# Methylnickel compounds containing bridging and monodentate carboxylate ligands*

Hans-F. Klein, Thomas Wiemer
*Eduard-Zintl-Institut für Anorganische Chemie der Technischen Hochschule Darmstadt, Hochschulstrasse 10, D-6100 Darmstadt (FRG)*

Michèle Dartiguenave and Yves Dartiguenave
*Laboratoire de Chimie Inorganique, Université Paul Sabatier, 118 route de Narbonne, F-31007 Toulouse-Cédex (France)*

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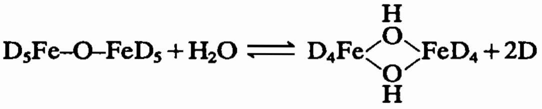
## Abstract

Dinuclear methylnickel carboxylates $[NiMe(OOCR)(PMe_3)]_2$ (R = cyclohexyl (**1**); $CH(C_6H_5)_2$ (**2**); $C(C_6H_5)_3$ (**3**); 9-anthracenyl (**4**); bicyclo[3.2.2]nonane-1-yl (**5**); $C_6H_5$ (**6**); 2-$NH_2$-$C_6H_4$ (**7**); 4-OH-$C_6H_4$ (**8**); 1-naphthyl (**9**); 2-naphthyl (**10**); $CF_3$ (**11**); $CH_2Cl$ (**12**); $CHCl_2$ (**13**); $CH_2Br$ (**14**)) were prepared by reacting $[NiMe(OMe)(PMe_3)]_2$ and the corresponding carboxylic acid. Spectroscopic data indicate $\mu$-carboxylato ligands in eight-membered metallocycles $(NiOCO)_2$, while mononuclear methylnickel carboxylates $NiMe(OOCR)(PMe_3)_2$ (**1a**, **2a**, **4a**–**10a**, **12a**–**14a**) contain unidentate carboxylate anions. Upon reaction with trimethylphosphine **11** forms an ionic methylnickel complex $[NiMeL_4]^+CF_3COO^-$ (**15**) rather than **11a**. Compound **6** crystallizes in the monoclinic space group $C_2/c$ with $a = 12.327(3)$, $b = 12.885(4)$, $c = 16.495(6)$ Å, $\beta = 102.93(2)°$, $V = 2553(2)$ Å$^3$, $Z = 4$. Final discrepancy indices are $R = 0.0631$ and $R_w = 0.0659$. The molecule **6** contains two square planar nickel centres (Ni–C = 1.907(7), Ni–P = 2.119(2), Ni–O = 1.955(5) and 1.919(6) Å) with parallel coordination planes (non-bonding Ni–Ni = 2.865(2) Å).

## Introduction

Nature has utilized ($\mu$-oxo)bis($\mu$-carboxylato) units in hemerythrin for reversible oxygenation reactions, and when the structure of methemerythrine was detected a number of ($\mu$-oxo)bis($\mu$-carboxylato)-Fe(III) synthetic models were developed [1]. In these investigations the role of $\mu$-carboxylato groups as auxiliary ligands in iron complexes has received less attention than the chemical nature of the Fe–O–Fe unit. Apparently one exchange of neutral or anionic ligands D in octahedral Fe(III) compounds can favour bis($\mu$-hydroxo)iron(III) complexes in an equilibrium [2].



$$D_5Fe{-}O{-}FeD_5 + H_2O \rightleftharpoons D_4Fe(\mu\text{-}OH)_2FeD_4 + 2D$$

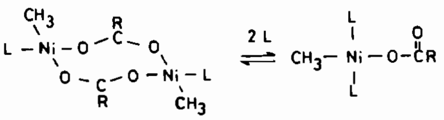
D = O-donor function

In general, coordination or dissociation of anionic or neutral molecules often induces dramatic changes in reactivity and in the catalytic activity of metal centres due to different coordination numbers.

At fixed coordination numbers different coordination modes of bidentate ligands like carboxylate anions are expected to cause smaller effects.

For instance little is known about the role of carboxylate ions that accumulate in homogeneous carboxylation reactions of olefins or in the synthesis of acrylic acid from acetylene and carbon monoxide with $Ni(CO)_4$ as catalyst [3].

In dinuclear methylnickel carboxylates phosphines reversibly convert both carboxylate bridges to monodentate ligands according to eqn. (1) with retention of square planar coordination at the nickel atom [4].



(1)

For R = H a dramatic change in reactivity is observed. Spontaneous decarboxylation proceeds below 0 °C in the mononuclear complex, while decomposition of the dinuclear methylnickel formate requires heating above 85 °C [4a].

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*Th. Wiemer, Doctoral Thesis, TH Darmstadt, 1991.

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This example illustrates how metal-induced fragmentations of organonickel functions can depend on the coordination mode of carboxylate ions.

We have investigated the syntheses and properties of mononuclear and dinuclear methylnickel compounds containing bridging and monodentate O-donor functions. Haloalkyl groups were tested for compatibility with Ni–C bonds and amino groups were introduced for competition with O-bridging donors as in natural systems.

## Experimental

### *General procedures and materials*

All air-sensitive and volatile material was handled by standard vacuum techniques and kept under argon. Microanalyses were carried out in the microanalytical laboratory of the institute for organic chemistry, highly air-sensitive samples were sent to Malissa and Reuter, Microanalytical Laboratory, D-5250 Engelskirchen.

Melting points (m.p.) and decomposition temperatures were obtained from sealed capillaries under argon and are uncorrected.

Trimethylphosphine [5] was prepared from triphenylphosphite and methylmagnesium chloride. Other chemicals (Merck-Schuchardt) were used as purchased but degassed prior to synthesis.

IR spectra were recorded on a Perkin-Elmer type 397 spectrophotometer; $^1$H NMR were obtained on a Varian EM 360 (60 MHz) and Bruker WM 300 (300 MHz), where $^{13}$C (75.5 MHz) and $^{31}$P (121.5 MHz) NMR spectra were also recorded.

### *Di-μ(cyclohexanecarboxylato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (1)*

500 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ [4a] (1.38 mmol) and 354 mg of cyclohexanecarboxylic acid (2.76 mmol) were combined in 70 ml of ether to give a red–brown solution. After 1 h this was filtered and cooled to −30 °C: orange–brown crystals (700 mg, 92%), m.p. 114–117 °C (decomp.).

*Anal.* Calc. for $C_{22}H_{46}Ni_2O_4P_2$ (553.9): C, 47.70; H, 8.37. Found: C, 46.98; H, 8.44%.

$^1$H NMR (60 MHz, $CD_2Cl_2$, 308 K, $Me_4Si$ external reference, $\delta$0): $\delta(NiCH_3)$ −0.68 (d, 6H, $^3J$(PH) 6.4 Hz); $\delta(PCH_3)$ 1.40 (d, 18H, $^2J$(PH) 10.0 Hz); $\delta(CH_2)$ 1.48 (m, 22H).

