Trimethylphosphine Complexes of Diorganonickel(IV) Moieties

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When coordinated to 2-oxobenzoyl-*C,O* chelating ligands (O⌒C=O) (⌒ = 3-*tert*-butyl-5-methylphenyl, 3,5-di-*tert*-butylphenyl, 3-methoxyphenyl, 3,4-benzocyclohexenyl, cyclohexenyl), 18 electron nickel(II) complexes Ni(O⌒C=O)(PMe₃)₃ (**1–5**) oxidatively add iodomethane affording thermally labile Ni^IV compounds *trans-mer*-Ni(Me)I(O⌒C=O)(PMe₃)₂ (**6–10**) or react with iodine in a ligand dismutation reaction to form stable molecules of *trans*-Ni(O⌒C=O)₂-(PMe₃)₂ (**21–25**), which contain cisoidal acylphenolato chelate rings. Acylphenolato compounds **1–5** react with larger electrophiles [C₂H₅I, (CH₃)₂CHI, *n*-C₄H₉I, *cyclo*-C₆H₁₁I, CH₃COCl, PhCOCl, (CH₃)₃COCl] in different regioselectivities affording ketones or esters. The square pyramidal bis[*n*-butyl 2-oxophenyl ketone]nickel(II) complex **16** crystallizes in the monoclinic space group C2/c, while the square planar chloro(phenyl)nickel(II) complex **19** with an ester group in the 2-position crystallizes in the triclinic space group P$\bar{1}$. Steric control of C,C-coupling reactions is demonstrated in three transformations, starting either from (acylphenolato)nickel(II) or from metastable diorganonickel(IV) compounds.

Introduction

The late transition elements are characterized by a distinctly lower stability of high formal oxidation states, which is most pronounced for first-row metals.[1] While Zn(H₂O)₆²⁺ cannot be oxidized under ambient conditions, the hexafluorometalates(III,IV) MF₆$^{z-}$ (M = Cu, Ni; z = 2, 3) once generated are highly oxidizing. Disregarding the effects of π-bonding and ligand noninnocence, this property of the metal center falls off with the electronegativity of donor atoms. Nonexistent tetramethylnickel is expected to behave as a reductant in most reactions similar to WMe₆. However, the thermal stability of a metastable compound is controlled by a kinetic barrier, which is difficult to predict. Therefore all doubts that have been cast on the existence of organonickel(IV) compounds beyond the kinetically labile organonickel(III) intermediates do not really rest on solid ground. Using chelating 2-acylphenolato ligands we have recently synthesized two novel types of hexacoordinate nickel complexes in which the organometal can be said to be in an unusual ligand field (Figure 1). Molecular structures and properties of both types of diorgano-nickel(IV) complexes (**6**, **7**, **21**, **22**) have been previously published.[2,3] As generated via oxidative addition of iodoalkanes to nickel(II) complexes the first examples for the formal oxidation state of IV in organonickel chemistry challenge the current view of C,C-coupling processes using nickel(II) compounds[4] in stoichiometric reactions or as catalysts. It is generally
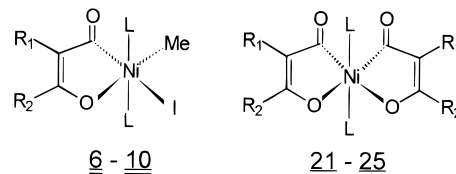
Figure 1. Types of diorganonickel(IV) compounds.

believed that highly reactive organonickel(III) intermediates play an important role in such transformations. Chemical properties and reactions of the new nickel(IV) complexes therefore warranted further investigations, and in this paper a detailed account of pertinent studies is presented.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Solvents were reagent grade and were dried with Na/benzophenone and by distillation under argon. 2-Hydroxy-3-methoxybenzaldehyde (Aldrich) was used as purchased. Iodoalkanes and carbonic acid chlorides were freshly distilled under argon. Literature procedures were followed in the preparation of 2-formyltetralone,[5] 1-formylcyclohexan-2-one,[6] and [Ni(μ-OMe)MeL]₂.[7] Methods of characterization and spectroscopic instruments used in this study have been previously described.[8]

Preparations. Synthesis of (3-Methoxy-2-oxobenzoyl)-tris(trimethylphosphine)nickel (3). [NiMe(μ-OMe)(PMe₃)]₂

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(2090 mg, 5.78 mmol) and 2-hydroxy-3-methoxybenzaldehyde (1760 mg, 11.57 mmol) in 80 mL of ether at 20 °C formed an orange red mixture, to which was condensed at −70 °C in vacuo trimethylphosphine (1770 mg, 23.26 mmol). After 5 h of stirring at 20 °C a dark red solution was obtained. Removing a small amount of solid by filtration and cooling the solution to −27 °C afforded 3610 mg of dark red crystals (71%), mp 61−63 °C. Anal. Calcd for $C_{17}H_{33}NiO_3P_3$ (437.1): C, 46.72; H, 7.61; P, 21.26. Found: C, 46.91; H, 7.45; P, 21.38. IR (Nujol mull, 2000−1500 cm⁻¹): 1607 (s), 1575 (s) ν(C=O); 1547 (w). ¹H NMR (300 MHz, acetone-d_6, 273 K): δ(PCH_3) 1.30 (d, 27 H, ²J(PH) = 7.4 Hz), δ(OCH_3) 3.86 (s, 3 H), δ(CH) 5.96 (m, 1 H), δ(CH) 6.63 (d, 1 H, ³J(HH) = 7.2 Hz), δ(CH) 6.75 (d, 1 H, ³J(HH) = 7.9 Hz). ¹³C NMR (75.4 MHz, acetone-d_6, 273 K): δ(PCH_3) 17.2 (d, ¹J(PC) = 18.3 Hz), δ(OCH_3) 57.0, δ(CH) 110.7, 116.5, 117.0; δ(C) 133.6, 152.6, 170.4; δ(CO) 231.2.

Synthesis of (3-Carbonyl-4-oxo-1,2-dihydronaphthalenyl)tris(trimethylphosphine)nickel (4). [NiMe(μ-OMe)(PMe₃)]₂ (1620 mg, 4.48 mmol) and 2-formyltetralone (1560 mg, 8.96 mmol) in 80 mL of THF at 20 °C formed a clear brown solution which was evaporated to dryness within 30 min. The residue was dissolved in 60 mL of pentane containing excess PMe₃ (1780 mg, 23.4 mmol). After 2 h a slight turbidity of the dark red solution was removed by filtration, and at −27 °C dark red crystals were obtained (3870 mg, 95%), dec > 110 °C. Anal. Calcd for $C_{20}H_{35}NiO_2P_3$ (459.1): C, 52.32; H, 7.68; P, 20.23. Found: C, 52.28; H, 7.93; P, 20.30. IR (Nujol mull, 2000−1500 cm⁻¹): 1605 (w), 1570 (s) ν(C=O); 1530 (m) ν(C=C). ¹H NMR (300 MHz, THF-d_8, 297 K): δ(PCH_3) 1.28 (m, 27 H), δ(CH_2) 2.38 (m, 2 H), δ(CH_2) 2.66 (m, 2 H), δ(CH) 7.11 (m, 3 H), δ(CH) 7.90 (m, 1 H). ³¹P NMR (121.5 MHz, THF-d_8, 297 K): δ(P) −12.7.

