2944 *Organometallics* **1994,** *13,* 2944–2950

# Ligand-Induced Fragmentation of Methylnickel Phenolates Containing a 2-Aldehyde Function: Structure of (3-*tert*-Butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)nickel

Hans-Friedrich Klein,* Alfred Bickelhaupt, and Birgit Hammerschmitt

*Eduard-Zintl-Institut für Anorganische Chemie der Technischen Hochschule Darmstadt,*
*Hochschulstrasse 10, 64289 Darmstadt, FRG*

Ulrich Flörke and Hans-Jürgen Haupt

*Anorganische und Analytische Chemie der Universität/GH Paderborn,*
*Warburger Strasse 100, 33095 Paderborn, FRG*

*Received March 7, 1994*⊗

O-bridging salicylaldehyde derivatives in dimeric methylnickel compounds NiMe(OR)($\mathrm{PMe_3}$) showing equilibria of *cis* and *trans* forms (OR = 2-oxobenzaldehyde (**1**), 3-*tert*-butyl-5-methyl-2-oxobenzaldehyde (**2**), 3,5-di-*tert*-butyl-2-oxobenzaldehyde (**3**), 2-oxonaphthaldehyde (**4**)) spontaneously undergo, upon addition of trimethylphosphine, a fragmentation reaction forming 2-oxobenzoyl-*C,O* chelating ligands in 18-electron mononuclear complexes $\mathrm{Ni(O\overset{\frown}{C}{=}O)(PMe_3)_3}$ ($\mathrm{O\overset{\frown}{C}{=}O}$ = 2-oxobenzoyl (**5**), 3-*tert*-butyl-5-methyl-2-oxobenzoyl (**6**), 3,5-di-*tert*-butyl-2-oxobenzoyl (**7**), 2-oxonaphthoyl (**8**)). The molecular structure of **6** contains pentacoordinate nickel with a chelate bite angle C—Ni—O = 85.5(1)°. Dissociation of phosphine ligands in **5** gives $\mathrm{Ni(O\overset{\frown}{C}{=}O)(PMe_3)_2}$ (**9**) and $\mathrm{[Ni(O\overset{\frown}{C}{=}O)(PMe_3)]_2}$ (**10**), but no mobilization of carbonyl ligands could be observed in the presence of $\mathrm{Ni(PMe_3)_4}$ as CO acceptor.

## Introduction

Electron-rich metal complexes can remove formyl groups under mild conditions by mobilizing and coordinating carbonyl ligands from steroid precursors.[1] As an initiating step of such aldehyde reactions using the Wilkinson catalyst, according to eq 1, coordination and

$$\mathrm{RCHO} + \mathrm{RhClL_3} \rightarrow [\mathrm{RhH(COR)ClL_3}] \rightarrow \mathrm{RH} + \mathrm{RhCl(CO)L_2} + \mathrm{L} \qquad (1)$$

$$\mathrm{L} = \mathrm{P(C_6H_5)_3}$$

oxidative addition of the activated CH unit are assumed. The postulated acyl intermediate undergoes a rapid transformation due to a reversed carbonylation reaction.

Indeed, stable hydrido(acyl) complexes of zerovalent iron have been synthesized and subjected to a decarbonylation reaction.[2] A necessary prerequisite for the aldehyde reaction to occur appears to be an electron-rich and coordinatively unsaturated metal center ($\mathrm{Rh^I}$ or $\mathrm{Fe^0}$ with 16 valence electrons) which must fulfill two requirements: (a) coordination and oxidative addition of the aldehyde group and (b) decarbonylation and coordination of CO. If the metal center is deactivated by CO the reaction remains stoichiometric, but will become catalytic when CO dissociates.

We report here on a new stoichiometric aldehyde reaction with methylnickel(II) complexes (eq 2) that proceeds under mild conditions and which is initiated

$$\mathrm{RCHO} + \mathrm{Ni(CH_3)XL_2} + \mathrm{L} \rightarrow \mathrm{Ni(COR)XL_3} + \mathrm{CH_4} \qquad (2)$$

$$\mathrm{L} = \mathrm{P(CH_3)_3}$$

by coordination of trimethylphosphine, giving methane, and affords the first acylnickel compound (18 valence electrons) containing three monodentate neutral ligands.

While all reported acylnickel complexes with a square planar configuration (16 valence electrons) are decarbonylated by CO-accepting compounds,[3] no CO ligand is mobilized under conditions of thermal dissociation of trimethylphosphine from the title compound.

## Experimental Section

**General Procedures and Materials.** Standard vacuum techniques were used in manipulations of volatile and air-sensitive material.[5] Salicylaldehyde and 2-hydroxonaphthalenecarbaldehyde (Fluka) were used as purchased. Literature procedures were followed in the synthesis of 3-*tert*-butyl-5-methylsalicylaldehyde,[6] 3,5-di-*tert*-butylsalicylaldehyde,[6] $\mathrm{[NiMe(OMe)(PMe_3)]_2}$,[4a] $\mathrm{NiMeCl(PMe_3)_2}$,[4a] and $\mathrm{NiMe_2(PMe_3)_3}$.[7]

Microanalyses were carried out by Dornis & Kolbe, microanalytical laboratory, Mülheim (FRG). Infrared spectra

---

⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1994.

[1] Tsuji, J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977.

[2] Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

[3] (a) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524. (b) Cámpora, J.; Gutiérrez, E.; Monge, A.; Poveda, M. L.; Carmona, E. *Organometallics* **1992**, *11*, 2644.

[4] (a) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1973**, *106*, 1433. (b) Klein, H.-F.; Wiemer, T.; Menu, M.-J.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chim. Acta* **1991**, *189*, 35.

[5] Klein, H.-F.; Mager, M.; Flörke, U.; Haupt, H.-J.; Breza, M.; Boca, R. *Organometallics* **1992**, *11*, 2912.

[6] (a) Ligget, R. W.; Diehl, H. *Proc. Iowa Acad. Sci.* **1945**, *52*, 191. (b) Hess, D. Doctoral thesis, Technische Hochschule Darmstadt, 1987.

[7] Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1972**, *105*, 2628.

0276-7333/94/2313-2944$04.50/0

(4000−400 cm$^{-1}$), as obtained from Nujol mulls between KBr windows, were recorded on a Perkin-Elmer, type 397, spectrophotometer. $^{1}$H NMR spectra were obtained from a Bruker WM 300 (300-MHz) spectrometer equipped with a low-temperature unit that was calibrated with a standard methanol sample. Melting points were determined in capillaries sealed under argon and are uncorrected.

**Preparations. Synthesis of Bis(μ-2-oxobenzaldehyde)bis[methyl(trimethylphosphine)nickel] (1).** [NiMe(OMe)PMe$_3$]$_2$ (500 mg, 1.55 mmol) and salicylaldehyde (380 mg, 3.11 mmol) in 70 mL of THF changed color from yellow brown to orange red. After 3 h at 20 °C the volatiles were removed in vacuo and the residue was extracted with 70 mL of pentane over a glass−sinter disk (G3). Freezing at −70 °C afforded 600 mg of a dark red oil (72% crude yield): $C_{22}H_{34}Ni_2O_4P_2$ (541.8), mixture of *cis* and *trans* isomers (*cis* (43%), *trans* (57%)), no correct elemental analysis. IR (Nujol mull, 2000−1600 cm$^{-1}$): 1620 (vs), 1600 (vs) ν(C=O). $^{1}$H NMR (300 MHz, THF-$d_8$, 25 °C): δ(NiC*H*$_3$, *trans*) −0.67 (s, 3H), δ(NiC*H*$_3$, *cis*) −0.50 (s, 3 H), δ(PC*H*$_3$) 1.25 (d, 18 H, $^{2}J$(PH) = 10.1 Hz), δ(C*H*) 6.37 (dd, 2 H, $^{3}J$(HH) = 7.3 and 7.3 Hz), δ(C*H*) 6.48 (d, 1 H, $^{3}J$(HH) = 7.7 Hz), δ(C*H*) 6.64 (m, 1 H), δ(C*H*) 7.19 (m, 4 H), δ(C*H*O) 9.04 (s, 2 H). $^{13}$C NMR (75.4 MHz, THF-$d_8$, 25 °C): δ(P*C*H$_3$) 13.27 (d, $^{1}J$(PC) = 29.0 Hz), δ(3-*C*) 114.4, δ(1-*C*) 122.7, δ(5-*C*) 124.8, δ(6-*C*) 135.5, δ(4-*C*) 136.9, δ(2-*C*) 171.9, δ(*C*HO) 188.9.