### *Di-μ(diphenylacetato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (2)*

610 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.69 mmol) and 716 mg of diphenylacetic acid in 80 ml of ether were kept at 20 °C for 1 h. The solution was concentrated to 5 ml and 60 ml of pentane were added. At −30 °C 730 mg of brown crystals were obtained (60% yield), m.p. 93–95 °C (decomp.).

*Anal.* Calc. for $C_{36}H_{46}Ni_2O_4P_2$ (722.1): C, 59.88; H, 6.42. Found: C, 59.50; H, 6.49%.

$^1$H NMR (300 MHz, $(CD_3)_2CO$, 295 K, $Me_4Si$ external reference, $\delta$0): $\delta(NiCH_3)$ −0.65 (d, 6H, $^3J$(PH) 6.2 Hz); $\delta(PCH_3)$ 1.09 (d, 18H, $^2J$(PH) 10.0Hz); $\delta(CH)$ 4.67 (s, 2H), d(CH aromat.) 7.18 (m, 20H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $(CD_3)_2CO$, 295 K, $CD_3$ (acetone-d6) internal reference, $\delta$ 29.8): $\delta(NiCH_3)$ −14.0 (d, $^2J$(CP) 45.3 Hz); $\delta(PCH_3)$ 13.49 (d, $^1J$(CP) 29.7 Hz); $\delta(CH)$ 60.85(s); $\delta(CO_2)$ 180.3(s).

### *Di-μ(triphenylacetato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (3)*

Solutions of 500 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.52 mmol) in 20 ml of ether and 876 mg of triphenylacetic acid (3.04 mmol) in 30 ml of ether were combined at 20 °C under stirring. After 1 h an orange–brown solid was filtered and washed with ether: 125 mg (94% yield), m.p. 121–123 °C (decomp.).

*Anal.* Calc. for $C_{48}H_{54}Ni_2O_4P_2$ (874.3): C, 65.94; H, 6.22. Found: C, 65.56; H, 6.49%.

$^1$H NMR (60 MHz, THF-d8, 308 K, $Me_4Si$ external reference, $\delta$0): $\delta(NiCH_3)$ −0.79 (d, 6H, $^3J$(PH) 6.2 Hz); $\delta(PCH_3)$ 0.92 (d, 18H, $^2J$(PH) 10.0 Hz); $\delta(CH)$, 7.14 m (30H).

### *Di-μ(9-anthracenecarboxylato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (4)*

510 mg of $[NiCH_3(OCH_3)(PMe)_3]_2$ (1.41 mmol) and 625 mg of 9-anthracenecarboxylic acid (2.82 mmol) in 50 ml of THF were kept for 1 h at 20 °C. The red–brown solution was concentrated *in vacuo* to 10 ml and diluted with 50 ml of pentane to give yellow–brown microcrystals: 900 mg (86% yield), m.p. 139–141 °C (decomp.).

*Anal.* Calc for $C_{38}H_{42}Ni_2O_4P_2$ (742.1): C, 61.50; H, 5.70. Found: C, 61.82; H, 5.93%.

$^1$H NMR (60 MHz, toluene-d8, 308 K, $Me_4Si$ external reference, $\delta$0): $\delta(NiCH_3)$ 0.08 (d, 6H, $^3J$(PH) 6.0 Hz), 0.93 (d, 18H, $^2J$(PH) 9.4 Hz); $\delta(CH)$ 7.77 (m, 18H).

### *Di-μ(bicyclo{3.2.2.}nonane-1-carboxylato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (5)*

630 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.74 mmol) and 586 mg of bicyclo{3.2.2}nonane-1-carboxylic acid (3.48 mmol) in 80 ml of ether were kept at 20 °C for 1 h. Filtration and cooling to −70 °C afforded 1030 mg of red–brown crystals (93% yield), m.p. 158–161 °C (decomp.).

*Anal.* Calc. for $C_{28}H_{54}Ni_2O_4P_2$ (634.1): C, 53.04; H, 8.58. Found: C, 52.81; H, 8.88%.

$^1$H NMR (300 MHz, $C_6D_6$, 295 K, $Me_4Si$ external reference, δ0): δ(Ni$CH_3$) −0.41 (d, 6H, $^3J$(PH) 6.8 Hz); δ(P$CH_3$) 0.86 (d, 18H, $^2J$(PH) 10.0 Hz); δ($CH_2$) 1.74 (m, 30H). $^{13}C\{^1H\}$ NMR (75.5 MHz, 295 K, $C_6D_6$, benzene-d6 internal reference, δ128.00): δ(Ni$CH_3$) −14.14 (d, $^2J$(PC) 43.1 Hz); δ(P$CH_3$) 13.31 (d, $^1J$(PC) 27.6 Hz); δ(CH) 22.47 (s), 26.28 (s), 29.84 (d, $^4J$(PC) 9.0 Hz), 31.16 (s), 34.79 (s), 36.13 (s), 44.51 (s); δ($CO_2$) 187.61 (s).

*Di-μ(benzoato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (6)*

800 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.05 mmol) in 50 ml of THF at −70 °C were reacted with 505 mg of benzoic acid (4.10 mmol) by slow warming up to 20 °C. The red–brown solution was filtered and evaporated to dryness. The raw product was crystallized from 50 ml of acetone to give 800 mg of red–brown crystals (72% yield), decomp. > 170 °C.

*Anal.* Calc. for $C_{12}H_{34}Ni_2O_4P_2$ (541.9): C, 48.76; H, 6.32. Found: C, 48.65; H, 6.68%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, $Me_4Si$ external reference, δ0): δ(Ni$CH_3$) −0.05 (d, 6H, $^3J$(PH) 6.5 Hz); δ(P$CH_3$) 0.97 (d, 18H, $^2J$(PH) 10.0 Hz); δ(CH) 7.07 (m, 2H), 7.16 (m, 4H), 8.27 (m, 4H).

*Di-μ(2-aminobenzoato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (7)*

370 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.02 mmol) in 50 ml of THF and 280 mg of 2-aminobenzoic acid (2.04 mmol) in 20 ml of THF were combined at −70 °C to give an orange–brown solution. The volatiles were removed *in vacuo* and the residue was extracted with 50 ml of ether over a glass-sinter disc. Crystallization at −30 °C gave 500 mg of orange–brown crystals (85% yield), m.p. 147–149 °C (decomp.).

