinement for **3a**

Formula	$C_{18}H_{39}Ni_2O_3P_3$
Formula weight	513.85
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.784(4)
b (Å)	9.095(2)
c (Å)	16.796(4)
α (°)	96.83(2)
β (°)	101.99(3)
γ (°)	102.85(3)
V (Å^3)	1260.5(2)
Z	2
D_{calc} (g/cm^3)	1.353
μ (Mo Kα) (cm^{-1})	16.18
Temperature (°C)	20±2
Scan method	ω
Data collection range, θ (°)	$1 \leq \theta \leq 24$
No. reflections measured	4085
No. unique data with $(I) > 3\sigma(I)$	2939
No. parameters refined	247
R[a]	0.0398
R_w[b]	0.0439

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

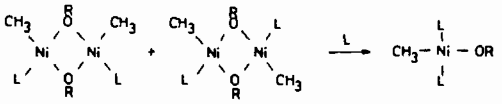
The selected crystal that belongs to the triclinic system, was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer. Matrix transformation and least-squares fit of settings angles of 25 reflections led to the cell constants given in Table 1. Data reduction was performed [5]. Intensity standards showed a linear decrease of about 3%. Empirical absorption corrections were made [6]. All non-zero reflections (2939) were used in the subsequent calculations.

Structure solution and refinement

The structure was solved by the heavy-atom method. The position of the nickel atoms was revealed from a Patterson map. Least-squares refinement was performed when all non-hydrogen atoms were located. Hydrogen atoms were refined isotropically. All other atoms were refined anisotropically. The last refinement cycle led to $R = 0.040$ and $R_w = 0.044$. Atom coordinates are given in Table 2.

Results and discussion

Non-chelating phenolate ligands with $NiCH_3(PMe_3)$ moieties form μ-phenoxo bridged dinuclear complexes. These are broken up by trimethylphosphine according to eqn. (1)



(1)

R = aryl, L = PMe_3

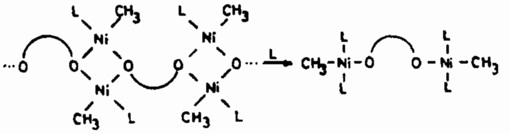
giving mononuclear methyl(phenolato)nickel compounds. With difunctional phenols formation of coordination polymers and, in the presence of phosphine, breakup into dinuclear complexes is expected

TABLE 2. Positional parameters for non-hydrogen atoms of **3a**[a]

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni(1)	0.12712(9)	0.39068(9)	0.15017(5)
C(1)	−0.0629(8)	0.2246(8)	0.1270(4)
P(1)	0.1611(2)	0.3265(2)	0.0319(1)
C(11)	−0.005(1)	0.245(1)	−0.0562(4)
C(12)	0.278(1)	0.4781(9)	−0.0062(5)
C(13)	0.277(1)	0.184(1)	0.0337(5)
Ni(2)	−0.01678(9)	0.33266(9)	0.32606(5)
C(2)	−0.1598(8)	0.2162(9)	0.3832(5)
P(2)	0.1492(2)	0.1845(2)	0.3533(1)
C(21)	0.137(1)	0.068(1)	0.4305(6)
C(22)	0.152(1)	0.056(1)	0.2665(5)
C(23)	0.3597(9)	0.290(1)	0.3909(7)
P(3)	−0.1860(2)	0.4752(2)	0.3024(1)
C(31)	−0.124(1)	0.635(1)	0.2526(6)
C(32)	−0.236(1)	0.565(1)	0.3924(5)
C(33)	−0.3760(9)	0.377(1)	0.2329(5)
O(1)	0.1250(5)	0.4423(4)	0.2640(2)
O(2)	0.3076(5)	0.5630(5)	0.1738(3)
O(3)	0.5666(6)	0.8291(6)	0.2419(4)
C(9)	0.504(1)	0.888(1)	0.1743(6)
C(3)	0.2380(7)	0.5734(6)	0.3012(4)
C(4)	0.2616(8)	0.6416(7)	0.3824(4)
C(5)	0.3826(9)	0.7737(8)	0.4147(5)
C(6)	0.4809(8)	0.8367(8)	0.3668(5)
C(7)	0.4574(7)	0.7675(7)	0.2862(4)
C(8)	0.3360(7)	0.6345(6)	0.2506(4)

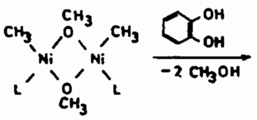
[a] e.s.d.s. given in parentheses.

according to eqn. (2). This type of behaviour has been found with 4-hydroxobenzoic acid [3].