**Preparation of Bis(μ-3-*tert*-butyl-5-methyl-2-oxobenzaldehyde)bis[*cis*-methyl(trimethylphosphine)nickel] (2).** [NiMe(OMe)PMe$_3$]$_2$ (800 mg, 2.21 mmol) and 3-*tert*-butyl-5-methylsalicylaldehyde (870 mg, 4.53 mmol) in 100 mL of THF at −70 °C gave an orange red solution. Warming to 20 °C and removing the volatiles afforded a red brown residue. Extraction with 50 mL of pentane and cooling to −30 °C gave 1160 mg of red brown needles (68%); dec pt >99 °C. Anal. Calcd for $C_{32}H_{54}Ni_2O_4P_2$ (682.1): C, 56.35; H, 7.98. Found: C, 56.48; H, 7.95. IR (Nujol mull, 2000−1560 cm$^{-1}$): 1615 (m), 1585 (vs) ν(C=O). $^{1}$H NMR (300 MHz, THF-$d_8$, 25 °C): δ(NiC*H*$_3$) −0.43 (d, 3 H, $^{3}J$(PH) = 6.6 Hz), δ(PC*H*$_3$) 1.27 (d, 9 H, $^{2}J$(PH) = 9.9 Hz), δ[C(C*H*$_3$)$_3$] 1.36 (s, 9 H), δ(CC*H*$_3$) 2.15 (s, 3 H), δ(C*H*) 6.79 (s, 1 H), δ(C*H*) 7.10 (d, 1 H, $^{4}J$(HH) = 2.3 Hz), δ(C*H*O) 8.91 (s, 1 H). $^{13}$C NMR (75.4 MHz, THF-$d_8$, 25 °C): δ(Ni*C*H$_3$) −12.30 (d, $^{2}J$(PC) = 43.0 Hz), δ(P*C*H$_3$) 12.69 (d, $^{1}J$(PC) = 30.2 Hz), δ(C*C*H$_3$) 29.13, δ[C(*C*H$_3$)$_3$] 34.91, δ(1-*C*) 121.5, δ(6-*C*) 131.0, δ(4-*C*) 134.6, δ(5-*C*) 142.4, δ(2-*C*) 168.9, δ(*C*HO) 187.5.

**Preparation of Bis(μ-3,5-di-*tert*-butyl-2-oxobenzaldehyde)bis[*cis*-methyl(trimethylphosphine)nickel] (3).** [NiMe(OMe)PMe$_3$]$_2$ (1500 mg, 4.15 mmol) and di-*tert*-butylsalicylaldehyde (1950 mg, 8.32 mmol) in 30 mL of pentane gave a red brown solution. After 15 min the solution was filtered which failed to give a solid at −27 °C. The volatiles were removed in vacuo to afford 3180 mg of a red brown solid (crude yield 99%). Anal. Calcd for $C_{38}H_{66}Ni_2O_4P_2$ (766.3): C, 59.56; H, 8.68. Found: C, 58.73; H, 8.61. IR (Nujol mull, 2000−1560 cm$^{-1}$): 1590 (s) ν(C=O). $^{1}$H NMR (300 MHz, THF-$d_8$, 24 °C): δ(NiC*H*$_3$) −0.44 (d, 3 H, $^{3}J$(PH) = 6.5 Hz); δ(CC*H*$_3$) 1.25 (s, 9 H); δ(PC*H*$_3$) 1.27 (d, 9 H, $^{2}J$(PH) = 10.0 Hz); δ(CC*H*$_3$) 1.36 (s, 9 H); δ(C*H*) 6.95 (d, 1 H, $^{4}J$(HH) = 2.7 Hz), 7.39 (d, 1 H, $^{4}J$(HH) = 2.7 Hz); δ(C*H*O) 8.96 (s, 1 H). $^{13}$C NMR (75.4 MHz, 24 °C, THF-$d_8$): δ(P*C*H) 11.44 (d, $^{1}J$(PC) = 29.6 Hz); δ(C*C*H$_3$) 27.96, 29.63; δ(*C*CH$_3$) 32.58, 34.10; δ(*C*) 120.0; δ(*C*H) 126.16, 128.89; δ(*C*) 133.75, 140.89; δ(*C*O) 167.72; δ(*C*HO) 186.86.

**Preparation of Bis(μ-2-oxonaphthalene-1-carbaldehyde)bis[methyl(trimethylphosphine)nickel] (4).** [NiMe(OMe)PMe$_3$]$_2$ (630 mg, 1.74 mmol) and 2-hydroxonaphthalene-1-carbaldehyde (600 mg, 3.49 mmol) in 70 mL of ether at 20 °C gave a red brown solution. After 18 h this was evaporated to dryness and the resulting solid extracted with 25 mL of pentane. Cooling to −30 °C afforded 270 mg of red brown needles (24%); dec pt >78 °C. Anal. Calcd for $C_{30}H_{38}Ni_2O_4P_2$ (642.0): C, 56.13; H, 5.97. Found: C, 55.84; H, 5.98. IR (Nujol mull, 2000−1600 cm$^{-1}$): 1613 (vs), 1600 (vs) ν(C=O). $^{1}$H NMR (300 MHz, THF-$d_8$, 25 °C) (isomers: *cis* (44%), *trans* (56%)): δ(NiC*H*$_3$, *trans*) −0.59 (s, 3 H), δ(NiC*H*$_3$, *cis*) −0.55 (d, 3 H, $^{3}J$(PH) = 3.9 Hz), δ(PCH$_3$) 1.30 (d, 18 H, $^{2}J$(PH) = 10.2 Hz), δ(C*H*, *trans*) 6.62 (d, 1 H, $^{3}J$(HH) = 9.3 Hz), δ(C*H*, *cis*) 6.78 (d, 1 H, $^{3}J$(HH) = 9.3 Hz), δ(C*H*) 7.16 (ddd, 2 H, $^{3}J$(HH) = 6.9 and 7.8 Hz, $^{4}J$(HH) = 0.9 Hz), δ(C*H*) 7.36 (q, 2 H, $^{3}J$(HH) = 6.9 Hz), δ(C*H*) 7.55 (d, 2 H, $^{3}J$(HH) = 7.8 Hz), δ(C*H*) 7.61 (t, 2 H, $^{3}J$(HH) = 9.3 and 9.3 Hz), δ(C*H*) 8.04 (d, 1 H, $^{3}J$(HH) = 8.4 Hz), δ(C*H*) 8.10 (d, 1 H, $^{3}J$(HH) = 8.4 Hz), δ(C*H*O, *trans*) 9.89 (s, 1 H), δ(C*H*O, *cis*) 9.92 (s, 1 H). $^{13}$C NMR (75.4 MHz, THF-$d_8$, 25 °C): δ(P*C*H$_3$) 13.15 (d, $^{1}J$(PC) = 21.8 Hz); δ(*C*) 113.7; δ(*C*H) 118.7, 118.8, 123.3, 127.2, 127.6, 128.5, 129.6, 135.9; δ(*C*) 137.7; δ(2-*C*) 173.3; δ(*C*HO) 181.8.