Synthesis of ((2-Oxocyclohexen-1-yl)carbonyl)tris(trimethylphosphine)nickel (5). [NiMe(μ-OMe)(PMe₃)]₂ (430 mg, 1.19 mmol) and 1-formylcyclohexan-2-one (300 mg, 2.37 mmol) in 70 mL of THF at 20 °C formed a clear brown solution which was evaporated to dryness within 30 min. The residue was dissolved in 70 mL of pentane containing excess PMe₃ (900 mg, 11.8 mmol). After 2 h a slight turbidity of the dark red solution was removed by filtration, and at −27 °C dark red crystals were obtained (650 mg, 66%). Anal. Calcd for $C_{16}H_{35}NiO_2P_3$ (411.1): C, 46.75; H, 8.85. Found: C, 47.28; H, 8.61. IR (Nujol mull, 2000−1500 cm⁻¹): 1587 (m) ν(C=O); 1535 (s), 1507 (m) ν(C=C). ¹H NMR (300 MHz, C_6D_6, 297 K): δ(PCH_3) 1.09 (m, 27 H), δ(CH_2) 1.67 (m, 4 H), δ(CH_2) 2.46 (m, 2 H), δ(CH_2) 2.66 (m, 2 H). ¹³C NMR (75.4 MHz, C_6D_6, 297 K): δ(PCH_3) 18.1, δ(CH_2) 25.0, 25.5, 25.9, 34.6; δ(C) 105.0; δ(C−O) 187.0.

Attempted Synthesis of 8. Onto **3** (1.00 g, 2.09 mmol) in 70 mL of ether at −70 °C was condensed CH₃I (0.79 mL, 12.6 mmol). The mixture was allowed to warm and was kept at 20 °C for 17 h. Fractional crystallization gave yellow solids containing up to 10% of residual NiI₂(PMe₃)₃. IR (Nujol mull, 2000−1500 cm⁻¹): 1715 (s) ν(C=O).

Synthesis of *mer-trans*-Iodo(methyl)(3-carbonyl-4-oxo-1,2-dihydronaphthalenyl)bis(trimethylphosphine)nickel (9). Onto **4** (770 mg, 1.68 mmol) in 80 mL of ether at −70 °C was condensed in vacuo excess iodomethane (600 mg, 4.22 mmol). After warming of the mixture to 20 °C within 5 h a precipitation of tetramethylphosphonium iodide (IR) was filtered off yielding a greenish yellow solution which was kept at −27 °C. A yellow solid was isolated by decantation and drying in vacuo (400 mg, 45%), dec > 10 °C. IR (Nujol mull, 2000−1500 cm⁻¹): 1687 (s), 1603 (w) ν(C=O); 1519 (m) ν(C=C).

Synthesis of *mer-trans*-Iodo(methyl)((2-oxocyclohexen-1-yl)carbonyl)bis(trimethylphosphine)nickel (10). Upon **5** (900 mg, 2.19 mmol) in 80 mL of ether at −70 °C was condensed in vacuo excess iodomethane (770 mg, 5.42 mmol). Attaining 20 °C within 30 min, the red solution turned greenish yellow depositing tetramethylphosphonium iodide (IR). From the filtered solution at −27°C orange-yellow crystals were obtained (590 mg, 56%), dec > 95 °C. Anal. Calcd for $C_{14}H_{29}NiO_2P_2I$ (476.9): C, 35.26; H, 6.13. Found: C, 35.56;

H, 6.09. IR (Nujol mull, 2000−1500 cm⁻¹): 1700 (s, broad) ν(C=O); 1530 (w) ν(C=C). ¹H NMR (300 MHz, THF-d_8, 248 K): δ(NiCH_3) 0.95 (t, 3 H, ³J(PH) = 8.4 Hz), δ(PCH_3) 1.48 (virtual t, 18 H, |²J(PH) + ⁴J(PH)| = 8.3 Hz), δ(CH_2) 1.54 (m, 2 H), δ(CH_2) 1.66 (m, 2 H), δ(CH_2) 2.21 (m, 4 H).

Synthesis of Bis[2-acetyl-3-*tert*-butyl-5-methylphenolato-O,O]-bis(trimethylphosphine)nickel (11). Method a. Onto **12**² (190 mg, 0.348 mmol) in 50 mL of pentane at −70 °C was condensed trimethylphosphine (230 mg, 3.02 mmol) causing the greenish brown solution to turn orange brown. At −27 °C 200 mg of brown needles was obtained (92%). **Method b. 6** (1240 mg, 2.28 mmol) in 70 mL of ether containing excess trimethylphosphine (1330 mg, 17.5 mmol) after 24 h at 20 °C changed from orange to light green and after 5 d turned dark green. The volatiles were removed in vacuo, and the dark green residue was extracted with 70 mL of pentane. At −27 °C a crystalline solid was isolated by decantation, washing with refluxing pentane, and drying in vacuo to afford 410 mg of dark brown needles (29%); mp 140−142 °C. Anal. Calcd for $C_{32}H_{52}O_4NiP_2$ (621.4): C, 61.85; H, 8.44; P, 9.97. Found: C, 62.07; H, 8.54; P, 10.05. IR (Nujol mull, 2000−1500 cm⁻¹): 1585 (vs) ν(C=O); 1510 (vs) ν(C=C). ¹H NMR (300 MHz, THF-d_8, 297 K): broad lines with paramagnetic shift. MS (EI; m/e(⁵⁸Ni) (%)): 468 (100), M − 2 PMe₃.

Synthesis of [3-*tert*-Butyl-5-methyl-2-oxybenzaldehyde 1′,3′-propanediyl dithioacetal]methylbis(trimethylphosphine)nickel(II) (13). [NiMe(μ-OMe)(PMe₃)]₂ (470 mg, 1.30 mmol) and 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde 1′,3′-propandiyl dithioacetal (730 mg, 2.58 mmol) in 70 mL of THF at 20 °C formed an orange brown mixture, to which was condensed at −70 °C in vacuo trimethylphosphine (990 mg, 13.0 mmol). After 30 min an orange brown solution was evaporated to dryness, and the residue was dissolved in 70 mL of pentane. From the filtered solution at −27 °C brown needles were obtained (410 mg, 31%). Anal. Calcd for $C_{22}H_{42}$-NiOP₂S₂ (507.4): C, 52.08; H, 8.34; Ni, 11.57; P, 12.21. Found: C, 51.92; H, 8.30; Ni, 11.36; P, 11.78. IR (Nujol mull, 2000−1500 cm⁻¹): 1595 (w); 1535 (w) ν(C=C). ¹H NMR (300 MHz, THF-d_8, 297 K): δ(NiCH_3) −1.06 (s, 3 H), δ(PCH_3) 1.17 (s, 18 H), δ(C(CH_3)₃) 1.33 (s, 9 H), δ(CH_2) 1.51 (d, 2 H, ³J(HH) = 11.0 Hz), δ(CCH_3) 2.07 (s, 3 H), δ(CH_2) 2.93 (dt, 2 H, ³J(HH) = 14.0 Hz, ⁴J(HH) = 3.5 Hz), δ(CH_2) 3.34 (ddd, 2 H, ³J(HH) = 12.2 and 14.4 Hz, ⁴J(HH) = 2.2 Hz), δ(CH) 6.65 (d, 1 H, ⁴J(HH) = 2.5 Hz), δ(CH) 6.99 (d, 1 H, ⁴J(HH) = 2.3 Hz), δ(CHSS) 8.91 (s, 1 H). ¹³C NMR (75.4 MHz, THF-d_8, 297 K): δ(PCH_3) 13.01 (d, ¹J(PH) = 18.8 Hz), δ(CCH_3) 21.1, δ(CH_2) 29.8, 34.3; δ(C(CH_3)₃) 30.7, δ(C(CH₃)₃) 36.1, δ(SCS) 49.6, δ(C) 119.3, 124.2, 139.5; δ(CH) 127.6, 128.4; δ(C−O) 163.6.