(2)

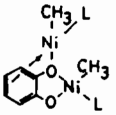
Surprisingly, 1,2-hydroxobenzene and dimeric methyl(methoxo)(trimethylphosphine)nickel in a reaction according to eqn. (3) gave unexpected products under partial decomposition.



$$\underset{\mathbf{1}}{(C_6H_4OO)Ni_2(CH_3)_2L_2} + \underset{\mathbf{1a}}{(C_6H_4OO)Ni_2(CH_3)_2L_3} + Ni + \dots \quad (3)$$

In solution the reactants first produce a brown solid. This is redissolved within 20 h at 20 °C to give a dark red solution, from which **1** and **1a** are crystallized in fractions.

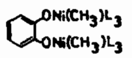
Addition of phosphine prevents decomposition and gives **1a** exclusively. Both compounds are extremely sensitive to oxygen in solution and in the crystalline state. In the IR spectrum of **1** all typical bands of the pyrocatechol anion are absent in the regions of aromatic fingerprint. Two low intensity bands at 1530 and 1496 cm,$^{-1}$ are supposed to indicate coordinated C=C functions. The magnetic resonances of ring protons are shifted to higher field showing a pattern of two doublets (at 6.04 and 6.19 ppm) and two triplets (at 4.97 and 5.05 ppm) each containing $^2J(HH) = 6.5$ Hz which is consistent with a π-olefin type coordination of one Ni center in **1**.



1

At 20 °C crystals of **1** slowly decompose to nickel and **1a** as the main product, as expected from eqn. (2). Consequently, **1a** formed in 80% yield when one equivalent of trimethylphosphine is supplied in a synthesis according to eqn. (3). Excess phosphine is tolerated. Although this gives a deep red colour to the solutions as expected for equilibrium (4) **1a** is exclusively crystallized from the system.

$$\mathbf{1a} \underset{-L}{\overset{+L}{\rightleftharpoons}} (C_6H_4OO)Ni_2(CH_3)_2L_4 \underset{-L}{\overset{+L}{\rightleftharpoons}} (C_6H_4OO)Ni_2(CH_3)_2L_5 \underset{-L}{\overset{+L}{\rightleftharpoons}}$$



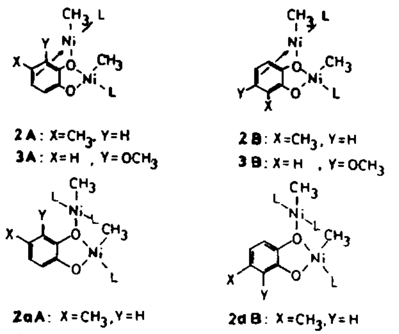
(4)

4-Methyl- and 3-methoxo-pyrocatechols form analogous compounds **2** and **3** in a synthesis according to eqn. (3) within 24 h. After prolonged reaction times the yields drop below 30% because of decomposition that increases the yields of **2a** and **3a**. Again excess phosphine gives deeply coloured solutions, but no ligand-rich compound as in eqn. (4) is crystallized.

IR spectra of **2** and **3** contain strong ν(C=C) bands at 1480 and 1462 cm^{-1} (**2**) and at 1465 cm^{-1} (**3**). ^{1}H NMR spectra display CH signals with high-field shifts and couplings similar to **1**. A striking difference lies in the presence of twice the number of all signals for **2**, **2a**, **3** and **3a**, respectively, that arise from isomers **A** and **B** as given in Scheme 1.

Structure of 3a

Unstable compounds **1**, **2** and **3** gave no crystals that would appear suitable for X-ray diffraction. **2a** was obtained as an oil. Only **3a** upon slow cooling was obtained from acetone as dark brown cubes. A specimen 0.15 × 0.15 × 0.2 mm was fixed in a 0.3 mm quartz capillary and sealed under argon. **3a** crystallizes in the triclinic space group $P\bar{1}$. No second sort of crystals has been detected under the microscope.



Scheme 1. Isomeric methylnickel pyrocatecholates.