**(2-Oxobenzoyl)tris(trimethylphosphine)nickel (5).** From salicylaldehyde (270 mg, 2.23 mmol) and [NiMe(OMe)PMe$_3$]$_2$ (400 mg, 1.11 mmol) was generated an orange solution of **1**, and trimethylphosphine (170 mg, 2.22 mmol) was added by condensation at −70 °C. After 2 h at 20 °C a dark red solution resulted, which was dried in vacuo, and the resulting red solid was extracted with 70 mL of pentane. At −30 °C 160 mg of red needles was obtained (18%); mp 130−132 °C. (Subsequent extraction with 70 mL of ether in an otherwise similar procedure yielded 230 mg of dark red crystals of **9** (30%); mp 172−174 °C.) Anal. Calcd for $C_{16}H_{31}NiO_2P_3$ (407.0): C, 47.21; H, 7.67; P, 22.83. Found: C, 47.20; H, 7.70; P, 22.95. IR (Nujol mull, 2000−1560 cm$^{-1}$): 1650 (w), 1600 (vs), 1570 (s) ν(C=O). $^{1}$H NMR (300 MHz, THF-$d_8$, 25 °C): δ(PC*H*$_3$) 1.25 (d, 27 H, $^{2}J$(PH) = 7.2 Hz), δ(C*H*) 6.00 (ddd, 1 H, $^{3}J$(HH) = 7.7 and 6.7 Hz, $^{4}J$(HH) = 1.0 Hz), δ(C*H*) 6.61 (dd, 1 H, $^{3}J$(HH) = 8.4 Hz, $^{4}J$(HH) = 1.0 Hz), δ(C*H*) 6.93 (ddd, 1 H, $^{3}J$(HH) = 8.4 and 6.7 Hz, $^{4}J$(HH) = 1.8 Hz), δ(C*H*) 7.01 (dd, 1 H, $^{3}J$(HH) = 7.7 Hz, $^{4}J$(HH) = 1.8 Hz). $^{13}$C NMR (75.4 MHz, THF-$d_8$, 32 °C): δ(P*C*H$_3$) 17.23 (d, $^{1}J$(PC) = 18.1 Hz); δ(*C*H) 111.2, 120.0, 123.5; δ(*C*) 132.2; δ(*C*H) 133.0; δ(*C*) 178.7; δ(*C*=O) 230.6. $^{31}$P NMR (121.5 MHz, THF-$d_8$): (32 °C) δ(*P*) −17.56 (s), (−75 °C) δ(P) −14.80 (s).

**Preparation of (3-*tert*-Butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)nickel (6).** (a) NiMe$_2$(PMe$_3$)$_3$ (980 mg, 3.09 mmol) and 3-*tert*-butyl-5-methylsalicylaldehyde (600 mg, 3.12 mmol) in 70 mL of THF were allowed to react upon warming from −70 to +20 °C. The volatiles were removed in vacuo, and the residue was extracted with 70 mL of pentane. At −30 °C 950 mg of dark red crystals (64%) was obtained. (b) To a solution of 3-*tert*-butyl-5-methylsalicylaldehyde (930 mg, 4.84 mmol) in 70 mL of THF at −70 °C was added through a syringe 3.1 mL of a 1.6 M solution of CH$_3$Li in ether (4.96 mmol). In a stream of argon, NiMeCl(PMe$_3$)$_2$ (1230 mg, 4.71 mmol) was added under stirring to give an orange brown solution. To this was condensed in vacuo PMe$_3$ (740 mg, 9.73 mmol), producing a dark red color within 5 min. Warming to 20 °C and working up as above yielded 650 mg of red crystals (32%). (c) From [NiMe(OMe)PMe$_3$]$_2$ (1780 mg, 4.92 mmol) and 3-*tert*-butyl-5-methylsalicylaldehyde (1900 mg, 9.88 mmol) in 70 mL of THF at −70 °C an orange red solution of **2** was prepared and trimethylphosphine (2140 mg, 28.1 mmol) was added by condensation in vacuo. Within 15 min a dark red color was observed. After warming to 20 °C, the volatiles were removed in vacuo and the cherry red solid was extracted with 70 mL of ether. Crystallization at −30 °C yielded 3910 mg of red prisms (83%); dec pt >157 °C. Anal. Calcd for $C_{21}H_{41}NiO_2P_3$ (477.2): C, 52.86; H, 8.87. Found: C, 53.24; H, 8.85 IR (Nujol mull, 2000−1560 cm$^{-1}$): 1595 (s), 1575 (vs) ν(C=O). $^{1}$H NMR (300 MHz, THF-$d_8$, 25 °C): δ(PC*H*$_3$) 1.27 (d, 27 H, $^{2}J$(PH) = 7.2 Hz), δ[C(C*H*$_3$)$_3$] 1.47 (s, 9 H), δ(C*H*$_3$) 2.09 (s, 3 H), δ(C*H*) 6.74 (dd, 1 H, $^{4}J$(HH) = 2.2 Hz, $^{4}J$(HH) = 0.9 Hz), δ(C*H*) 6.83 (d, 1 H, $^{4}J$(HH) = 2.2 Hz). $^{13}$C NMR (75.4 MHz, THF-$d_8$, 25 °C): δ(P*C*H$_3$) 17.47 (d, $^{1}J$(PC) = 17.8 Hz); δ(*C*H$_3$) 20.71; δ[C(*C*H$_3$)$_3$] 30.16; δ[*C*(CH$_3$)$_3$] 35.23; δ(*C*) 118.9; δ(*C*H) 121.8, 130.7; δ(*C*) 132.6, 138.5, 176.1; δ(*C*=O) 230.3. $^{31}$P NMR (121.5 MHz, THF-$d_8$): (22 °C) δ(P) −18.49 (s); (−40 °C) δ(P) −16.97; (−100 °C) δ(P) −21.02 (s, broad), −4.54 (s, broad).

**Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$)**

| atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Ni | 1388(1) | 5076(1) | 640(1) | 41(1) |
| P(1) | 2295(1) | 5150(1) | 615(1) | 61(1) |
| P(2) | 1434(1) | 4668(1) | 1869(1) | 62(1) |
| P(3) | 860(1) | 3749(1) | 127(1) | 59(1) |
| O(1) | 1191(1) | 6581(2) | 990(1) | 42(1) |
| O(2) | 1339(1) | 5280(3) | −929(2) | 58(1) |
| C(1) | 835(2) | 8971(4) | −161(3) | 49(2) |
| C(2) | 824(2) | 8537(4) | −880(3) | 50(2) |
| C(3) | 965(2) | 7477(4) | −937(2) | 41(2) |
| C(4) | 1101(2) | 6831(4) | −297(2) | 35(2) |
| C(5) | 1088(2) | 7249(4) | 422(2) | 37(2) |
| C(6) | 965(2) | 8374(4) | 492(2) | 41(2) |
| C(7) | 988(2) | 8890(4) | 1262(3) | 55(2) |
| C(8) | 667(2) | 9256(4) | −1563(3) | 79(2) |
| C(9) | 1280(2) | 5697(4) | −336(2) | 41(2) |
| C(11) | 2547(2) | 4939(6) | −245(3) | 124(3) |
| C(12) | 2764(2) | 4235(6) | 1191(3) | 125(4) |
| C(13) | 2595(2) | 6437(5) | 901(4) | 144(4) |
| C(21) | 1865(2) | 5592(5) | 2506(2) | 88(3) |
| C(22) | 773(2) | 4837(5) | 2193(3) | 83(2) |
| C(23) | 1672(2) | 3362(5) | 2278(3) | 100(3) |
| C(31) | 1271(2) | 2755(4) | −283(3) | 113(3) |
| C(32) | 478(2) | 2882(4) | 668(3) | 90(3) |
| C(33) | 298(2) | 4021(5) | −661(3) | 88(3) |
| C(71) | 1577(2) | 8748(5) | 1723(3) | 82(3) |
| C(72) | 561(2) | 8362(4) | 1676(3) | 74(2) |
| C(73) | 876(2) | 10118(4) | 1219(3) | 86(3) |

[a] Equivalent isotropic *U* calculated as $U(\mathrm{eq}) = {}^1/_3(\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j)$.