Reaction of 1 with Iodoethane. 1 (1560 mg, 3.27 mmol) and C₂H₅I (2.1 mL, 4.03 g, 25.9 mmol) in 70 mL of ether within 2 d at 20 °C formed a dark green solution. After 4 d a dark green solid was obtained by cooling the solution to −27 °C: NiI₂(PMe₃)₃ (630 mg, 36%). The liquor after evaporation yielded 580 mg of a light green solid, which was chromatographed in ether (ICN-alumina N, deactivated with 5 parts of water). The yellow zone was eluted to afford 400 mg of 3-*tert*-butyl-2-hydroxy-5-methylphenyl ethyl ketone (**14**) as a yellow solid (56%); mp 61−63 °C. Anal. Calcd for $C_{14}H_{20}O_2$ (220.3): C, 76.32; H, 9.15. Found: C, 77.51; H, 9.66. IR (KBr disk, 2000−1500 cm⁻¹): 1620 (vs) ν(C=O); 1575 (m) ν(C=C). ¹H NMR (300 MHz, THF-d_8, 297 K): δ(CH_2CH_3) 1.17 (t, 3 H, ³J(HH) = 7.3 Hz), δ(C(CH_3)₃) 1.40 (s, 9 H), δ(CCH_3) 2.28 (s, 3 H), δ(CH_2) 3.07 (quart, 2 H, ³J(HH) = 7.3 Hz), δ(CH) 7.30 (d, 1 H, ⁴J(HH) = 2.2 Hz), δ(CH) 7.55 (d, 1 H, ⁴J(HH) = 2.2 Hz), δ(OH) 13.09 (s, 1 H). ¹³C NMR (75.4 MHz, THF-d_8, 297 K): δ(CH_2CH₃) 8.6, δ(CCH_3) 21.0 s, δ(C(CH_3)₃) 29.4, δ(C(O)CH_2) 32.2, δ(C(CH₃)₃) 35.1, δ(C) 119.0, 127.2, 138.5; δ(CH) 127.9, 134.8; δ(CO) 160.2, δ(C=O) 208.3. MS (EI, m/e(⁵⁸Ni) (%)): 220 (50), M; 205 (100), M − CH₃; 191 (54), M − C₂H₅.

Synthesis of Bis[3-*tert*-butyl-5-methyl-2-oxyphenyl isopropyl ketone-O,O](trimethylphosphine)nickel (15). 1 (1480 mg, 3.11 mol) and 2-iodopropane (4660 mg, 27.4 mmol)

in 70 mL of ether within 7 d formed a dark green mixture, from which 670 mg of $NiI_2(PMe_3)_3$ was obtained. The mother liquor was evaporated and the residue extracted with 100 mL of pentane. At −80 °C 100 mg of $NiI_2(PMe_3)_3$ was crystallized, and the remaining solution was evaporated to 10 mL and kept at −27 °C. A 150 mg amount of brown solid was collected (8%), which still contained <3% of $NiI_2(PMe_3)_3$. IR (Nujol mull, 2000−1500 cm^{-1}): 1622 (m), 1612 (m), 1570 (vs) ν(C=O); 1550 (m) ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): broad lines with paramagnetic shift. MS (FD, m/e(^{58}Ni) (%)): 524 (100), M − PMe$_3$.

Synthesis of Bis[3-*tert*-butyl-5-methyl-2-oxyphenyl *n*-butyl ketone-*O,O*](trimethylphosphine)nickel (16). 1 (2080 mg, 4.36 mol) and 1-iodobutane (3950 mg, 21.5 mmol) in 70 mL of ether within 5 d formed a dark green mixture, from which 640 mg of $NiI_2(PMe_3)_3$ were obtained. The mother liquor was evaporated and the residue extracted with 100 mL of pentane. At −27 °C 100 mg of $NiI_2(PMe_3)_3$ was crystallized, and the remaining solution was evaporated to 20 mL and kept at −27 °C. A 290 mg amount of greenish brown leaflets was collected (11%), which still contained dark green needles of $NiI_2(PMe_3)_3$ (<3%). The byproduct was removed mechanically. Analytical data were obtained from selected crystals, mp 143−144 °C. Anal. Calcd for $C_{35}H_{55}NiO_4P$ (629.5): C, 66.78; H, 8.81; Ni 9.32; P, 4.92. Found: C, 67.08; H, 9.09; Ni, 9.26; P, 5.00. IR (Nujol mull, 2000−1500 cm^{-1}): 1605 (m), 1575 (vs) ν(C=O); 1515 (s) ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): broad lines with paramagnetic shift. MS (FD, m/e(^{58}Ni) (%)): 552 (100), M − PMe$_3$.

Synthesis of Bis[3-*tert*-butyl-5-methyl-2-oxyphenyl cyclohexyl ketone-*O,O*](trimethylphosphine)nickel (17). 1 (1690 mg, 3.54 mol) and iodocyclohexane (2320 mg, 10.6 mmol) in 70 mL of ether within 5 d formed a dark green mixture, from which 530 mg of $NiI_2(PMe_3)_3$ was obtained. The mother liquor was evaporated and the residue extracted with 70 mL of pentane. At −27 °C 110 mg of brown needles was crystallized (5%) and a second extraction of the residue with 70 mL of ether gave brown needles and dark green leaflets (630 mg). Brown needles of the first fraction were used for analysis and spectroscopy, dec > 131 °C. IR (Nujol mull, 2000−1500 cm^{-1}): 1610 (m), 1580 (vs) ν(C=O); 1512 (s) ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): broad lines with paramagnetic shift. MS (EI, m/e(^{58}Ni) (%)): 604 (100), M − PMe$_3$.

Synthesis of *trans*-Chloro[3-*tert*-butyl-5-methyl-2-(acetyloxy)phenyl]bis(trimethylphosphine)nickel (18). 1 (1580 mg, 3.31 mmol) in 70 mL of ether and acetyl chloride (0.50 mL, 533 mg, 7.04 mmol) were combined at −70 °C. The mixture immediately turned dark red and then orange depositing a solid of acetyltrimethylphosphonium chloride, which was removed by filtration. From the solution at −27 °C orange brown needles were obtained (710 mg, 47%), mp 98−99 °C. Anal. Calcd for $C_{19}H_{35}ClNiO_2P_2$ (451.6): C, 50.53; H, 7.81; P, 13.71. Found: C, 50.15; H, 8.64; P, 13.65. IR (Nujol mull, 2000−1500 cm^{-1}): 1730 (vs), 1724 (m) ν(C=O); 1570 (s), 1540 (s) ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): δ(PCH_3) 1.05 (t′, 18 H, |^2J(PH) + ^4J(PH)| = 7.9 Hz), δ(C(CH_3)$_3$) 1.27 (s, 9 H), δ(CCH_3) 2.18 (s, 3 H), δ(C(O)CH_3) 2.49 (s, 3 H), δ(CH) 6.60 (s, 1 H), δ(CH) 6.96 (s, 1H). ^{13}C NMR (75.4 MHz, THF-d_8, 297 K): δ(PCH_3) 13.4 (t′, |^1J(PC) + ^3J(PC)| = 27.2 Hz), δ(CCH_3) 21.5, δ(C(O)CH_3) 22.8, δ(C(CH_3)$_3$) 31.2, δ(C(CH$_3$)$_3$) 34.9, δ(CH) 122.6, 136.4; δ(C) 133.6, 140.2, 148.5 (t, ^2J(PC) = 34.7 Hz); δ(C−O) 152.5 (t, ^3J(PC) = 4.1 Hz); δ(C=O) 171.3. ^{31}P NMR (121.5 MHz, THF-d_8, 297 K): δ(P) −9.98 s.