TABLE 3. Important distances (Å) and angles (°) of **3a**

Bond distances			
Ni1–C1	1.920(7)	P3–C31	1.80(2)
Ni1–P1	2.104(2)	P3–C32	1.810(9)
Ni1–O1	1.919(5)	P3–C33	1.796(7)
Ni1–O2	1.900(4)	O1–C3	1.356(6)
P1–C11	1.795(7)	O2–C8	1.320(7)
P1–C12	1.796(9)	O3–C9	1.38(1)
P1–C13	1.82(2)	O3–C7	1.395(9)
Ni2–C2	1.943(8)	C3–C4	1.382(9)
Ni2–P2	2.213(2)	C3–C8	1.406(9)
Ni2–P3	2.187(2)	C4–C5	1.380(8)
Ni2–O1	1.966(4)	C5–C6	1.38(1)
P2–C21	1.78(2)	C6–C7	1.38(2)
P2–C22	1.77(1)	C7–C8	1.395(8)
P2–C23	1.823(7)		
Bond angles			
C1–Ni1–P1	90.2(2)	C21–P2–C23	98.9(5)
C1–Ni1–O1	93.5(2)	C22–P2–C23	102.8(6)
C1–Ni1–O2	176.7(3)	Ni2–P3–C31	115.9(3)
P1–Ni1–O1	171.8(1)	Ni2–P3–C32	116.0(3)
P1–Ni1–O2	91.5(1)	Ni2–P3–C33	114.2(3)
O1–Ni1–O2	85.3(2)	C31–P3–C32	102.4(4)
Ni1–P1–C11	122.2(4)	C31–P3–C33	101.3(5)
Ni1–P1–C12	114.4(3)	C32–P3–C33	105.3(4)
Ni1–P1–C13	110.5(3)	Ni1–O1–Ni2	128.4(2)
C11–P1–C12	101.7(4)	Ni1–O1–C3	111.2(4)
C11–P1–C13	102.7(4)	Ni2–O1–C3	120.5(4)
C12–P1–C13	103.2(4)	Ni1–O2–C8	111.0(4)
C2–Ni2–P2	89.4(3)	C9–O3–C7	115.9(7)
C2–Ni2–P3	88.4(3)	O1–C3–C4	124.4(6)
C2–Ni2–O1	177.3(2)	O1–C3–C8	114.2(5)
P2–Ni2–P3	177.79(9)	C4–C3–C8	121.5(5)
P2–Ni2–O1	89.7(1)	C3–C4–C5	119.7(7)
P3–Ni2–O1	92.5(1)	C4–C5–C6	120.4(7)
Ni2–P2–C21	121.8(4)	C5–C6–C7	119.7(6)
Ni2–P2–C22	114.2(4)	O3–C7–C6	117.6(6)
Ni2–P2–C23	113.6(3)	O3–C7–C8	120.2(7)
C21–P2–C22	103.3(5)	C6–C7–C8	122.1(7)
O2–C8–C3	118.3(4)	C3–C8–C7	116.8(6)
O2–C8–C7	124.9(6)		

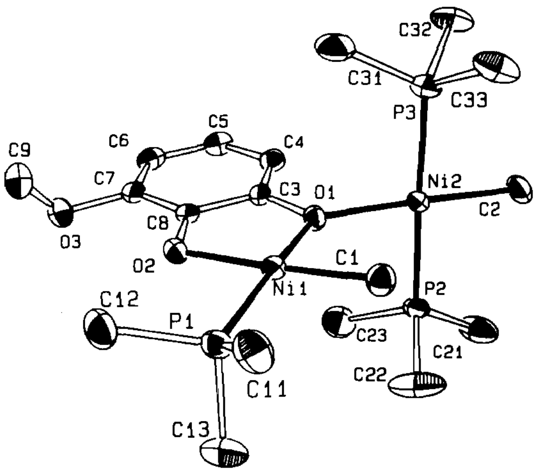


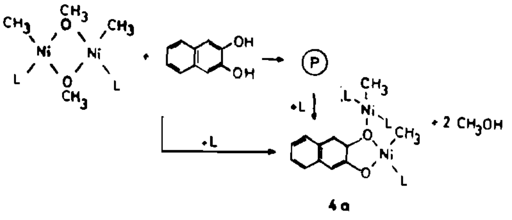
Fig. 1. Molecular structure of **3a** (isomer A).

TABLE 4. Calculated planes in compound **3a**

Plane 1:	Ni1O1O2 $-0.7262x+0.6396y-0.2519z-1.4742=0$
Plane 2:	Ni2O1P2 $-0.2048x-0.5094y-0.8358z+5.0388=0$
Dihedral angle between plane 1 and 2: 88.08 ± 0.14°	

Figure 1 displays the molecular structure of **3a** (isomer A). The molecule contains two nickel atoms in square planar surroundings. Table 3 gives some bond distances and angles. Ni1 with its donor atoms (P1, O2, O1, C1) lies in a plane that is almost perpendicular (Table 4) to that of Ni2 (with P2, O1, P3, C2). The oxygen atom belonging to both planes is in a trigonal planar environment (sum of angles at O1: 360°). Its *trans*-influence causes a long NiC bond (Ni2C2 1.943(8) Å) and a short NiP bond (Ni1P1 2.104(2) Å) while the other NiC bond (Ni1C1 1.920(7) Å) is short as in methyl(8-oxoquinolato)(trimethylphosphine)nickel [5] (NiC 1.917(5) Å).