**Table 2. Selected Bond Lengths (Å) and Angles (deg)**

| | | | |
|---|---|---|---|
| Ni−P(1) | 2.227(1) | Ni−P(2) | 2.269(1) |
| Ni−P(3) | 2.188(1) | Ni−O(1) | 2.042(3) |
| Ni−C(9) | 1.904(4) | P−C(av) | 1.814 |
| O(1)−C(5) | 1.308(5) | O(2)−C(9) | 1.223(5) |
| C(1)−C(2) | 1.405(7) | C(1)−C(6) | 1.383(6) |
| C(2)−C(3) | 1.359(7) | C(2)−C(8) | 1.517(7) |
| C(3)−C(4) | 1.399(6) | C(4)−C(5) | 1.408(6) |
| C(4)−C(9) | 1.467(6) | C(5)−C(6) | 1.427(7) |
| C(6)−C(7) | 1.525(6) | C(7)−C(71) | 1.545(7) |
| C(7)−C(72) | 1.532(7) | C(7)−C(73) | 1.537(7) |
| P(1)−Ni−P(2) | 98.5(1) | P(1)−Ni−P(3) | 122.5(1) |
| P(2)−Ni−P(3) | 100.3(1) | P(1)−Ni−O(1) | 104.9(1) |
| P(2)−Ni−O(1) | 82.6(1) | P(3)−Ni−O(1) | 131.0(1) |
| P(1)−Ni−C(9) | 86.8(1) | P(2)−Ni−C(9) | 167.8(1) |
| P(3)−Ni−C(9) | 85.8(1) | O(1)−Ni−C(9) | 85.5(2) |
| Ni−P−C(av) | 117.4 | C−P−C(av) | 100.4 |
| Ni−O(1)−C(5) | 110.5(3) | C(2)−C(1)−C(6) | 123.8(4) |
| C(1)−C(2)−C(3) | 118.2(4) | C(1)−C(2)−C(8) | 119.8(5) |
| C(3)−C(2)−C(8) | 122.0(4) | C(2)−C(3)−C(4) | 120.7(4) |
| C(3)−C(4)−C(5) | 121.3(4) | C(3)−C(4)−C(9) | 122.1(4) |
| C(5)−C(4)−C(9) | 116.6(4) | O(1)−C(5)−C(4) | 117.8(4) |
| O(1)−C(5)−C(6) | 123.8(4) | C(4)−C(5)−C(6) | 118.4(4) |
| C(1)−C(6)−C(5) | 117.4(4) | C(1)−C(6)−C(7) | 121.9(4) |
| C(5)−C(6)−C(7) | 120.6(4) | C(6)−C(7)−C(71) | 109.4(4) |
| C(6)−C(7)−C(72) | 110.6(4) | C(71)−C(7)−C(72) | 109.7(4) |
| C(6)−C(7)−C(73) | 112.7(4) | C(71)−C(7)−C(73) | 106.3(4) |
| C(72)−C(7)−C(73) | 108.1(4) | Ni−C(9)−O(2) | 129.0(4) |
| Ni−C(9)−C(4) | 109.4(3) | O(2)−C(9)−C(4) | 121.6(4) |

**Preparation of [3,5-Di-*tert*-butyl-2-oxobenzoyl]tris(trimethylphosphine)nickel (7).** $[\mathrm{NiMe(OMe)PMe_3}]_2$ (1980 mg, 5.47 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (2630 mg, 11.22 mmol) in 70 mL of ether after 30 min at 22 °C formed an orange brown solution of **3**. To this was added by cooling and condensation in vacuo excess trimethylphosphine (2210 mg, 29.1 mmol). At 22 °C within 10 min, a dark red solution was obtained, which was evaporated to dryness. Extraction with 70 mL of fresh ether and cooling to −27 °C afforded 3800 mg of dark red prisms (67%), mp 166−168 °C. Anal. Calcd for $\mathrm{C_{24}H_{47}NiO_2P_3}$ (519.2): C, 55.52; H, 9.12. Found: C, 55.76; H, 9.00. IR (Nujol solution, 2000−1550 $\mathrm{cm^{-1}}$): 1780 (w), 1610 (vs), 1580 (vs) $\nu(\mathrm{C{=}O})$. $^1$H NMR (300 MHz, THF-$d_8$, 24 °C): $\delta(\mathrm{CC}H_3)$ 1.21 (s, 9 H); $\delta(\mathrm{PC}H_3)$ 1.28 (d, 27 H, $^2J(\mathrm{PH}) = 7.2$ Hz); $\delta(\mathrm{CC}H_3)$ 1.49 (s, 9 H); $\delta(\mathrm{C}H)$ 6.98 (d, 1 H, $^4J(\mathrm{HH}) = 2.7$ Hz), 7.14 (d, 1 H, $^4J(\mathrm{HH}) = 2.7$ Hz). $^{13}$C NMR (75.4 MHz, THF-$d_8$, 24 °C): $\delta(\mathrm{P}C\mathrm{H_3})$ 15.66 (d, $^1J(\mathrm{PC}) = 17.4$ Hz); $\delta(\mathrm{C}C\mathrm{H_3})$ 28.37, 30.55; $\delta(C\mathrm{CH_3})$ 32.54, 33.72; $\delta(C\mathrm{H})$ 115.87, 125.19; $\delta(C)$ 130.56, 130.96, 136.07, 174.11; $\delta(C\mathrm{HO})$ 228.48. $^{31}$P NMR (121.5 MHz, THF-$d_8$, 24 °C): $\delta$(P) −17.70 (s).

**Preparation of (2-Oxo-1-naphthoyl)tris(trimethylphosphine)nickel (8).** $[\mathrm{NiMe(OMe)PMe_3}]_2$ (450 mg, 1.24 mmol) and 2-hydroxynaphthalene-1-carbaldehyde (440 mg, 2.56 mmol) in 70 mL of ether were stirred for 1 h at 20 °C. The clear solution was condensed with trimethylphosphine (1240 mg, 16.3 mmol), causing a dark red color and precipitation of a violet solid (270 mg) which was filtered off. This solution at −30 °C afforded 550 mg of red crystals (48%); dec pt >115 °C. Anal. Calcd for $\mathrm{C_{20}H_{33}NiO_2P_3}$ (457.1): C, 52.55; H, 7.28. Found: C, 52.42; H, 7.24. IR (Nujol mull, 2000−1570 $\mathrm{cm^{-1}}$): 1605 (s), 1580 (m) $\nu(\mathrm{C{=}O})$. $^1$H NMR (300 MHz, THF-$d_8$, 25 °C): $\delta(\mathrm{PC}H_3)$ 1.27 (d, 27 H, $^2J(\mathrm{PH}) = 7.1$ Hz), $\delta(\mathrm{C}H)$ 6.90 (ddd, 1 H, $^3J(\mathrm{HH}) = 7.9$ and 6.8 Hz, $^4J(\mathrm{HH}) = 1.2$ Hz), $\delta(\mathrm{C}H)$ 6.93 (d, 1 H, $^3J(\mathrm{HH}) = 9.1$ Hz), $\delta(\mathrm{C}H)$ 7.17 (ddd, 1 H, $^3J(\mathrm{HH}) = 8.5$ and 6.8 Hz, $^4J(\mathrm{HH}) = 1.4$ Hz), $\delta(\mathrm{C}H)$ 7.42 (d, 1 H, $^3J(\mathrm{HH}) = 9.0$ Hz), $\delta(\mathrm{C}H)$ 7.43 (dd, 1 H, $^3J(\mathrm{HH}) = 7.9$ Hz, $^4J(\mathrm{HH}) = 1.4$ Hz), $\delta(\mathrm{C}H)$ 8.74 (d, 1 H, $^3J(\mathrm{HH}) = 8.5$ Hz). $^{13}$C NMR (75.4 MHz, THF-$d_8$, 25 °C): $\delta(\mathrm{P}C\mathrm{H_3})$ 15.41 (d, $^1J(\mathrm{PC}) = 17.0$ Hz); $\delta(C)$ 115.9; $\delta(C\mathrm{H})$ 118.1, 122.3, 123.1; $\delta(C)$ 125.2; $\delta(C\mathrm{H})$ 125.5, 125.7; $\delta(C)$ 131.2; $\delta(C\mathrm{H})$ 131.7; $\delta(C)$ 178.9.