Synthesis of *trans*-Chloro[3-*tert*-butyl-5-methyl-2-(benzoyloxy)phenyl]bis(trimethylphosphine)nickel (19). 1 (1800 mg, 3.77 mmol) in 70 mL of ether and benzoyl chloride (0.90 mL, 1060 mg, 7.55 mmol) were combined at −70 °C. After 30 min of stirring at 20 °C the mixture was yellow brown. Solid benzoyltrimethylphosphonium chloride was removed by filtration, and the solution at −27 °C afforded light brown needles (1470 mg, 76%), mp 143−144 °C. Anal. Calcd for $C_{24}H_{37}ClNiO_2P_2$ (513.6): C, 56.12; H, 7.26; P, 12.06. Found: C, 56.22;

H, 7.30; P, 12.35. IR (Nujol mull, 2000−1500 cm^{-1}): 1780 (w), 1700 (vs) ν(C=O); 1590 (s), 1580 (s) ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): δ(PCH_3) 1.03 (t′, 18 H, |^2J(PH) + ^4J(PH)| = 7.8 Hz), δ(C(CH_3)$_3$) 1.31 (s, 9 H), δ(CCH_3) 2.23 (s, 3 H), δ(CH) 6.67 (d, 1 H, ^4J(HH) = 1.2 Hz), δ(CH) 7.12 (dd, 1 H, ^4J(HH) = 1.8 and 0.8 Hz), δ(CH) 7.57 (m, 2 H), δ(CH) 7.66 (tt, 1 H, ^3J(HH) = 7.4 Hz, ^4J(HH) = 1.7 Hz), δ(CH) 8.29 (dt, 2 H, ^3J(HH) = 7.0 Hz, ^4J(HH) = 1.6 Hz). ^{13}C NMR (75.4 MHz, THF-d_8, 297 K): δ(PCH_3) 13.1 (t′, |^1J(PC) + ^3J(PC)| = 27.7 Hz), δ(CCH_3) 21.3, δ(C(CH_3)$_3$) 31.1, δ(C(CH$_3$)$_3$) 34.8, δ(CH) 122.5, 129.5, 130.8, 133.8; δ(CH) 135.8 (t, ^3J(PC) = 4.5 Hz); δ(C) 132.5, 133.2, 140.3, 148.7 (t, ^2J(PC) = 34.9 Hz); δ(C−O) 152.6, δ(C=O) 166.6. ^{31}P NMR (121.54 MHz, d$_8$-THF, 297 K): δ(P) −9.86 s.

Synthesis of *trans*-Chloro[3-*tert*-butyl-5-methyl-2-(pivaloyloxy)phenyl]bis(trimethylphosphine)nickel (20). 1 (2060 mg, 4.32 mmol) in 70 mL of ether and pivaloyl chloride (2080 mg, 17.25 mmol) were combined at 20 °C. After 24 h the mixture was red brown. Solid phosphonium chloride was removed by filtration, and the solution at −27 °C afforded honey colored plates (680 mg, 32%), mp 163−165 °C. Anal. Calcd for $C_{22}H_{41}ClNiO_2P_2$ (493.7): C, 53.53; H, 8.37; P, 12.44. Found: C, 54.30; H, 8.61; P, 12.16. IR (Nujol mull, 2000−1500 cm^{-1}): 1715 (s) ν(C=O); 1570 (s) ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): δ(PCH_3) 1.05 (t′, 18 H, |^2J(PH) + ^4J(PH)| = 7.9 Hz), δ(C(CH_3)$_3$) 1.26 (s, 9 H), δ(C(O)C(CH_3)$_3$ 1.56 (s, 9 H) δ(CCH_3) 2.19 (s, 3 H), δ(CH) 6.61 (d, 1 H, ^4J(HH) = 1.1 Hz), δ(CH) 7.02 (m, 1 H). ^{13}C NMR (75.4 MHz, THF-d_8, 297 K): δ(PCH_3) 13.5 (t′, |^1J(PC) + ^3J(PC)| = 27.7 Hz), δ(CCH_3) 21.7, δ(C(CH_3)$_3$) 29.0, 31.4; δ(C(CH$_3$)$_3$) 35.2, 40.6; δ(CH) 123.1, 136.1 (t, ^3J(PC) = 4.6 Hz); δ(C) 133.5, 140.6, 148.2 (t, ^2J(PC) = 35.2 Hz); δ(C−O) 153.5 (t, ^3J(PC) = 4.4 Hz), δ(C=O) 178.5. ^{31}P NMR (121.5 MHz, THF-d_8, 297 K): δ(P) −10.2 s. MS (FD, m/e(^{58}Ni) (%)): 492 (100), M; 457 (12), M − Cl.

Synthesis of Bis(3-*tert*-butyl-5-methyl-2-oxybenzoyl)-bis(trimethylphosphine)nickel (21).[3] **Method a. 1** (680 mg, 1.43 mmol) and diiodomethane (390 mg, 1.46 mmol) in 50 mL of ether at −70 °C formed a brown solution that within 12 h at 20 °C turned green. The volatiles were removed in vacuo, and the residue was extracted with 70 mL of pentane. At −27 °C small yellow crystals and a few long green needles of $NiI_2(PMe_3)_3$ were formed. After decantation and drying in vacuo the green needles were picked out, raw yield 450 mg. **Method b. 1** (1200 mg, 2.52 mmol) and 1,2-diiodoethane (710 mg, 2.52 mmol) in 70 mL of ether after 12 h gave a green solution that was worked up as above, yield 160 mg of **21** (11%) and 320 mg of $NiI_2(PMe_3)_3$ (24%).

Synthesis of Bis(3,5-di-*tert*-butyl-2-oxybenzoyl)bis-(trimethylphosphine)nickel (22). 2 (1070 mg, 2.06 mmol) in 70 mL of ether was combined with 1 mol equiv of iodine (550 mg, 2.09 mmol). After the mixture was stirred for 12 h at 20 °C, the color changed from red to dark green. The volatiles were removed in vacuo, and the residue was dissolved in 10 mL of acetone. Aqueous HCl (2 M) was added dropwise until precipitation was complete. Washing with 20 mL of H_2O, removing the solvent, and drying in vacuo afforded 240 mg of pure yellow solid (17%), dec > 168 °C. IR (Nujol mull, 2000−1500 cm^{-1}): 1745 (m), 1715 (vs) ν(C=O); 1585 (m) ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 223 K): δ(PCH_3) 0.95 (t′, 18 H, |^2J(PH) + ^4J(PH)| = 9.4 Hz), δ(C(CH_3)$_3$) 1.24 (s, 18 H), δ(C(CH_3)$_3$) 1.51 (s, 18 H) δ(CH) 7.02 (d, 2 H, ^4J(HH) = 2.3 Hz), δ(CH) 7.33 (d, 2 H, ^4J(HH) = 2.3 Hz). ^{13}C NMR (75.4 MHz, THF-d_8, 223 K): δ(PCH_3) 11.3 (t′, |^1J(PC) + ^3J(PC)| = 30.1 Hz), δ(C(CH_3)$_3$) 30.3, 32.4; δ(C(CH$_3$)$_3$) 35.2, 36.4; δ(CH) 118.9, 131.1; δ(C) 123.8, 136.2, 140.9; δ(C−O) 176.2, δ(C=O) 212.3 (t, ^2J(PC) = 10.6 Hz). ^{31}P NMR (121.5 MHz, THF-d_8, 297 K): δ(P) 7.07 s. MS (FD, m/e(^{58}Ni) (%)): 674 (100), M.