*Anal.* Calc. for $C_{22}H_{36}N_2Ni_2O_4P_2$ (571.9): C, 46.20; H, 6.35. Found: C, 46.07; H, 6.49%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, benzene-d5 internal reference, δ7.27): δ(Ni$CH_3$) −0.13 (d, 6H, $^3J$(PH) 4.2 Hz); δ(P$CH_3$) 0.94 (d, 18H, $^2J$(PH) 9.2 Hz); δ(N$H_2$) 5.44 (s (broad), 4H); δ(*CH-3*) 6.30 (dd, 2H, $^3J$(HH) 8 Hz); δ(*CH-5*) 6.62 (ddd, 2H, $^3J$(HH) 8 Hz); δ(*CH-4*) 7.12 (ddd, 2H, $^3J$(HH) 8 Hz); δ(*CH-6*) 8.34 (dd, $^3J$(HH) 8 Hz).

*Poly-μ(4-oxobenzoato-O:O)-[trans-methyl(trimethylphosphine)nickel] (8)*

To 270 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (0.75 mmol) in 30 ml of THF at −30 °C under stirring were added dropwise 104 mg of 4-hydroxobenzoic acid in 10 ml THF. The mixture was allowed to warm up to 20 °C. The orange–brown solid was filtered and washed with 20 ml of THF. Drying *in vacuo* at 20 °C gave a constant weight of 350 mg (90% yield). The product is insoluble in hydrocarbon or ether solvents, decomp. > 162 °C.

*Di-μ(1-naphthoato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (9)*

280 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (0.78 mmol) in 50 ml of THF at −70 °C were combined with 267 mg of 1-naphthoic acid (1.56 mmol). Under stirring the mixture was warmed up to 20 °C and filtered. From 10 ml of THF and 20 ml of pentane at −30 °C orange–brown crystals were obtained: 450 mg (90% yield), decomp. >103 °C.

*Anal.* Calc. for $C_{30}H_{38}Ni_2O_4P_2$ (642.0): C, 56.13; H, 5.97. Found: C, 55.98; H, 5.98%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, benzene-d5 internal reference, δ7.27): δ(Ni$CH_3$) 0.07 (d, 6H, $^3J$(PH) 6.4 Hz); δ(P$CH_3$) 1.00 (d, 18H, $^2J$(PH) 10.0 Hz); δ(CH) 7.71 (m, 14H).

*Di-μ(2-naphthoato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (10)*

In a similar synthesis 270 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (0.75 mmol) and 258 mg of 2-naphthoic acid (1.50 mmol) gave 420 mg of orange–brown crystals (87% yield), decomp. > 172 °C.

*Anal.* Calc. for $C_{30}H_{38}Ni_2O_4P_2$ (642.0): C, 56.13; H, 5.97. Found: C, 56.01; H, 6.04%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, benzene-d5 internal reference, δ7.27): δ(Ni$CH_3$L) −0.01 (d, 6H, $^3J$(PH) 6.8 Hz); δ(P$CH_3$) 1.05 (d, 18H, $^2J$(PH) 10.0 Hz); δ(CH) 7.98 (m, 14H).

*Di-μ(trifluoroacetato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (11)*

To 420 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.16 mmol) in 50 ml of ether at −70 °C were added dropwise 26.6 ml of 0.0087 M trifluoroacetic acid in ether. The orange–brown solution was evaporated to dryness and the residue was dissolved in 150 ml of refluxing pentane. Upon slow cooling to 0 °C 480 mg of dark brown crystals were obtained (79% yield), decomp. >90 °C.

*Anal.* Calc. for $C_{12}H_{24}F_6Ni_2O_4P_2$ (525.7): C, 27.42; H, 4.60. Found: C, 27.35; H, 4.52%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, benzene-d5 internal reference, δ7.27): δ(Ni$CH_3$) −0.40 (d, 6H, $^3J$(PH) 6.0 Hz); δ(P$CH_3$) 0.74 (d, 18H, $^2J$(PH) 8.3 Hz).

*Di-μ(chloroacetato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (12)*

In a similar procedure starting from 330 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (0.91 mmol) in 30 ml of ether and 172 mg of chloroacetic acid in 20 ml of ether, dark brown crystals (320 mg from 200 ml pentane, 72% yield) were obtained, m.p. 83–85 °C (decomp.).

*Anal.* Calc. for $C_{12}H_{28}Cl_2Ni_2O_4P_2$ (486.6): C, 29.62; H, 5.80. Found: C, 29.51; H, 5.80%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{NiC}H_3)$ −0.29 (d, 6H, $^3J$(PH) 6.0 Hz); $\delta(\mathrm{PC}H_3)$ 0.88 (d, 18H, $^2J$(PH) 10.1 Hz); $\delta(\mathrm{C}H_2)$ 3.68 (s, 4H).

### *Di-μ(dichloroacetato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (13)*

In a similar procedure starting from 540 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.49 mmol) in 30 ml of ether and 384 mg of dichloroacetic acid (2.98 mmol) in 30 of ml ether, dark brown crystals (620 mg from 400 ml pentane, 75% yield) were obtained, m.p. 72–74 °C (decomp.).

*Anal.* Calc. for $C_{12}H_{26}Cl_4Ni_2O_4P_2$ (555.5): C, 25.94; H, 4.72. Found: C, 25.80; H, 4.58%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{NiC}H_3)$ −0.30 (d, 6H, $^3J$(PH) 6.0 Hz); $\delta(\mathrm{PC}H_3)$ 0.86 (d, 18H, $^2J$(PH) 10.3 Hz); $\delta(\mathrm{C}H)$ 5.70 (s, 2H).

### *Di-μ(bromoacetato-O:O)-bis[trans-methyl(trimethylphosphine)nickel] (14)*

In a similar procedure starting from 410 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.13 mmol) and 314 mg of bromoacetic acid (2.26 mmol) in 50 ml of ether, dark brown sticklets (330 mg from 200 ml pentane, 51% yield) were obtained, m.p. 78–80 °C (decomp.).

*Anal.* Calc. for $C_{12}H_{28}Br_2Ni_2O_4P_2$ (575.5): C, 25.04; H, 4.90. Found: C, 25.69; H, 5.06%.

$^1$H NMR (60 MHz, $(CD_3)_2CO$, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{NiC}H_3)$ −0.60 (d, 6H, $^3J$(PH) 6.2 Hz); $\delta(\mathrm{PC}H_3)$ 1.30 (d, 18H, $^2J$(PH) 10.1 Hz); $\delta(\mathrm{C}H_2)$ 3.54 (s, 4H).

### *Cyclohexanecarboxylato-methyl-bis(trimethylphosphine)nickel (1a)*

(a) To 510 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.41 mmol) and 361 mg of cyclohexanecarboxylic acid (2.82 mmol) at −70 °C were condensed *in vacuo* 0.35 ml of trimethylphosphine (3.36 mmol) and 50 ml of THF. After 1 h at 20 °C the solution was filtered and the volume reduced to 20 ml *in vacuo*. Dilution with 50 ml of pentane gave yellow crystals that were dried *in vacuo* at 20 °C: 680 mg (68% yield).