**Preparation of (2-Oxobenzoyl)bis(trimethylphosphine)nickel (9).** (a) In the synthesis of **5**, after extraction with pentane, the red solid remaining on the glass−sinter was dissolved in 70 mL of ether. From this solution at −30 °C was obtained 230 mg of dark red crystals (30%). (b) Combining $\mathrm{NiMe_2(PMe_3)_3}$ (440 mg, 1.39 mmol) and salicylaldehyde (170 mg, 1.40 mmol) in 70 mL of ether at −70 °C resulted in a change of color from orange to dark red. After 24 h at 20 °C the volatiles were removed in vacuo and from the solid was obtained 110 mg of **5** (19%) by extraction with pentane. The violet residue was then extracted with 50 mL of toluene to give 250 mg of a red solid (50%) which had a satisfactory elemental analysis. Recrystallization from 80 mL of ether gave 120 mg of violet red needles; dec pt >172 °C. Anal. Calcd for $\mathrm{C_{13}H_{22}NiO_2P_2}$ (331.0): C, 47.18; H, 6.70; P, 18.72. Found: C, 47.28; H, 6.74; P, 18.86. IR (Nujol mull, 2000−1620 $\mathrm{cm^{-1}}$): 1680 (w), 1670 (w), 1615 (vs) $\nu(\mathrm{C{=}O})$. $^1$H NMR (300 MHz, THF-$d_8$): [(25 °C) **10** (29%)] $\delta(\mathrm{PC}H_3)$ 0.89 (d, 9 H, $^2J(\mathrm{PH}) = 9.8$ Hz), $\delta(\mathrm{C}H)$ 6.46 (ddd, 1 H, $^3J(\mathrm{HH}) = 7.7$ and 7.1 Hz, $^4J(\mathrm{HH}) = 0.9$ Hz), $\delta(\mathrm{C}H)$ 7.10 (dd, 1 H, $^3J(\mathrm{HH}) = 7.6$ Hz, $^4J(\mathrm{HH}) = 1.7$ Hz), $\delta(\mathrm{C}H)$ 8.28 (d, 1 H, $^3J(\mathrm{HH}) = 8.0$ Hz); [additional signals at 25 °C for **5** and **9** involved in rapid $\mathrm{PMe_3}$ exchange (together 71%)] $\delta(\mathrm{PC}H_3)$ 1.26 (d, 45 H, $^2J(\mathrm{PH}) = 7.2$ Hz), $\delta(\mathrm{C}H)$ 6.07 (2 H), 6.27 (1 H), 6.56 (1 H), 6.96 (4 H), exchange-broadened multiplets; [($\mathrm{PMe_3}$ signals at −90 °C) for **10** (33%)] $\delta(\mathrm{PC}H_3)$ 0.23 (d, 3 H, $^2J(\mathrm{PH}) = 10.3$ Hz), 0.96 (d, 3 H, $^2J(\mathrm{PH}) = 9.5$ Hz), 1.33 (d, 3 H, $^2J(\mathrm{PH}) = 8.3$ Hz); [($\mathrm{PMe_3}$ signals at −90 °C) for **5** and **9** (together 67%)] $\delta(\mathrm{PC}H_3)$ 1.25 (m, 45 H); [(CH signals at −90 °C) for **5** (29%)] $\delta(\mathrm{C}H)$ 6.07 (dd, 1 H, $^3J(\mathrm{HH}) = 7.3$ and 7.3 Hz), 6.59 (d, 1 H, $^3J(\mathrm{HH}) = 8.3$ Hz), 6.94 (ddd, 1 H, $^3J(\mathrm{HH}) = 6.7$ and 8.3 Hz, $^4J(\mathrm{HH}) = 1.7$ Hz), 6.99 (dd, 1 H, $^3J(\mathrm{HH}) = 7.7$ Hz, $^4J(\mathrm{HH}) = 1.7$ Hz); [(CH signals at −90 °C) for **9** (38%)] $\delta(\mathrm{C}H)$ 6.01 (dd, 1 H, $^3J(\mathrm{HH}) = 7.2$ Hz and 7.2 Hz), 6.27 (d, 1 H, $^3J(\mathrm{HH}) = 8.2$ Hz), 6.88 (dd, 1 H, $^3J(\mathrm{HH}) = 7.6$ Hz, $^4J(\mathrm{HH}) = 1.5$ Hz), 7.07 (m, 1 H); [(CH signals at −90 °C) for **10** (33%)] $\delta(\mathrm{C}H)$ 6.49 (dd, 1 H, $^3J(\mathrm{HH}) = 7.3$ and 7.3 Hz), 7.07 (m, 1 H), 7.33 (dd, 1 H, $^3J(\mathrm{HH}) = 6.8$ and 8.3 Hz), 8.26 (d, 1 H, $^3J(\mathrm{HH}) = 8.3$ Hz. $^{13}$C NMR (75.4 MHz, THF-$d_8$, 25 °C): $\delta(\mathrm{P}C\mathrm{H_3})$ 13.00 (d, $^1J(\mathrm{PC}) = 29.5$ Hz), 16.51 (d, $^1J(\mathrm{PC}) = 16.6$ Hz); $\delta(C)$ 117.0, 118.5, 122.7, 123.4, 133.2, 134.0, 135.6, 172.4. $^{31}$P NMR (121.5 MHz, THF-$d_8$): (32 °C) $\delta$(P) −20.44 (s, broad), 1.64 (s); (−25 °C) $\delta$(P) −26.34 (s, broad), −16.90 (s), 2.83 (s); (−75 °C) $\delta$(P) −25.16 (s), −15.82 (s, broad), 4.13 (s).

**Preparation of (2-Oxobenzoyl)(trimethylphosphine)nickel (10).** An orange solution of **1**, prepared from [NiMe-

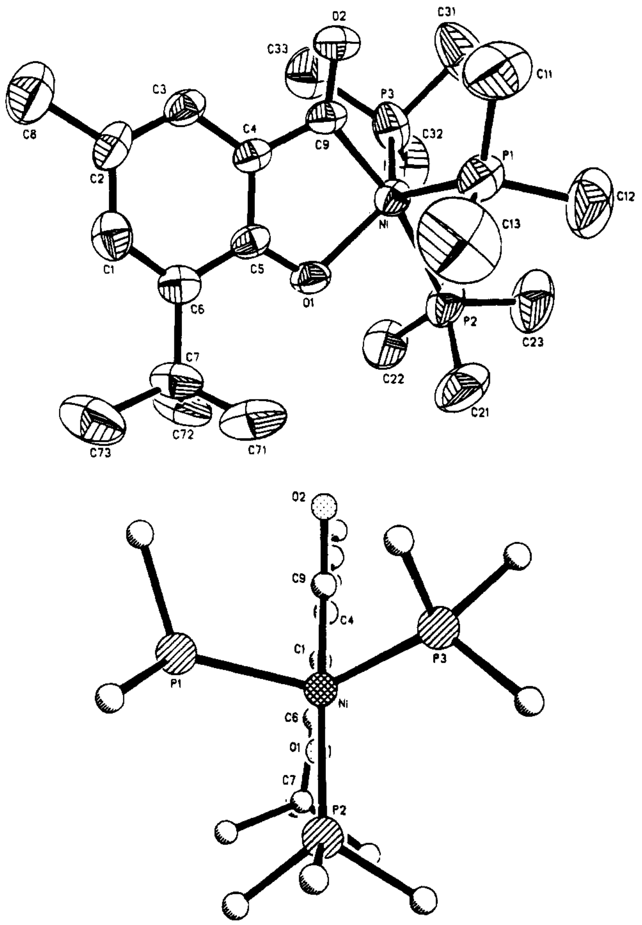


**Figure 1.** (a, top) Molecular structure of **6** and atom numbering. (b, bottom) View along the plane of rings.

(OMe)PMe$_3$]$_2$ (600 mg, 1.66 mmol) and salicylaldehyde (410 mg, 3.36 mmol) in 80 mL of ether, was kept at 20 °C for 7 days. Dark red crystals were deposited which were then washed with ether and dried in vacuo to yield 290 mg (34%); decomp pt >233 °C. Anal. Calcd for $C_{20}H_{26}Ni_2O_4P_2$ (509.8): C, 47.13; H, 5.14. Found: C, 47.47; H, 5.44. IR (Nujol mull, 2000–1560 cm$^{-1}$): 1620 (vs), 1570 (s) $\nu$(C=O). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$(PC*H*$_3$) 0.87 (d, 9 H, $^2J$(PH) = 9.8 Hz), $\delta$(C*H*) 6.50 (dd, 1 H, $^3J$(HH) = 7.6 and 7.1 Hz), $\delta$(C*H*) 7.12 (dd, 1 H, $^3J$(HH) = 7.6 Hz, $^4J$(HH) = 1.6 Hz), $\delta$(C*H*) 7.28 (ddd, 1 H, $^3J$(HH) = 8.1 and 7.1 Hz, $^4J$(HH) = 1.6 Hz), $\delta$(C*H*) 8.15 (d, 1 H, $^3J$(HH) = 8.1 Hz). $^{13}$C NMR (75.4 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$(PCH$_3$) 12.85 (d, $^1J$(PC) = 29.9 Hz); $\delta$(CH) 116.8, 117.7, 122.1, 133.9; $\delta$(C) 135.1, 171.7.