Attempted Synthesis of 23. In a similar procedure as for **22**, oxidation using excess $C_2H_4I_2$ afforded a yellow solid which started decomposing during workup. IR (Nujol mull, 2000−1500 cm^{-1}): 1724 (s) ν(C=O).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 16[a]

Ni(1)−O(2)	1.921(2)	O(2)−C(7)	1.301(3)
Ni(1)−O(1)	2.007(2)	C(1)−C(2)	1.452(3)
Ni(1)−P(1)	2.3284(14)	C(2)−C(7)	1.427(4)
O(1)−C(1)	1.249(3)		
O(2)−Ni(1)−O(2)[1]	151.5(2)	C(1)−O(1)−Ni(1)	129.5(2)
O(2)−Ni(1)−O(1)	87.73(8)	C(7)−O(2)−Ni(1)	129.9(2)
O(2)[1]−Ni(1)−O(1)	88.60(8)	O(1)−C(1)−C(2)	123.7(2)
O(1)−Ni(1)−O(1)[1]	165.06(13)	C(7)−C(2)−C(1)	122.0(2)
O(2)−Ni(1)−P(1)	104.26(8)	O(2)−C(7)−C(2)	123.4(2)
O(1)−Ni(1)−P(1)	97.47(7)		

[a] Symmetry transformations used to generate equivalent atoms: (1) $-x$, y, $-z + {}^1/_2$.

Synthesis of Bis(3-carbonyl-4-oxo-1,2-dihydronaphthalenyl)bis(trimethylphosphine)nickel (24). At −70 °C **4** (860 mg, 1.87 mmol) and 1,2-diiodoethane (280 mg, 0.99 mmol) in 80 mL of ether formed a red solution which upon warming to 20 °C turned yellow-green within 30 min. The volatiles were evaporated, and the residue was dissolved in 10 mL of acetone. Aqueous HCl (2 M) was added dropwise to precipitate a yellow solid until precipitation was complete. The solid was dissolved in 5 mL of fresh acetone and kept at −27 °C to yield yellow needles (400 mg, 96%), dec > 176 °C. Anal. Calcd for $C_{28}H_{34}NiO_4P_2$ (555.2): C, 60.57; H, 6.17. Found: C, 60.54; H, 6.27. IR (KBr disk, 2000−1500 cm^{-1}): 1693 (s) ν(C=O); 1515 (m) ν(C=C). ^{1}H NMR (300 MHz, acetone-d_6, 243 K): δ(PCH_3) 1.19 (virtual t, 18 H, $|^2J(PH) + {}^4J(PH)| = 9.3$ Hz), δ(CH_2) 2.58 (A_2B_2 spin system, 4 H, $^3J = 6.8$ Hz), δ(CH_2) 2.85 (A_2B_2, 4 H, $^3J = 6.8$ Hz), δ(CH) 7.34 (A*BCD* spin system, 6 H, $^3J_{BA} = {}^3J_{BC} = 7.2$ Hz, $^4J_{BD} = 1.6$ Hz), δ(CH) 8.04 (*ABCD*, 2 H, $^3J = 7.2$ Hz). ^{31}P NMR (121.5 MHz, acetone-d_6, 243 K): δ(P) 6.37 (s).

Attempted Synthesis of 25. In a similar procedure starting with **5** (780 mg, 1.9 mmol) small amounts of a yellow solid were precipitated with HCl but decomposed during workup at 0 °C.

X-ray Crystallography. The determinations of the X-ray structures of **16**, **19**, and **19a** were carried out using single crystals sealed in capillaries under argon.

Structure determination of 16: $C_{35}H_{55}NiO_4P$, $M_r = 629.5$, crystal size $0.62 \times 0.45 \times 0.20$ mm; monoclinic, space group $C2/c$ (No. 15); $a = 18.629(5)$ Å, $b = 7.303(2)$ Å, $c = 26.512(8)$ Å, $\beta = 91.35(2)°$, $V = 3606$ Å^3; refined from 35 reflections $18 < 2\theta < 39°$; $Z = 4$; $D_{calc} = 1.160$ g cm^{-3}; λ(Mo Kα) = 0.710 73 Å; $\mu = 0.615$ mm^{-1}; $T = 296$ K; Siemens R3m diffractometer; graphite monochromator, $\omega-2\theta$ scan; 4234 intensities collected $3 < 2\theta < 55°$; h, ±24; k, 0−9, l, 0−34; 3 standards recorded every 400 showed only random deviations; Lp correction, semi-empirical absorption correction via ψ-scans, min/max transmission 0.644/0.705; 4142 independent intensities; structure solved by direct and conventional Fourier methods; full-matrix least-squares refinement based on F^2 and 205 parameters (SHELXTL V5[9]). The methyl groups of the PMe$_3$ ligand which lies on a crystallographic 2-fold axis are disordered over two sites with half occupation each. Anisotropic refinement of non-hydrogen atoms converged at $R1$ ($F > 4\sigma(F)$) = 0.056, w$R2$ (F^2, all data) = 0.153, Gof = 1.053, and max(Δ/σ) = 0.001; min/max height in final ΔF map −0.68/1.09 e/Å^3. Selected bond lengths and angles are given in Table 1; Figure 4 shows the structure of the molecule.

Structure determination of 19: $C_{24}H_{37}ClNiO_2P_2$, $M_r = 513.6$, crystal size $0.52 \times 0.35 \times 0.33$ mm; triclinic, space group $P\bar{1}$ (No. 2); $a = 9.477(4)$ Å, $b = 17.377(8)$ Å, $c = 18.549(8)$ Å, $\alpha = 107.75(2)°$, $\beta = 96.25(2)°$, $\gamma = 105.07(2)°$, $V = 2749.8$ Å^3; refined from 25 reflections $13 < 2\theta < 28°$; $Z = 4$; $D_{calc} = 1.241$ g cm^{-3}; λ(Mo Kα) = 0.710 73 Å; $\mu = 0.936$ mm^{-1}; $T = 296$ K; Siemens R3m diffractometer; graphite monochromator, $\omega-2\theta$ scan; 13 096 intensities collected, $4 < 2\theta < 55°$; h, ±12; k, 0−9, l, 0−21;

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 19

Ni(1)−C(1)	1.895(8)	Ni(2)−C(31)	1.891(7)
Ni(1)−P(2)	2.199(3)	Ni(2)−P(4)	2.202(4)
Ni(1)−P(1)	2.200(3)	Ni(2)−P(3)	2.202(3)
Ni(1)−Cl(1)	2.213(4)	Ni(2)−Cl(2)	2.214(3)
O(1)−C(12)	1.341(8)	O(3)−C(42)	1.357(9)
O(1)−C(2)	1.430(9)	O(3)−C(32)	1.444(9)
O(2)−C(12)	1.203(9)		
C(1)−Ni(1)−P(2)	90.9(2)	C(31)−Ni(2)−P(4)	91.6(2)
C(1)−Ni(1)−P(1)	87.0(2)	C(31)−Ni(2)−P(3)	88.4(2)
P(2)−Ni(1)−P(1)	165.52(10)	P(4)−Ni(2)−P(3)	172.83(10)
C(1)−Ni(1)−Cl(1)	176.2(2)	C(31)−Ni(2)−Cl(2)	177.9(2)
P(2)−Ni(1)−Cl(1)	89.13(12)	P(4)−Ni(2)−Cl(2)	89.10(12)
P(1)−Ni(1)−Cl(1)	93.91(12)	P(3)−Ni(2)−Cl(2)	90.60(12)
C(12)−O(1)−C(2)	119.5(5)	C(42)−O(3)−C(32)	117.1(6)
C(2)−C(1)−Ni(1)	123.5(6)	C(32)−C(31)−Ni(2)	122.4(6)
C(1)−C(2)−O(1)	116.4(6)	C(31)−C(32)−O(3)	115.6(6)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 19a

Ni−C(1)	1.891(6)	Ni−P(2)	2.202(2)
Ni−P(1)	2.214(2)	Ni−Br	2.3641(10)
C(1)−C(6)	1.399(8)	C(1)−C(2)	1.413(8)
C(2)−C(3)	1.390(9)	C(6)−C(5)	1.385(9)
C(5)−C(4)	1.391(11)	C(3)−C(4)	1.382(10)
C(1)−Ni−P(2)	87.9(2)	C(1)−Ni−P(1)	87.6(2)
P(2)−Ni−P(1)	175.53(7)	C(1)−Ni−Br	179.0(2)
P(2)−Ni−Br	92.19(6)	P(1)−Ni−Br	92.28(5)

l, 0−24; 3 standards recorded every 400 showed only random deviations; Lp correction, semi-empirical absorption correction via ψ-scans, min/max transmission 0.629/0.724; 12 712 independent intensities; structure solved by direct and conventional Fourier methods; full-matrix least-squares refinement based on F^2 and 577 parameters (SHELXTL V5[9]); two independent molecules per asymmetric unit, disorder of the methyl groups at P(1) of molecule 1 and of the t-Bu group of molecule 2 was not fully resolved. Anisotropic refinement of non-hydrogen atoms converged at $R1$ ($F > 4\sigma(F)$) = 0.084, w$R2$-(F^2, all data) = 0.259, Gof = 1.129, and max(Δ/σ) = 0.001; min/max height in final ΔF map −0.57/0.93 e/Å^3. Selected bond lengths and angles are in Table 2; Figure 5 shows the structure of one of the two independent molecules.