(b) To 330 mg of **1** (0.60 mmol) in 80 ml of ether at −70 °C were condensed *in vacuo* 0.2 ml of trimethylphosphine (1.92 mmol). At −30 °C from a red solution 320 mg of yellow needles were obtained (76% yield), m.p. 94–96 °C (decomp.).

*Anal.* Calc. for $C_{14}H_{32}NiO_2P_2$ (353.1): C, 47.63; H, 9.13. Found: C, 47.48; H, 9.21%.

$^1$H NMR (60 MHz, $CD_2Cl_2$, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{NiC}H_3)$ −1.16 (s, 3H); $\delta(\mathrm{PC}H_3)$ 1.20 (s(broad), 18H); $\delta(\mathrm{C}H_2)$ 1.47 (m, 11H).

### *Methyl-diphenylacetato-bis(trimethylphosphine)nickel (2a)*

(a) To 540 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.49 mmol) and 633 mg of diphenylacetic acid (2.98 mmol) at −70 °C were condensed *in vacuo* 0.35 ml of trimethylphosphine (3.36 mmol) and 40 ml of THF. After 1 h at 20 °C the volatiles were removed *in vacuo*. The dark yellow residue was extracted with 150 ml of methylcyclohexane over a glass-sinter disc (G3) and the yellow solution kept at −30 °C overnight to give 870 mg of yellow needles (67% yield).

(b) To 600 mg of **2** (0.83 mmol) in 50 ml of ether were added *in vacuo* 0.5 ml of trimethylphosphine (4.80 mmol). The red solution was kept at −30 °C to give 570 mg of dark yellow crystals (79% yield), m.p. 85–87 °C, decomp. >100 °C.

*Anal.* Calc. for $C_{21}H_{32}NiO_2P_2$ (437.1): C, 57.70; H, 7.38. Found: C, 57.66; H, 7.44%.

$^1$H NMR (60 MHz, $(CD_3)_2CO$, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{NiC}H_3)$ −1.17 (s, 3H); $\delta(\mathrm{PC}H_3)$ 1.00 (d, 18H, $^2J$(PH) 8.3 Hz); $\delta(\mathrm{C}H)$ 4.74 (s, 1H); $\delta$(C*H* aromat.) 7.37 (m, 10H).

### *9-Anthracenecarboxylato-methyl-bis(trimethylphosphine)nickel (4a)*

(a) To 440 mg of $[\mathrm{NiCH_3(OCH_3)(PMe_3)}]_2$ (1.22 mmol) and 542 mg of 9-anthracenecarboxylic acid (2.44 mmol) at −70 °C were condensed *in vacuo* 0.35 ml of trimethylphosphine (3.36 mmol) and 60 ml of THF. After 1 h at 20 °C the solution was filtered and evaporated to 15 ml. 50 ml of pentane were added to give 860 mg of yellow crystals (81% yield).

(b) To 450 mg of **4** (0.61 mmol) in 80 ml of acetone were added 0.5 ml of trimethylphosphine (4.80 mmol). At −30 °C dark yellow bunches of needles were obtained (400 mg, 73% yield), m.p. 108–110 °C, decomp. >119 °C.

*Anal.* Calc. for $C_{22}H_{30}NiO_2P_2$ (447.1): C, 59.10; H, 6.76. Found: C, 58.86; H, 6.84%.

$^1$H NMR (300 MHz, THF-d8, 295 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{NiC}H_3)$ −0.95 (s, 3H); $\delta(\mathrm{PC}H_3)$ 1.22 (d, 18H, $^2J$(PH) 8.2 Hz); $\delta(\mathrm{C}H)$ 8–8.3 (m, 10H).

### *Bicyclo{3.2.2}nonyl-1-carboxylato-methyl-bis(trimethylphosphine)nickel (5a)*

To 800 mg of **5** (1.26 mmol) in 60 ml of ether at −70 °C were added 0.5 ml of trimethylphosphine

(4.80 mmol) *in vacuo*. After 1 h at 20 °C the volatiles were removed *in vacuo* and from 80 ml of pentane 720 mg of yellow crystals were obtained (73% yield), m.p. 104–106 °C, decomp. > 120 °C.

*Anal.* Calc. for $C_{17}H_{36}NiO_2P_2$ (393.1): C, 51.94; H, 9.23. Found: C, 51.25; H, 9.13%.

$^1$H NMR (300 MHz, toluene-d8, 295 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{Ni}CH_3)$ −0.88 (s, 3H); $\delta(\mathrm{P}CH_3)$ 0.90 (s, 18H); $\delta(CH_2)$ 1.86 (m, 15H).

### *Benzoato-methyl-bis(trimethylphosphine)nickel (**6a**)*

(a) To 930 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (2.57 mmol) and 633 mg of benzoic acid (5.14 mmol) in 40 ml of toluene at −70 °C were added 0.6 ml of trimethylphosphine (5.76 mmol). After 1 h at 20 °C the solution was filtered and cooled to −30 °C: 1200 mg yellow needles (67% yield).

(b) To 530 mg of **6** (0.98 mmol) were condensed *in vacuo* 100 ml of ether and 0.5 ml of trimethylphosphine (4.80 mmol). From a red solution at −30 °C 580 mg of yellow needles were obtained (85% yield), m.p. 92–93 °C (decomp.).

*Anal.* Calc. for $C_{14}H_{26}NiO_2P_2$ (347.0): C, 48.46; H, 7.55. Found: C, 48.25; H, 7.62%.

$^1$H NMR (60 MHz, toluene-d8, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{Ni}CH_3)$ −0.89 (s, 3H); $\delta(\mathrm{P}CH_3)$ 0.88 (d, 18H, $^2J$(PH) 8.0 Hz); $\delta(CH)$ 7.3–8.5 (m, 5H).

### *2-Aminobenzenecarboxylato-methyl-bis(trimethylphosphine)nickel (**7a**)*

(a) To 380 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.05 mmol) and 288 mg of 2-aminobenzoic acid (2.10 mmol) at −70 °C were added 0.3 ml of trimethylphosphine (2.88 mmol) and 60 ml of THF. After 1 h at 20 °C the volatiles were removed *in vacuo* and the residue was crystallized from 100 ml of acetone to give 590 mg of yellow brown crystals (78% yield).

(b) To 400 mg of **7** (0.70 mmol) in 80 ml of toluene were added 0.2 ml of trimethylphosphine (1.92 mmol). Filtration and cooling to −30 °C yields 290 mg of yellow microcrystals (57% yield), m.p. 109–111 °C, decomp. > 117 °C.