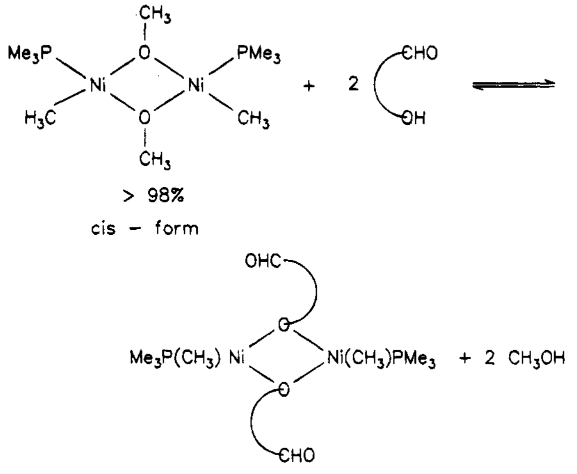
**Attempted Transformation of 2 by Triethylamine.** In 70 mL of pentane **2** (910 mg, 1.33 mmol) was combined with NEt$_3$ (800 mg, 7.9 mmol) and the resulting red brown solution was kept at 20 °C for 72 h. A slight turbidity was removed by filtration, and the solution was dried in vacuo to produce 910 mg of a dark brown solid identical with **2** by IR.

**Crystal structure determination**: $C_{21}H_{41}NiO_2P_3$; $M_r$ = 477.2; red crystal sealed in a capillary; size 0.25 x 0.40 x 0.69 mm; monoclinic, space group *C*2/*c*; $a$ = 24.453(3) Å; $b$ = 12.313(2) Å; $c$ = 18.132(3) Å; $\beta$ = 99.94(1)°; $V$ = 5377.4 Å$^3$; $Z$ = 8, $D_{calc}$ = 1.179 g cm$^{-3}$; $\mu$ = 0.91 mm$^{-1}$; $T$ = 296(1) K; Siemens R3m/V diffractometer; graphite monochromator; $\omega/2\theta$ scan; 7287 intensities collected ($3 \le 2\theta \le 55°$), 3034 unique intensities considered observed [$F \ge 4\sigma(F)$]; structure solved by Patterson and Fourier methods, empirical absorption correction via $\psi$ scans; $R$ = 0.052, $R_w$ = 0.039 [$1/w = \sigma^2(F) + 0.0001F^2$]; $S$ = 1.615, max($\Delta/\sigma$) = 0.001, max residuals −0.36/0.35 e/Å$^3$. Scattering factors were determined and refinement of the structure was by SHELXTL-Plus;[8] further programs were MISSYM[9] and PARST.[10]

Atomic coordinates are given in Table 1, and selected bond lengths and angles in Table 2; Figure 1 shows the molecular structure.

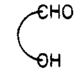
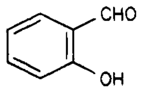
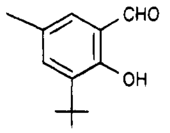
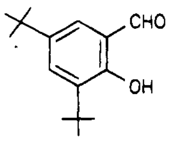
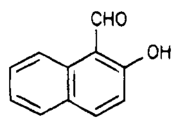
## Results and Discussion

Phenol functions generally replace both methoxo bridges in dinuclear methylnickel compounds[4] according to eq 3. Without utilizing their aldehyde functions,



(3)

1 – 4

| |  | cis : trans ( % )<br>¹H–NMR in d⁸–THF |
|---|---|---|
| 1 |  | 43 : 57 |
| 2 |  | > 95 : < 5 |
| 3 |  | > 95 : < 5 |
| 4 |  | 44 : 56 |

salicylaldehyde and its derivatives form phenoxo bridges in dinuclear methyl(trimethylphosphine)nickel compounds **1–4** with an equilibria of *cis* and *trans* configurations similar to that for phenol or *p*-cresol.[4a] Only in **2** and **3** does the *cis* configuration prevail due to the CMe$_3$ substituents crowding the $\mu$-oxo functions.

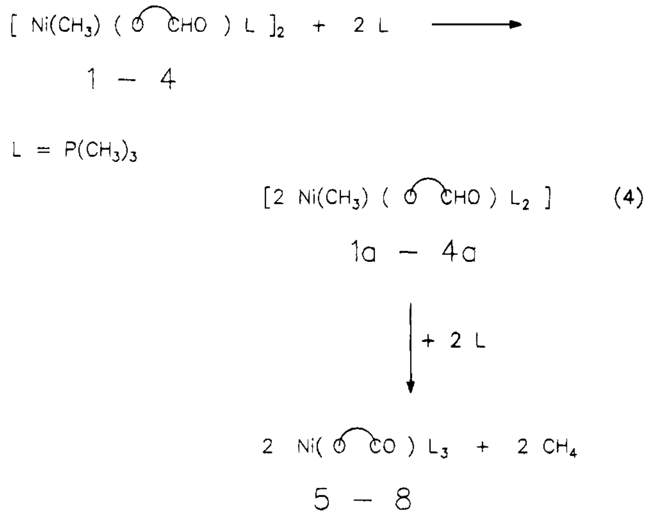
---

(8) Sheldrick, G. M. *SHELXTL-Plus Structure Determination Software Programs*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(9) LePage, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264.

(10) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

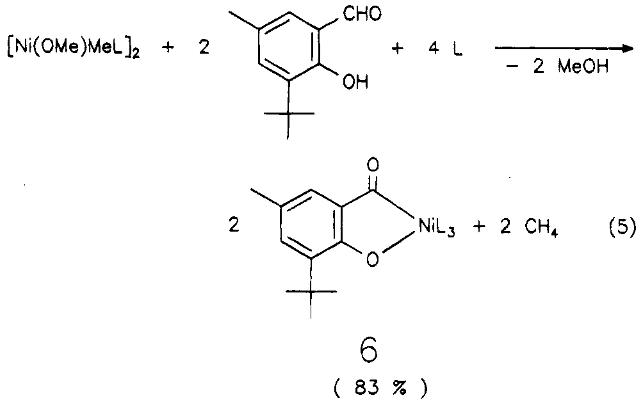
**Reaction with Trimethylphosphine.** Brown solutions of dinuclear methylnickel chloride $[NiMe(Cl)PMe_3]_2$ take up trimethylphosphine in ether at −70 °C, to give yellow *trans*-$NiMe(Cl)(PMe_3)_2$[4a] instantaneously and irreversibly. With a OMe replacing the Cl ligand, the solution yields crystals of dinuclear methylnickel methoxide exclusively,[4a] while mononuclear methylnickel phenolates may be crystallized although they release trimethylphosphine in vacuo. From these observations it follows that dinuclear compounds **1**−**4** will smoothly react with 2 equiv of ligand, according to eq 4, to give **1a**−**4a** as first intermediates. At −70 °C these undergo a spontaneous fragmentation reaction involving the aldehyde functions. From NiMe and CHO groups methane is formed and the phenolate ligands are transformed into chelating 2-oxophenacyl ligands of the new acylnickel complexes **5**−**8**.