Structure Determination of 19a. A sample was obtained from Ni(PMe$_3$)$_4$ and benzoyl chloride, followed by halide exchange using excess NaBr,[10] and was crystallized from pentane: $C_{12}H_{23}BrNiP_2$, $M_r = 367.9$, crystal size $0.25 \times 0.20 \times 0.23$ mm; monoclinic, space group $P2_1/c$ (No. 14); $a = 13.993$-(2) Å, $b = 10.708(1)$ Å, $c = 11.453(2)$ Å, $\beta = 108.29(1)°$, $V = 1629.4(4)$ Å^3, refined from 25 centered reflections; $Z = 4$; $D_{calc} = 1.500$ g cm^{-3}; λ(Mo Kα) = 0.710 73Å; $\mu = 3.816$ mm^{-1}, $T = 296$ K; PW 1100 diffractometer; graphite monochromator, $\omega-2\theta$ -scan, 2987 reflections collected, $2.7° < \theta < 25°$; h, 0−19; k, 0−15; l, −16 to −15; Lp correction, 2864 independent reflections; structure solved by direct methods (SHELXS-86)[11] and refined by Fourier methods (SHELXL-93)[12] (full-matrix least-squares refinement based on F^2 and 147 parameters). Anisotropic refinement of non-hydrogen atoms converged at R_1 ($F > 4\sigma(F)$) = 0.066, wR_2 (F^2, all data) = 0.1897, Gof = 1.041, and min/max height in final ΔF map −0.949/1.319 e Å^{-3}. Selected bond lengths and angles are in Table 3. Figure 6 shows the structure of the molecule.

Results and Discussion

Preparations. When combined with excess iodomethane pentacoordinate (acylphenolato)nickel(II) com-

(9) ShelXTL V5: Siemens Industrial Automation, Inc., Analytical Instrumentation, Madison, WI.
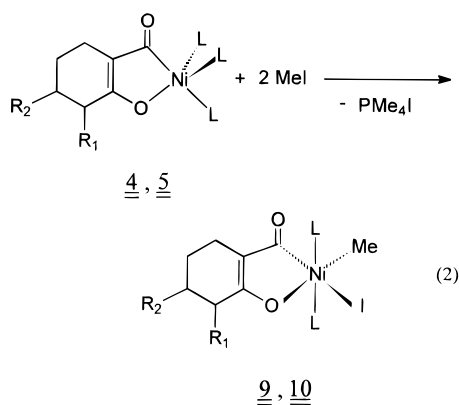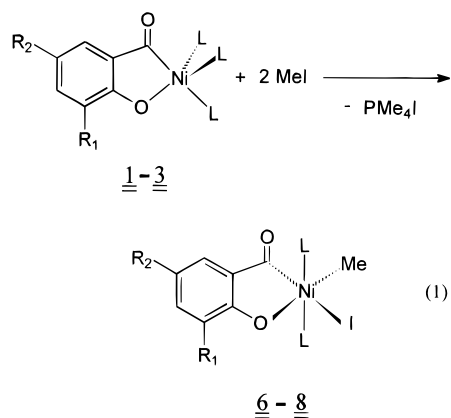
(10) Klein, H.-F.; Wenninger, J. unpublished information.
(11) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(12) Sheldrick, G. M. SHELXL-93, University of Göttingen, 1993.
(13) Tsumaki, T. *Bull. Chem. Soc. Jpn.* **1938**, *13*, 252.

plexes **1**−**5** undergo an oxidative addition reaction (eq 1) affording methyl(acyl)nickel(IV) complexes **6**−**10** as metastable crystalline materials.

$$ \text{(1)} $$

$$ \text{(2)} $$

	R_1	R_2	
1[a]	$C(CH_3)_3$	CH_3	**6**[b]
2[a]	$C(CH_3)_3$	$C(CH_3)_3$	**7**[b]
3[c]	OCH_3	H	**8**[c]
4[c]	Benzo		**9**[c]
5[c]	H	H	**10**[c]

L = PMe_3

[a]   reference [8]
[b]   reference [2]
[c]   this work

A 5-fold molar excess of iodomethane can bring about this unusual oxidative addition to a nickel(II) complex while a 2-fold excess of iodomethane proved to exert insufficient mass action. Alkyl substituents in 2,5 positions of the aromatic ring or a 2-methoxo group appears to support an oxidative addition, while the corresponding chelates derived from benzene or naphthalene did not. An olefinic skeleton can replace the aromatic ring as shown by a successful oxidative addition reaction with **4** and **5**, although at the expense of thermal stability of crystalline material. Orange crystals of **6** grown in cold ether formed both prisms and leaflets in a single batch. By means of two X-ray crystal structure determinations (153 K) a case of dimorphism was established for *trans-mer*-**6**.[2] Both types of crystals are represented in an MAS-CP-^{13}C NMR spectrum (Figure 2) by a 2-fold pattern of resonances, while all solution spectra[2] display only one set of signals. In
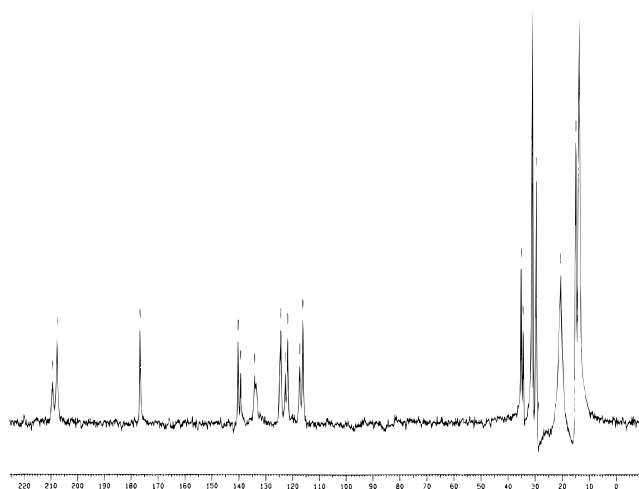

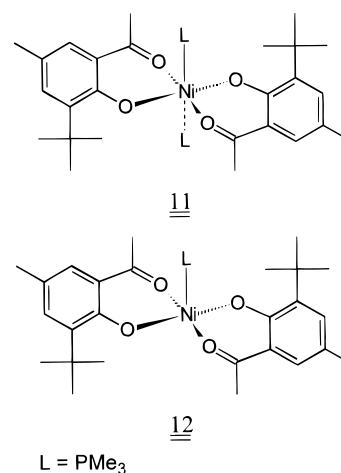**Figure 2.** MAS-CP-^{13}C NMR spectrum of **6**.