*Anal.* Calc. for $C_{14}H_{17}NNiO_2P_2$ (362.0): C, 46.45; H, 7.52; N, 3.87. Found: C, 46.44; H, 7.52; N, 3.87%.

$^1$H NMR (60 MHz, THF-d8, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{Ni}CH_3)$ −1.12 (s, 3H); $\delta(\mathrm{P}CH_3)$ 1.13 (d, 18H, $^2J$(PH) 7.8 Hz); $\delta(\mathrm{N}H_2)$ 6.33 (s(broad), 2H); $\delta(CH)$ 7.03 (m, 4H).

### *Dimethyl-(benzenecarboxylato-4-oxo)-tetrakis(trimethylphosphine)dinickel (**8a**)*

To 580 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.60 mmol) and 221 mg of 4-hydroxobenzoic acid (1.60 mmol) at −70 °C were condensed *in vacuo* 0.4 ml of trimethylphosphine (3.84 mmol) and 60 ml of THF. After 2 h stirring at 20 °C the volatiles were removed *in vacuo* and the residue was extracted with 100 ml of ether over a glass-sinter disc. Cooling to −30 °C afforded 690 mg of orange-brown needles (73% yield), m.p. 162–164 °C (decomp.).

*Anal.* Calc. for $C_{21}H_{46}Ni_2O_3P_4$ (587.9): C, 42.90; H, 7.89. Found: C, 42.66; H, 7.96%.

$^1$H NMR (60 MHz, $(CD_3)_2CO$, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{Ni}CH_3)$ −1.13 (s, 6H); $\delta(\mathrm{P}CH_3)$ 1.19 (s, 18H), 1.09 (d, 18H, $^2J$(PH) 8.0 Hz); $\delta(CH\text{-}3,5)$ 6.84 (d, 2H, $^3J$(HH) 8.4 Hz); $\delta(CH\text{-}2,6)$ 7.63 (d, 2H, $^3J$(HH) 8.4 Hz).

### *Methyl-1-naphthalenecarboxylato-bis(trimethylphosphine)nickel (**9a**)*

(a) To 440 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.22 mmol) and 420 mg of 1-naphthoic acid (2.44 mmol) at −70 °C were added 0.35 ml of trimethylphosphine (3.36 mmol) and 50 ml of THF. After 1 h at 20 °C the red–brown solution was filtered and reduced to 10 ml. Adding 50 ml of pentane and cooling to −30 °C afforded 720 mg of yellow crystals (74% yield).

(b) To 470 mg of **9** (0.73 mmol) in 80 ml of toluene were added 0.2 ml of trimethylphosphine (1.92 mmol). At 30 °C a clear solution was obtained that on slow cooling gave 330 mg of yellow leaflets (57% yield), m.p. 107–109 °C, decomp. > 119 °C.

*Anal.* Calc. for $C_{18}H_{28}NiO_2P_2$ (397.1): C, 54.44, H, 7.11. Found: C, 54.66; H, 7.10%.

$^1$H NMR (60 MHz, THF-d8, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{Ni}CH_3)$ −1.05 (s, 3H); $\delta(\mathrm{P}CH_3)$ 1.17 (d, 18H, $^2J$(PH) 7.1 Hz); $\delta(CH)$ 7.67 (m, 7H).

### *Methyl-2-naphthalinecarboxylato-bis(trimethylphosphine)nickel (**10a**)*

(a) To 520 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.44 mmol) and 495 mg of 2-naphthoic acid (2.88 mmol) at −70 °C were added 0.35 ml of trimethylphosphine (3.36 mmol) and 60 ml of THF. Workup as for **9a** gave a light yellow powder that was recrystallized from 200 ml of toluene (40 °C) to give 850 mg of yellow leaflets (74% yield).

(b) To 470 mg of **10** (0.73 mmol) in 100 ml of toluene at −70 °C were added 0.15 ml of trimethylphosphine (1.44 mmol). At 50 °C a clear yellow solution was obtained. Slow cooling gave 420 mg of yellow leaflets (72% yield), m.p. 129–131 °C, decomp. > 144 °C.

*Anal.* Calc. for $C_{18}H_{28}NiO_2P_2$ (397.1): C, 54.44; H, 7.11. Found: C, 54.20; H, 7.08%.

$^1$H NMR (60 MHz, $C_6D_6$, 308 K, $Me_4Si$ external reference, $\delta 0$): $\delta(\mathrm{Ni}CH_3)$ −0.87 (s, 3H); $\delta(\mathrm{P}CH_3)$ 0.93 (d, 18H, $^2J$(PH) 5.8 Hz); $\delta(CH)$ 7.99 (m, 7H).

### *Chloroacetato-methyl-bis(trimethylphosphine)nickel (12a)*

To 560 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.55 mmol) in 30 ml of ether containing 0.5 ml of trimethylphosphine (4.80 mmol) at −70 °C were added 295 mg of chloroacetic acid (3.10 mmol) in 20 ml of ether. The solution was allowed to warm up to 20 °C and the volatiles were removed *in vacuo*. Extraction with 90 ml of pentane and cooling the yellow solution gave 690 mg of yellow needles (70% yield), m.p. 70–72 °C (decomp.).

*Anal.* Calc. for $C_9H_{23}ClNiO_2P_2$ (319.4): C, 33.84; H, 7.26. Found: C, 34.01; H, 7.38%.

$^1H$ NMR (60 MHz, $C_6D_6$, 308 K, $Me_4Si$ external reference, δ0): δ(NiC$H_3$) −0.84 (s, 3H); δ(PC$H_3$) 0.93 (s, 18H); δ(C$H_2$) 4.01 (s, 2H).

### *Dichloroacetato-methyl-bis(trimethylphosphine)nickel (13a)*

In a similar procedure starting from 400 mg of $[NiCH_3(OCH_3)(PMe_3)]_2$ (1.11 mmol) and 285 mg of dichloroacetic acid (2.21 mmol) 460 mg of yellow leaflets (from 80 ml of pentane) were obtained (59% yield), m.p. 58–60 °C, decomp. >65 °C.

*Anal.* Calc. for $C_9H_{22}Cl_2NiO_2P_2$ (353.8): C, 30.55; H, 6.27. Found: C, 30.34; H, 6.29%.

$^1H$ NMR (60 MHz, $C_6D_6$, 308 K, $Me_4Si$ external reference, δ0): δ(NiC$H_3$) −0.93 (s, 3H); δ(PC$H_3$) 1.00 (s, 18H); δ(C$H$) 5.99 (s, 1H).

### *Methyl-tetrakis(trimethylphosphine)nickel-trifluoroacetate (15)*

To 430 mg of **11** (0.83 mmol) in 100 ml of ether at −70 °C was added 1.0 ml of trimethylphosphine (9.60 mmol). At 20 °C the red solution was filtered and cooled to −30 °C to give 690 mg of dark red crystals (85% yield), m.p. 61–63 °C (decomp.).