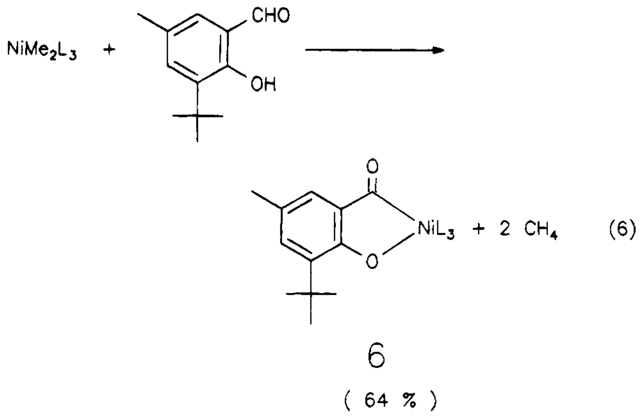


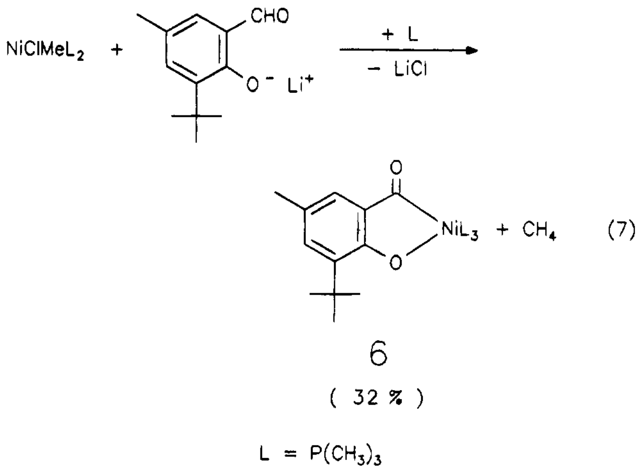
Tiethylamine, although a stronger base, even when present in excess cannot induce fragmentation of **2**, which is completely recovered after 72 h at 20 °C. With only 2 equiv of trimethylphosphine transformation is incomplete, because 18-electron tris(phosphine) compounds **5**−**8** are formed that do not readily dissociate neutral ligands. In particular **6** is smoothly formed according to eq 4 when **2** is reacted with 4 equiv of phosphine or in a one-pot reaction according to eq 5.

A synthesis starting from the highly reactive dimethylnickel complex according to eq 6 does not require additional ligand but is prone to side reactions. **6** crystallizes from ether in dark red prisms, and from pentane in cherry-red crystals. These crystals are freely soluble in toluene or THF and are oxidized in air within 2 min. Thermal decomposition begins under argon above 157 °C. Although this process liberates some trimethylphosphine, no compounds containing less than three phosphines per nickel could be obtained, either under normal pressure or in vacuo.

Compounds derived from the unsubstituted salicylaldehyde show a different behavior. Syntheses according to eq 4 or eq 6 afford mixtures of products. By extraction with pentane red needles of **5** (18% and 19%, respectively) are obtained, and subsequent extraction with ether yields dark red crystals of coordinatively unsaturated **9** (30% and 52%, respectively). In a one-pot reaction with excess phosphine, according to eq 5, only **5** (51%) is isolated. Under argon this material starts to melt at 130−132 °C, with a slow transformation into **9** which decomposes above 173 °C. Compounds **5** and **9** are more sensitive to oxygen than **6**.

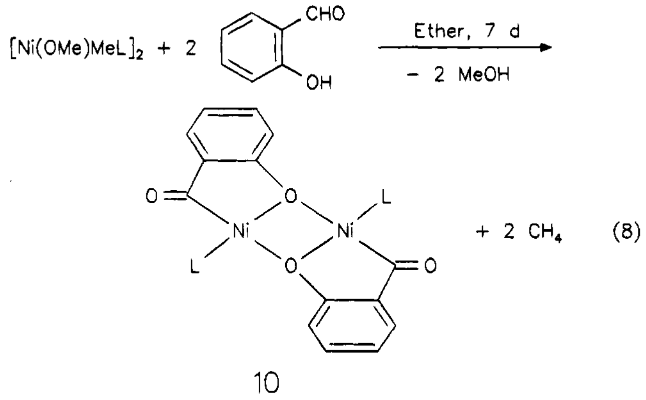




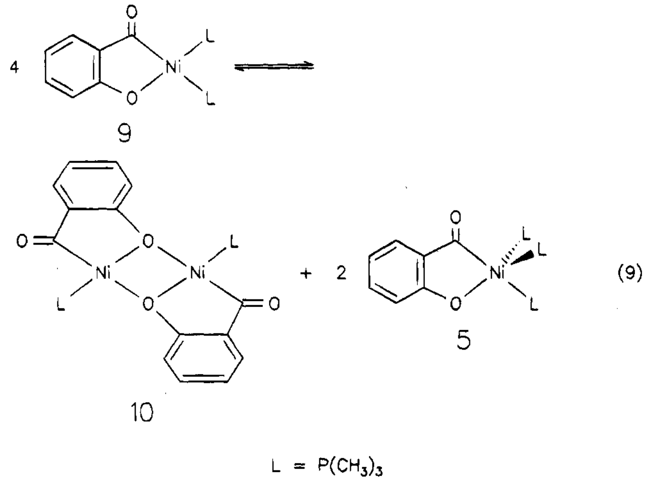


Solutions of **9** in THF are unstable. At varying temperatures, the $^1H$ NMR spectra indicate formation of **5** and of a new species **10**, that contains only one trimethylphosphine per chelating ligand. At 25 °C, **9** and **5** (together 71%) show one $PMe_3$ doublet and one group of aromatic CH signals, indicating fast exchange of neutral ligands that does not involve **10** (29%). At −90 °C separate signals for **5** (29%) and for **9** (38%) are observed, while for **10** (33%) a freezing of the $PMe_3$ rotation is recognized. However, a structural model for the coordination geometry around the nickel atom in **10** remains speculative. Most likely a 16-electron *trans*-dinickel compound is formed through a $\mu$-oxo-bridging function of the C,O-chelating ligand. This requires adjacent C=O and $PMe_3$ groups in the plane of coordination and results in steric congestion that could explain the hindered $PMe_3$ rotation.

For a convenient synthesis of **10**, a slow transformation of **1** by catalytic amounts of trimethylphosphine proceeds according to eq 8. From homogeneous solution at 20 °C dark red cubes are deposited within 1 week which are stable under argon up to 233 °C.



Using 2-hydroxynaphthaldehyde in a synthesis, according to eq 5, red crystals of **8** (48%) are obtained. These turn black under argon above 115 °C due to decomposition. The transformation of diamagnetic **9** into **5** and **10** by ligand dismutation (eq 9) suggests that the usual square planar geometry at the nickel atom is unfavorable for this particular set of ligands. Only the low solubility of **9** allows for its isolation. There are no bis(phosphine) pendants for **6**–**8**.



One reason for the preferred pentacoordination in **6** is based on the steric requirements of the C,O-chelating ligand. While the metallocycle formed should be equally apt to span a right angle either between *cis* positions in a square planar geometry or between axial–equatorial positions in a trigonal bipyramid, the exocyclic C=O group should cause in-plane repulsion only in the former. Therefore, the atomic positions in the crystal of **6** were of particular interest.

**Molecular Structure of 6.** The monoclinic cell of **6** contains eight molecules of the same configuration (Figure 1). The packing does not show significant intermolecular contacts (such as hydrogen bridges). The nickel atom holds two trimethylphosphine ligands at normal[11] distances Ni–P = 2.20 ± 0.02 Å and a third at the longer distance Ni–P = 2.269(1) Å. The angles are close to the sterically relaxed value[12] around 100°, although the first mentioned two ligands approach the ideal angle between equatorial positions in a trigonal bipyramid (P1–Ni–P3 = 122.5(1)°). However, the sum of equatorial bond angles is 358.4° and consists of very different values (P1–Ni–O1 = 104.9(1)° and P3–Ni–O1 = 131.0(1)°). Although the rotational orientation of the chelating ligand above the triangle P1P2P3 corresponds with type II (Figure 2) of the systematic[13] overview and is related to the trigonal bipyramid, the observed structure can also be derived from a square pyramidal geometry (P1 apical) by deformation of bond angles.