L = PMe_3

Figure 3. Molecular bis(phenolato)nickel(II) complexes.

ether at 20 °C an orange solution of **6** slowly turns light green and becomes dark green after 5 d indicating formation of $NiI_2(PMe_3)_3$ as a stoichiometric byproduct. Fractional crystallization in the presence of excess trimethylphosphine gives an equivalent amount of dark brown **11**. A dramatic acceleration of C,C-coupling is observed in the presence of catalytic amounts of NiL_4. At a phosphine/Ni ratio of 2 and with $NiI_2(PMe_3)_3$ as an invariant byproduct the overall stoichiometry leads to the bis(2-acetylphenolato)nickel complex **12** containing only one trimethylphosphine.[2] Transformation of salicylaldehydes to Schiff base ligands leads into the well-known chemistry of salicylaldiminato complexes which is characterized by stable six-membered (N,O) chelate rings.[11] Consequently, C−H reactivity cannot be initiated to afford (iminoacyl)nickel(II) complexes.[14] Using propanedithiol as a protecting group which raises the CH acidity[15] reduces the reactivity of the salicylaldehyde derivative to that of a phenol (eq 3).

Substitution of methoxide and addition of trimethylphosphine affords the stable methylnickel phenolate **13** as brown needles which decompose above 155 °C but do not form a chelate ring compound.

Reactions. Chemical reactions were investigated using **6** as a representative material. After 5 h under 1 bar of carbon monoxide at 0 °C **6** was recovered

(14) Klein, H.-F.; Bickelhaupt, A. *Inorg. Chim. Acta* **1996**, *248*, 111.
(15) Truce, R. *J. Org. Chem.* **1963**, *28*, 961.

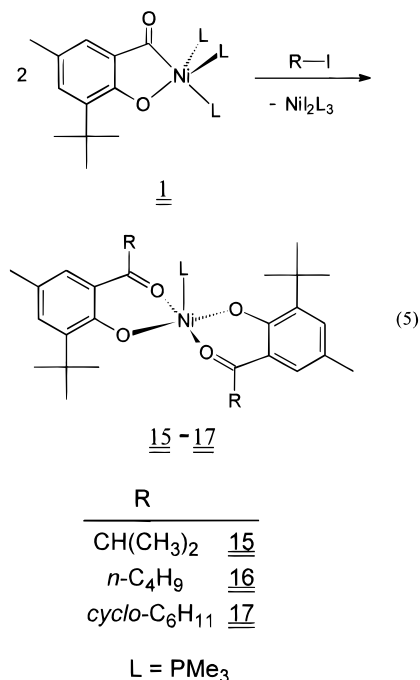## Scheme 1. Carbonylation Reactions of Methylnickel Complexes
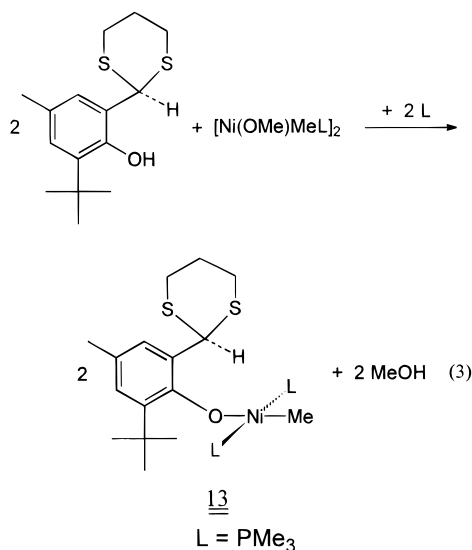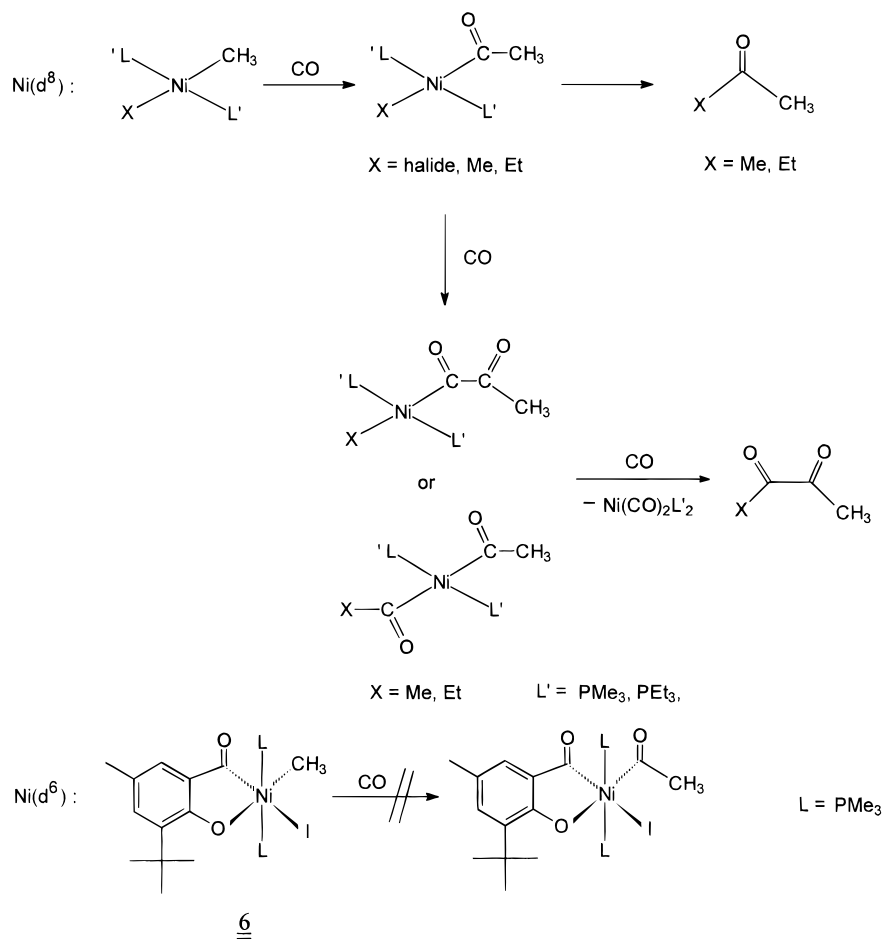
unchanged from ether solution. Under these conditions a normal Ni$-$CH$_3$ function is expected to undergo a carbonylation reaction,[16-20] which is not observed with **6** (Scheme 1). Methyllithium at -70 °C caused a dark green coloration. Workup yielded a brown solid showing

intense infrared absorptions where expected for an O-coordinated phenacetyl group and singlet proton resonances of NiMe and COCH$_3$ groups (1:1). Methylation of the NiI function appears to be rapidly followed by C,C-coupling, but separation of products has not been achieved in this reaction. The C,C-coupling reaction of the diorganonickel(IV) complex **6** in the presence of trimethylphosphine, although the added ligand serves to suppress side reactions, still needs considerable activation when compared with the sluggish thermal decomposition of **6** in the crystalline state or in ether at 20 °C. As this barrier is lowered by the presence of Ni(PMe$_3$)$_4$, the effect is probably due to the formation of a diorganonickel(III) intermediate.[2] At 0 °C solutions of **6** in THF spontaneously decompose and at lower temperatures in ether react with catalytic amounts of Ni(PMe$_3$)$_4$ much faster than without the catalyst, which would support formation of an ion-pair intermediate as the rate-determining step, until kinetic data become available. Larger iodoalkanes transform the acylnickel function to an O-coordinated ketone. Iodoethane is likely to attack the nickel and in a subsequent multistep reaction converts the chelating oxo acyl ligand to the metal-free 2-propanoylphenol **14** (eq 4). Still bulkier iodoalkanes appear to attack at the acyl function forming phenolato(iodo)nickel intermediates, which undergo a dismutation reaction as expected for a set of hard and soft anionic ligands and in an equilibrium afford the bis(phenolato)nickel(II) complexes **15$-$17** together with diiodotris(trimethylphosphine)nickel (eq 5). This result of a cooperative effect is based on