*Anal.* Calc. for $C_{15}H_{39}F_3NiO_2P_4$ (491.1): C, 36.69; H, 8.01. Found: C, 35.89; H, 8.38%.

$^1H$ NMR (300 MHz, $(CD_3)_2CO$, 193 K, $Me_4Si$ external reference, δ0): δ(NiC$H_3$) −0.18 (quartet, 3H, $^3J$(PH) 12.3 Hz); δ(PC$H_3$) 1.34 (s(broad), 27H), 1.51 (s, 9H). $^{19}F$ NMR (56.4 MHz, $(CD_3)_2CO$, 308 K, $CCl_3F$ external reference, δ0): δ −75.2 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, $(CD_3)_2CO$, 193 K, $H_3PO_4$ external reference, δ0): δ($P_{eq}$) −22.11 (d, 3P, $^2J$(PP) 52.2 Hz); δ($P_{ax}$) (quartet, 1P, $^2J$(PP) 52.2 Hz).

### *Data collection and reduction: complex 6*

Reflections were collected at 20 °C on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. The cell parameters were determined from a least-squares fitting of 25 centered reflections with $2q$ between 17 and 30°. The space group determination showed the systematic absences (*hkl* with $h+k$ odd, *h0l* with $l$ odd) identified in full data set. A summary of crystal and intensity collection data is given in Table 1. Successful refinement was carried out in the centrosymmetric space group $C_2/c$. A total of 6722 independent reflections, 1604 with $I > 3\sigma(I)$ was measured using θ/2θ scans for 2θ from 1 to 56°. Intensities of three reflections measured every 2 h during data collection varied less than 5%. The data were corrected for the Lorentz, polarization and absorption effects. The nickel atom was located from a Patterson synthesis, remaining non-hydrogen atoms were then found from a $\Delta F$ map (Table 2). Refinement was done by full-matrix least-squares based on $|F_o|$ by using the SHELX package [6]. After anisotropic refinement for all non-H atoms, the hydrogen atoms were fixed at idealized positions (C–H = 0.97 Å, $U$ = 0.6 Å$^2$ kept fixed) and repositioned after each least-squares cycle. Final parameters are $R = 0.0631$ and $R_w = 0.0659$ for 136 variables, with shift mean 0.01 σ, max. 0.04 σ in final cycle. The scattering factors were taken from Cromer and Mann [7] for Ni, P, O and C; from Stewart *et al.* [8] for H.

TABLE 1. Crystal data, details of data collection and structure refinement for $[Ni(CH_3)P(CH_3)_3(CO_2C_6H_5)]_2$

| | |
|---|---|
| Formula | $Ni_2P_2O_4C_{22}H_{34}$ |
| Molecular weight | 428.86 |
| Crystal system | monoclinic |
| Space group | $C_2/c$ |
| $a$ (Å) | 12.327(3) |
| $b$ (Å) | 12.885(4) |
| $c$ (Å) | 16.495(6) |
| $\beta$ (°) | 102.93(2) |
| $V$ (Å$^3$) | 2553(2) |
| $Z$ | 4 |
| $D_{calc}$ (g/cm$^3$) | 1.409 |
| $\mu$ (Mo Kα) (cm$^{-1}$) | 15.46 |
| Temperature (°C) | 20 ± 2 |
| Scan method | θ/2θ |
| Data collection range (2θ) (°) | $1 < 2\theta < 56$ |
| No. reflections measured | 6722 |
| No. unique data with $(I) > 3\sigma(I)$ | 1604 |
| No. parameters refined | 136 |
| $R^a$ | 0.0631 |
| $R_w{}^b$ | 0.0659 |

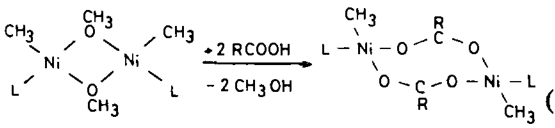
$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

## Results and discussion

Carboxylic acids protonate alkoxo bridges in dinuclear methylnickel alkoxides forming eight-membered metallocycles of methylnickel carboxylates according to eqn. (2).

TABLE 2. Fractional atomic coordinates with e.s.d.s in parentheses

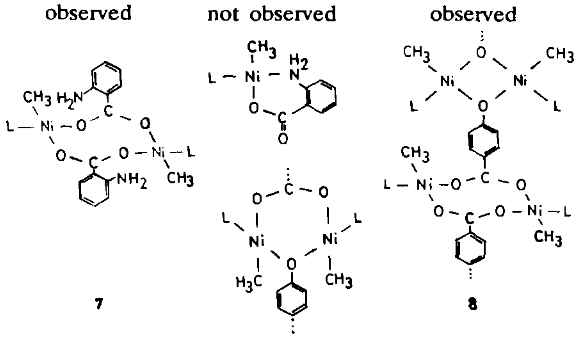
| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Ni(1) | 0.3808(1) | 0.54878(7) | 0.22759(6) |
| P(1) | 0.3110(3) | 0.4340(2) | 0.2926(1) |
| C(11) | 0.343(1) | 0.4492(8) | 0.4041(5) |
| C(12) | 0.339(1) | 0.2982(7) | 0.2793(6) |
| C(13) | 0.1602(9) | 0.4415(9) | 0.2659(7) |
| O(1) | 0.4017(5) | 0.6439(4) | 0.3222(3) |
| O(2) | 0.4137(6) | 0.6591(4) | 0.1587(3) |
| C(1) | 0.3513(8) | 0.4588(7) | 0.1334(5) |
| C(2) | 0.494(1) | 0.6806(6) | 0.3580(5) |
| C(3) | 0.4957(9) | 0.7539(5) | 0.4290(4) |
| C(4) | 0.401(1) | 0.7757(7) | 0.4561(5) |
| C(5) | 0.405(1) | 0.8418(8) | 0.5230(6) |
| C(6) | 0.502(1) | 0.8867(7) | 0.5619(6) |
| C(7) | 0.597(1) | 0.8658(7) | 0.5350(6) |
| C(8) | 0.5940(8) | 0.8002(6) | 0.4690(5) |



(2)

Table 3 gives the yields and some properties of compounds **1**–**14**.

Fluoro or chlorocarbon functions in **11**–**13** do not interfere with methylnickel groups but the lower yield of **14** is due to such side-reactions. Trichloroacetic acid, dibromoacetic acid and iodoacetic acid attack methylnickel groups and initiate deposition of dark solids and accelerate decomposition during workup. The *ortho*-amino group in **7** does not give rise to a six-membered chelate ring, but a 4-hydroxy group causes precipitation of **8** as a coordination polymer.