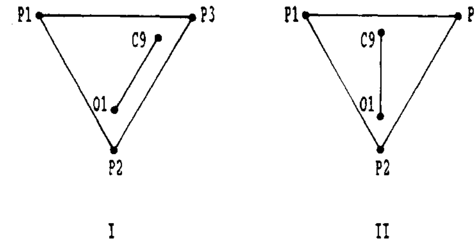


**Figure 2.** Structural types of pentacoordination for compounds $M(\eta^2\text{-ligand})(\eta^1\text{-ligand})_3$.

Disregarding the ligands with atoms P1 and P3, we observe the phenyl ring and the metal chelate ring in one plane that also contains the P2 atom (Figure 1b). The angles (O1–Ni–C9 = 85.5(2)°, O1–Ni–P2 = 82.6(1)°, and C9–Ni–P2 = 167.8(1)°) in this plane leave a vacant coordination site, which, for instance, could be occupied by the ligand with the P3 atom at the observed angle P3–Ni–C9 = 85.8(1)°. This would cause an angle P2–Ni–P3 ≈ 106° or, in ideal square planar geometry with right angles O1–Ni–P2 and C9–Ni–P2, would lead to a sterically tolerable value of 94.5°, which is close to that found in the structure of $NiCH_3(PMe_3)_4(BPh_4)$.[14] As opposed to the structure of *trans*-$Ni(COCH_3)Cl(PMe_3)_2$[15] the CO group with the typical angle Ni–C9–O2 = 129.0(4)° lies in the coordination plane and not perpendicular to it.

Let us again examine the molecular structure of **6** (Figure 1) and suppose we have a composition as in **9** with the known tendency for square planar coordination. Such an in-plane arrangement would cause repulsion with $PCH_3$ groups. Probably for this reason, the position in the chelate plane remains unoccupied, and the 14-electron fragment instead coordinates two phosphine ligands above and below this plane at angles P1–Ni–C9 = 86.8(1)° and P3–Ni–C9 = 85.8(1)° which occupy staggered rotational positions with respect to the CO group.

Repulsion with electrons of an $a_1$ type molecular orbital in an ideal square pyramidal geometry (P1 apical) can be assumed to be a reason for the oblique coordination of P1 and P3 relative to O1 (Figure 1b). We observe Ni–P2 = 2.269(1) Å to be almost opposite

---

[11] Pauling, L. *Die Natur der chemischen Bindung*, 3rd ed.; Verlag Chemie: Weinheim, 1976; p 216.

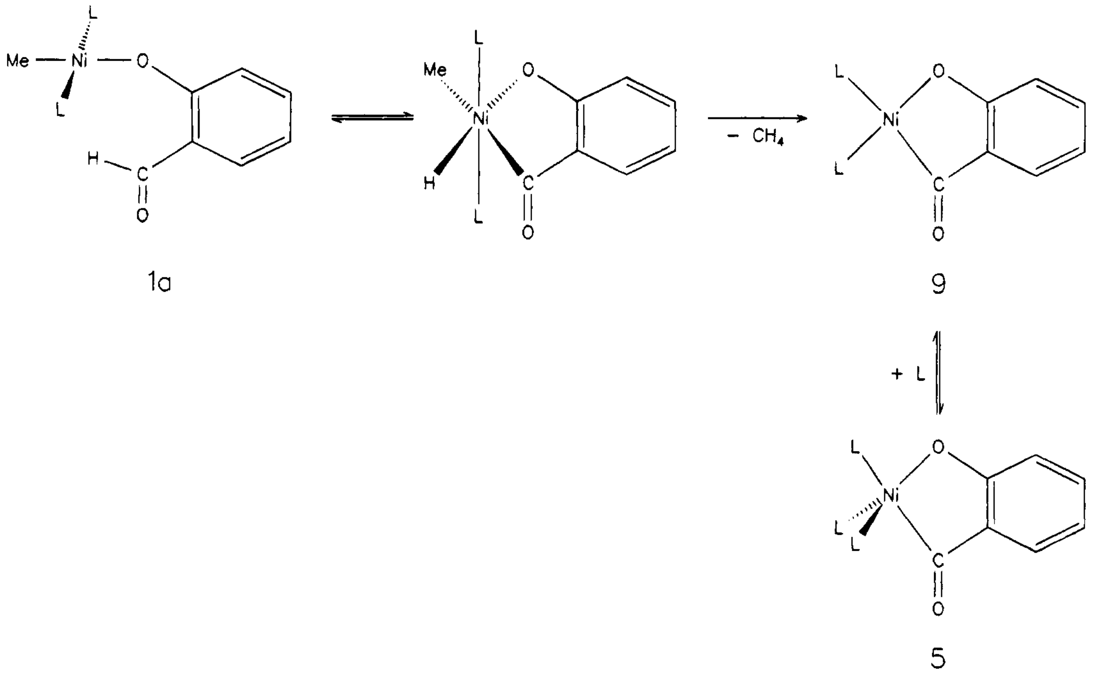
[12] Dawson, J. W.; McLennan, T. J.; Robinson, W.; Merle, A.; Dartiguenave, M.; Dartiguenave, Y.; Gray, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 4428.

[13] Kepert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 1, p 31.

[14] Gleizes, A.; Kerkeni, A.; Dartiguenave, M.; Dartiguenave, Y.; Klein, H.-F. *Inorg. Chem.* **1981**, *20*, 2372.

[15] Huttner, G.; Orama, O.; Bejenke, V. *Chem. Ber.* **1976**, *109*, 2533.

**Scheme 1. Addition/Elimination Reaction Sequence in Ligand-Induced Fragmentation Processes**



to the acyl ligand (C9−Ni−P2 = 167.8(1)°) and elongated by a *trans* influence which is significantly above the upper 25th percentile of expectation (2.245 Å).[16] The distance Ni−C9 = 1.904(4) Å is equal to the sum of Ni(II) and sp$^2$-C radii and therefore represents the expected $\sigma$-bond. The C−O distance (O2−C9 = 1.223(5) Å) and the angle Ni−C9−C4 (109.4(3)°) are as those for ketones, and the normal distance of the two sp$^2$-C atoms (C4−C9 = 1.467(6) Å) does not suggest an easy mobilization of CO, in accord with experimental findings.

Normal angles in the five-membered metal chelate ring (angle sum = 540°) indicate relaxed coordination of an axial acyl function as a soft $\sigma$-donor and an equatorial phenolate O atom as a hard $\sigma$- and $\pi$-donor ligand.

**Attempted Decarbonylation of 5−10.** From boiling methylcyclohexane **6** is recovered unchanged after 2 h. Thermal decomposition of a crystalline material of **5**−**9** at 160 °C under argon proceeds with black coloration from elemental nickel. Infrared spectra of incompletely decomposed samples display characteristic bands of educts, but no bands are observed in the region of terminal or bridging carbonyl ligands.

Solutions of **5**−**9** differ from those of *trans*-NiCl(COCH$_3$)(PMe$_3$)$_2$[3a] in that they have no tendency to decarbonylate toward Ni(PMe$_3$)$_4$. However, when **6** is cooled in THF under 1 bar of CO to −70 °C, the dark red color lightens, indicating reaction, while after 24 h at 20 °C **6** is recovered from the dark red solution as the sole product. Under normal conditions compounds **5**−**10** are neither decarbonylated nor carbonylated. The acylphenolate ligand forms a stable metal chelate ring.

This observation suggests syntheses of **5** by the ring-opening reaction from benzofuran-2,3-dione or oligosalicylide and Ni(PMe$_3$)$_4$ which so far have met with failure.

## Conclusion

Fragmentation reactions involving a nickel-d$^8$ center in square planar coordination geometry may be induced by addition of a second trimethylphosphine ligand, which breaks up the oxo-bridged dinuclear methylnickel phenolates into mononuclear *trans* complexes of suitable design. The methylnickel function appears to be essential in a transient acylnickel(IV) species[17] (Scheme 1).

Subsequent elimination of methane affords a chelating acylphenolate ligand supporting the nickel(II) center. The unusual stability of the 18-electron acylnickel complex is favorable for electrophilic attack and subsequent C,C-coupling reactions, which are under study.[17]

**Acknowledgment.** We thank *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* for financial support of this work.

**Supplementary Material Available:** A figure showing the structure of **6** and tables of atomic coordinates, bond lengths and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

OM940173V

---

[16] Orpen, G.; Brammer, L.; Allen, F. H.; Kennard, D. G.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S54.

[17] Acylnickel(IV) complexes have been recently characterized: Klein, H.-F.; Bickelhaupt, A.; Cordier, G.; Jung, T. *Organometallics* **1994**, *13*, .