While only circumstantial evidence points to C6 and C7 (Fig. 1) supporting π-olefin coordination in **3** (and likewise in **1** and **2**) it was of interest to learn how 2,3-hydroxonaphthalene would react. According to eqn. (5) an orange coordination polymer is formed that, in the presence of trimethylphosphine, gives **4a** in virtually quantitative yield.

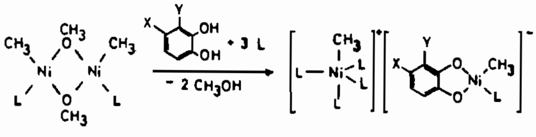


(5)

P = methylnickel polymer

There was no indication of a dinuclear intermediate **4** and **4a**, like **1a–3a**, cannot hold additional phosphine ligands in a crystal.

This situation is quite different with strongly accepting nitro or formyl groups as substituents X or Y. 2,3-Dihydroxobenzaldehyde or 3,4-dihydroxobenzaldehyde or 4-nitro-pyrocatechol, in a reaction according to eqn. (3) at −70 °C, give mainly decomposition products from which dark red crystals may be recovered in about 20% yield. Decomposition is not fully prevented in reactions where the ratio $PMe_3/Ni = 2$, but $PMe_3/Ni = 2.5$ is sufficient for high yield syntheses according to eqn. (6).



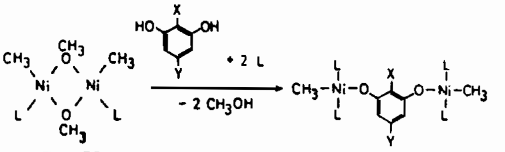
(6)

$L = PMe_3$
5: $X = H$, $Y = NO_2$
6: $X = CHO$, $Y = H$
7: $X = H$, $Y = CHO$

As shown by their solubility in polar solvents and by dynamic ^1H and ^{31}P NMR spectra all three complexes contain the methyltetrakis(trimethylphosphine)nickel cation [6] and new methyl(dioxobenzene)(trimethylphosphine)nickel anions.

The square planar anion geometry gives rise to two isomers of **5**, **6** and **7** with different orientations of substituents with respect to the methylnickel function, that are present in solution in about equal parts. All attempts to remove phosphine ligands from **5**, **6** or **7** resulted in decomposition.

Surprisingly, resorcinol derivatives with or without methoxo or nitro substituents afford only one type of complex according to eqn. (7).



(7)

8a: $X = Y = H$
9a: $X = H$, $Y = OCH_3$
10a: $X = NO_2$, $Y = H$

Without additional trimethylphosphine 1,3-dihydroxo-2-nitrobenzene causes decomposition while 1,3-dihydroxobenzene and 1,3-dihydroxo-5-methoxobenzene form orange–brown coordination polymers that may be cleaved according to eqn. (2) and are not formed in the early stages of the reaction according to eqn. (7). Resorcinols appear to react with both hydroxo groups just as phenols do. No dinuclear intermediates and no ionic species formed through uptake and dismutation of phosphine ligands have been observed.

Conclusions

Dioxobenzene dianions when coordinated to methylnickel moieties display a rich coordination chemistry depending on their structure and the concentration of trimethylphosphine donors. With a ratio $PMe_3/Ni = 1$, 1,2-dioxobenzenes act as μ-O:O-bridging anions that probably exert an additional π-olefin type coordination in positions 4 and 5 of the aromatic ring. If these positions are blocked as in the naphthalene-2,3-dioxo dianion or if $PMe_3/Ni = 1.5$ the anion relaxes to a μ-O:O-bridging conformation where one oxygen atom is sp^2 hybridized. Further uptake of trimethylphosphine requires nitro or formyl substituents and leads to methylnickel anions containing chelating dioxo ligands and methyltetrakis(trimethylphosphine)nickel counter-ions. Independent of donor or acceptor substituents 1,3-dioxobenzenes form dinuclear methylnickel compounds with a ratio $PMe_3/Ni = 2$.

Acknowledgements

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