L=PMe$_3$

Again this material does not contain six-membered rings but alternating four- and eight-membered metallocycles. All our attempts to construct metallocycles from different oxo anions gave symmetric products.

(i) Using only one equivalent of acid in a synthesis according to eqn. (1) leaves half of the starting material unreacted.

(ii) Using each one mole equivalent of benzoic acid and trifluoroacetic acid in a synthesis according to eqn. (1) gives a crystalline material consisting of **6** and **11** in a 1:1 ratio ($^1$H NMR).

Trimethylphosphine cleaves all metallocycles usually giving quantitative yields of methylbis(trimethylphosphine)nickel carboxylates according to eqn. (3) (Table 4).

TABLE 3. Dinuclear methylnickel carboxylates

| Compound | R | Yield (%) | Decomposition | |
|---|---|---|---|---|
| | | | of microcrystals (1 bar argon) | of crystal surface (in air 20 °C) |
| **1** | cyclo-$C_6H_{11}$ | 92 | 114–117 °C | 2 h |
| **2** | $CH(C_6H_5)_2$ | 60 | 93–95 °C | 1 h |
| **3** | $C(C_6H_5)_3$ | 94 | 121–123 °C | 5 min |
| **4** | 9-anthracenyl | 86 | 139–141 °C | 1 h |
| **5** | bicyclo(3.2.2)-nonane-1-yl | 93 | 158–161 °C | 5 h |
| **6** | $C_6H_5$ | 72 | 170–172 °C | 5 h |
| **7** | 8-$NH_2$-$C_6H_4$ | 85 | 147–149 °C | 5 h |
| **8** | 4-OH-$C_6H_4$ | 90 | 162–164 °C | 5 h |
| **9** | 1-naphthyl | 90 | 103–105 °C | 24 h |
| **10** | 2-naphthyl | 87 | 172–174 °C | 5 h |
| **11** | $CF_3$ | 79 | 90–92 °C | 1 min |
| **12** | $CH_2Cl$ | 70 | 83–85 °C | 1 min |
| **13** | $CHCl_2$ | 75 | 72–74 °C | 1 min |
| **14** | $CH_2Br$ | 51 | 78–80 °C | 1 min |

TABLE 4. Mononuclear methylnickel carboxylates

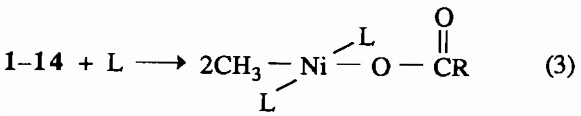
| Compound | R | Crystal habitus | Melting point[a] (°C) |
|---|---|---|---|
| **1a** | cyclo-$C_6H_{11}$ | yellow needles | 94–96 (d) |
| **2a** | $CH(C_6H_5)_2$ | yellow needles | 85–87 |
| **3a** | $C(C_6H_5)_3$ | [b] | |
| **4a** | 9-anthacenyl | yellow needles | 108–110 |
| **5a** | bicyclo(3.2.2)-nonane-1-yl | yellow–brown needles | 104–106 |
| **6a** | $C_6H_5$ | yellow needles | 92–93 (d) |
| **7a** | 8-$NH_2$-$C_6H_4$ | yellow needles | 109–111 |
| **8a** | 4-OH-$C_6H_4$ | orange–brown needles | 162–164 (d) |
| **9a** | 1-naphthyl | yellow leaflets | 107–109 |
| **10a** | 2-naphthyl | yellow leaflets | 129–131 |
| **11a** | $CF_3$ | [c] | [c] |
| **12a** | $ClCH_2$ | yellow needles | 70–72 (d) |
| **13a** | $Cl_2CH$ | yellow leaflets | 58–60 |
| **14a** | $BrCH_2$ | [b] | |

[a] (d) = with decomposition. [b] Not analytically pure. [c] See text for **15**.

TABLE 5. $\nu$(CO) bands of OCO-bridging and unidentate carboxylate functions

| Compound | $\nu_1$(CO) | $\nu_2$(CO) | $\Delta\nu$ | Compound | $\nu_1$(CO) | $\nu_2$(CO) | $\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| **1** | 1580vs | 1446vs | 131 | **1a** | 1590vs | 1372vs | 218 |
| **2** | 1606vs | 1400vs<br>1390vs | 211 | **2a** | 1611vs | 1371vs | 240 |
| **3** | 1605vs | 1379vs<br>1370vs | 228 | **4a** | 1594vs | 1362s | 232 |
| **4** | 1605vs | 1478s<br>1440s<br>1429s | 159 | **5a** | 1586vs | 1367vs<br>1349s | 225 |
| **5** | 1580vs | 1406s | 174 | **6a** | 1611s<br>1605vs | 1370s<br>1355vs | 246 |
| **6** | 1602vs<br>1561vs | 1405vs<br>1391vs | 184 | **7a** | 1614vs | 1365vs | 249 |
| **7** | 1610vs<br>1573vs | 1415s | 177 | **8a**[b] | 1595vs | 1355vs | 240 |
| **8**[a] | 1597s<br>1574s | 139vs | 187 | **9a** | 1620s<br>1610s | 1345s<br>1335s | 275 |
| **9** | 1596vs<br>1579vs<br>1565vs | 1419s<br>1410s | 166 | **10a** | 1600s | 1350s<br>1341s | 255 |
| **10** | 1600vs<br>1569vs | 1416vs<br>1395vs | 179 | **12a** | 1605vs | 1381vs | 224 |
| **11** | 1670vs<br>1601s | 1416vs | 231 | **13a** | 1665vs | 1355vs | 310 |
| **12** | 1630vs | 1421vs<br>1410vs | 215 | **15** | 1690vs | [c] | |
| **13** | 1650vs | 1410vs<br>1399vs | 246 | | | | |
| **14** | 1620vs | 1434s<br>1415s<br>1399s | 204 | | | | |

[a] Coordination polymer, see text. [b] Dinuclear complex. [c] Band not observed.



$$1\text{–}14 + L \longrightarrow 2CH_3-\overset{L}{\underset{L}{Ni}}-O-\overset{O}{\overset{\|}{C}}R \qquad (3)$$

$L = PMe_3$ 1a–14a

With **11** we did not observe a square planar mononuclear compound **11a** because ionic species $NiCH_3L_4{}^+CF_3COO^-$ ($L = PMe_3$) (**15**) prevailed in all experiments. From ether **15** is obtained within 10 min according to eqn. (4) in 85% yield.

$$11 + 6L \longrightarrow \underset{\mathbf{15}}{2[NiCH_3L_4][CF_3COO]} \qquad (4)$$

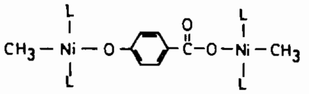
The dark red crystals of **15** are hygroscopic in moist air but in dry air (desiccator) remain unchanged for 2 h. Under argon in the dark at 25 °C they appear to be indefinitely stable. Above 61 °C trimethylphosphine dissociates.

### *IR and $^1H$ NMR spectra*

IR spectra obtained from suspensions **1–14** or solutions **1a–14a** (nujol) contain the bands of coordinated trimethylphosphine in narrow regions ($cm^{-1}$): 1311–1273, two or three bands with medium and strong intensities, $\delta_sPCH_3$; 1176–1145 m, $\delta_s$ $NiCH_3$; 959–940 vs, two bands for **1–15**, one band for **1a–14a**, $\rho_1PCH_3$; 864–840 m, one or two bands $\rho_2PCH_3$; 741–721 s, split for **1–3**, $\nu_{as}PC_3$; 679–668 s, split for **4** and **4c**, $\nu_sPC_3$; 538–508 m or w, $\nu NiC$. Both **7** and **7a** display broad bands at 3440 and 3335 and at 3435 and 3312 $cm^{-1}$, respectively, that indicate uncoordinated amino groups.

Anions of 4-hydroxybenzoic acid are coordinated in **8** or **8a** without remaining OH functions.

While square planar $CH_3(PMe_3)NiO_2$ groups are mutually *trans* in eight-membered carboxylate rings of **8**, their orientation in four-membered phenoxo rings may be *cis* or *trans* or both in irregular sequence. Phosphine cleaves all metallocycles giving **8a** as a dinuclear complex containing 4-oxobenzoate dianions as remaining bridges.



**8a**

Very strong bands of OCO vibrations indicate the mode of coordination by their difference of frequencies $\nu_{as}(OCO)^-\nu_s(OCO)$ for symmetric and $\nu(C{=}O)(\nu_1)$–$\nu(C\text{–}O)(\nu_2)$ for asymmetric carboxylate groups [9]. Table 5 gives assignments and likely coordination modes for dinuclear and mononuclear compounds. $^1H$ NMR spectra of compounds **1–14** contain a $NiCH_3$ doublet at highest field with $^3J(PH) = 6\text{–}7$ Hz; $^{31}P$ coupling is lost in **1a–13a** due to fast exchange of ligands.

### *Molecular structure of complex 6*

Eight-membered metallocycles $Ni_2O_4C_2$ of dimeric methylnickel carboxylates should be flexible and are expected to adopt either chair or boat configuration with the planar $CH_3(PMe_3)NiO_2$ groups in mutual *trans* positions. NMR spectra are not conclusive on this point. Therefore an X-ray crystal structure determination was undertaken with complex **6** that forms suitable single crystals. Figure 1 gives a perspective view of a molecule **6** and the atom numbering. Important bond lengths and angles are presented in Table 6. The structure consists of discrete dinuclear molecules containing nickel in square planar surroundings of atoms C P O and O′ in the expected *trans* configuration. The folding of the eight-membered metallocycle $Ni_2O_4C_2$ in an overall boat con-

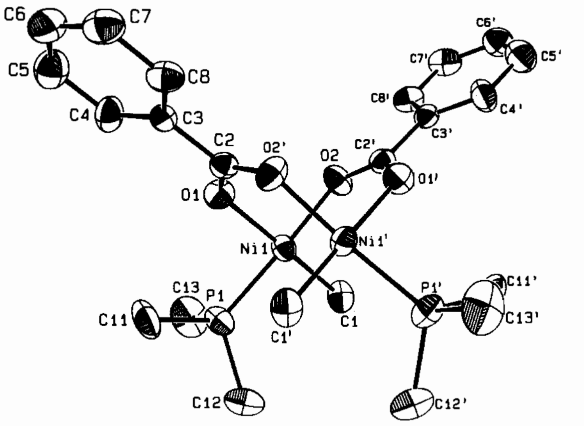


Fig. 1. Molecular structure of **6**

TABLE 6. Important distances (Å) and angles (°) of **6**

| | | | |
|---|---|---|---|
| Bond distances | | | |
| Ni–Ni′ | 2.865(2) | O1–C2 | 1.26(1) |
| Ni–P1 | 2.119(2) | C2–C3 | 1.50(1) |
| Ni–O1 | 1.955(5) | C3–C4 | 1.37(1) |
| Ni–O2 | 1.919(6) | C4–C5 | 1.39(1) |
| Ni–C1 | 1.907(7) | C5–C6 | 1.35(1) |
| P1–C11 | 1.802(8) | C6–C7 | 1.37(1) |
| P1–C12 | 1.806(9) | C7–C8 | 1.37(1) |
| P1–C13 | 1.81(1) | C8–C3 | 1.38(1) |
| Bond angles | | | |
| O1–Ni–P1 | 91.7(2) | O2–Ni–P1 | 168.5(2) |
| O1–Ni–O2 | 90.0(2) | O1–Ni–C1 | 176.5(3) |
| O2–Ni–C1 | 89.8(3) | P1–Ni–C1 | 87.8(3) |
| Ni–P1–C11 | 114.8(3) | Ni–P1–C12 | 120.4(4) |
| Ni–P1–C13 | 110.5(4) | C11–P1–C12 | 102.7(5) |
| C11–P1–C13 | 102.9(5) | C12–P1–C13 | 103.5(5) |
| Ni–O1–C2 | 123.7(6) | O1–C2–C3 | 117(1) |
| Ni–Ni′–O1 | 81.4(2) | O1–C2–O2′ | 125.7(8) |

formation through normal angles OCO = 125.7(8), NiOC = 123.76(7) and ONiO = 90.0(2)° brings the two nickel atoms to a close approach Ni–Ni = 2.865(2) pm with roughly parallel planes of coordination (NiNi′O1 = 81.4(3)°) as in dimeric copper(II) acetate dihydrate (Cu–Cu = 2.62 Å and CuCuO = 84°) [10].

## Conclusions

Methyl(trimethylphosphine)nickel carboxylates dimerize forming eight-membered metallocycles.

Mixed dimers are not found as equilibria through exchange of anionic ligands favour symmetric products. Amino groups of 2-$NH_2$-$C_6H_4COOH$ do not participate as bridging ligands but the phenolic OH group of 4-OH-$C_6H_4COOH$ give rise to additional $Ni_2O_2$ rings in a coordination polymer. Both metallocycles are cleaved by trimethylphosphine giving square planar methylbis(trimethylphosphine)nickel carboxylates with monodentate O-donor functions and a 16-electron count for nickel. Fast exchange of neutral and anionic ligands and coordination of up to four phosphines as evidenced by $^1H$ NMR spectra indicate easy access to the metal in catalytic reactions.

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