(16) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524.
(17) Carmona, E.; Gonzalez, F.; Poveda, M. L.; Atwood, J.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2108.
(18) Yamamoto, T.; Kohara, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2161.
(19) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, 4115.
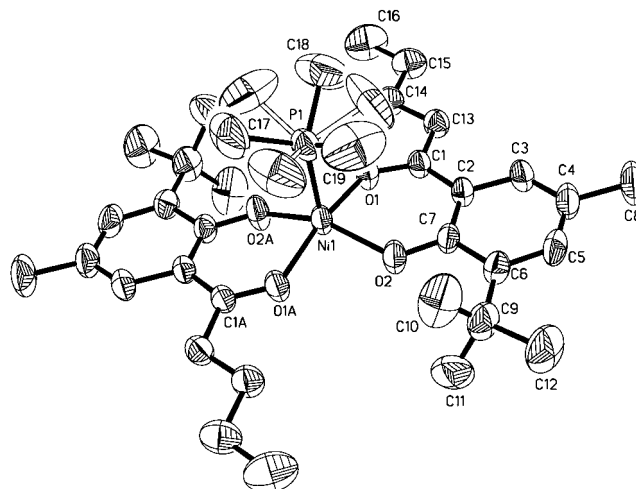(20) Younis, K.; Amer, I. *Organometallics* **1994**, *13*, 3120.

Figure 4. Molecular structure of **16**.
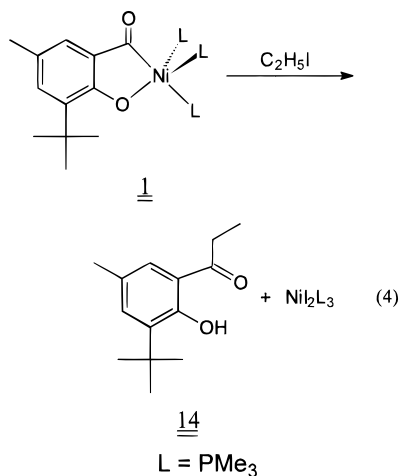
extensive dissociation of phosphines and an easily reversible formation of phenolato-bridged dinickel intermediates.

reaction of **6** with carbonic acid chlorides phenylnickel chlorides are generated (eq 6). Acetyl chloride in a fast

R	
$CH(CH_3)_2$	**15**
n-C_4H_9	**16**
$cyclo$-C_6H_{11}	**17**

L = PMe$_3$

R	
CH_3	**18**
C_6H_5	**19**
$C(CH_3)_3$	**20**

L = PMe$_3$

Bis(trimethylphosphine)bis(phenolato)nickel complexes form brown crystalline solids which are highly soluble in ether or toluene. NMR spectra showing broad lines and large paramagnetic shifts give little information, but strong infrared bands between 1570 and 1620 cm^{-1} (ν(C=O)) indicate O-coordinated keto functions. Proof for the unusual pentacoordination of a nickel diphenolate was obtained from an X-ray crystal structure determination of complex **16** (see below).
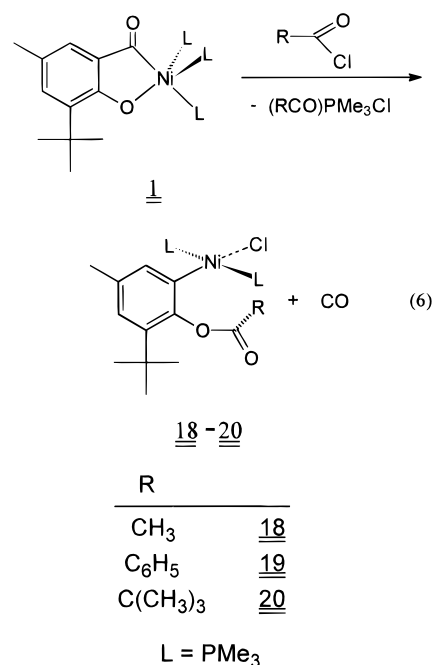
At variance with the tendency of unsubstituted bis-(phenolato)nickel to dissociate phosphine forming a coordination polymer, these mononuclear complexes will take up a second phosphine ligand as soon as supplied. This was exemplified by a quantitative conversion of **12** to **11** which is not reversed at 20 °C in vacuo. More conveniently, octahedral bis(trimethylphosphine)nickel bis(phenolates) of this type may be obtained from Ni-(PMe$_3$)$_4$, an appropriate phenol and dioxygen.[21] By

reaction at −70 °C, benzoyl chloride within 30 min at 20 °C, and pivaloyl chloride after 24 h form a white precipitate of acyl(trimethyl)phosphonium chloride suspended in an orange solution. After filtering of the mixture, crystallization affords the (2-(acyloxy)phenyl)-nickel(II) complexes **18−20**. As first indication of a missing CO group, the ^{13}C NMR spectrum of **18** failed to show a phenacylnickel carbon resonance around 230 ppm. On the other hand, one of the aromatic ring carbon nuclei gave a triplet resonance with J(PC) = 35 Hz, which is typical of a phenylnickel moiety and two *trans*-phosphines. The same pattern of signals was obtained from **19** and **20**. Proof came from an X-ray crystal structure determination of **19** (Figure 5). Generation of phenylnickel complexes via decarbonylation is a general method of synthesis,[22] but for this reaction (eq 6) the mechanism requires opening of the chelate ring in **6** through phenolic esterification as an initial

(21) Klein, H.-F.; Dal, A. Unpublished information.

(22) Yamamoto, T.; Kohara, T.; Osakada, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2147.
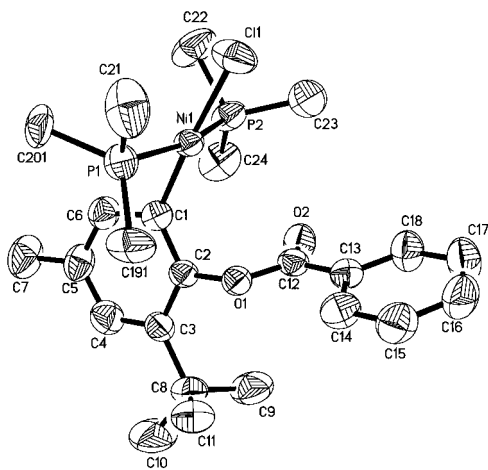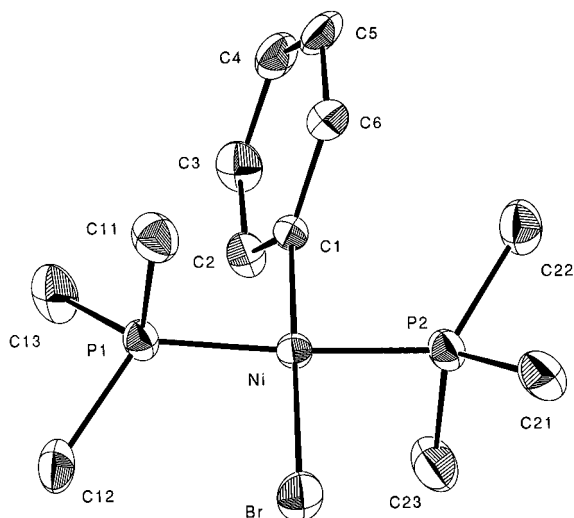
Figure 5. Molecular structure of **19**.

**Figure 6.** Molecular structure of **19a**.

step, which is followed by spontaneous decarbonylation of a chloro(acyl)nickel intermediate. Acetic acid anhydride within 48 h at 20 °C does not react with **6**.

Molecular structure of 16. The molecular units (Figure 4) have no contacts between each other and show a rare example of an 18-electron metal complex adopting a square pyramidal geometry. This is defined by four oxygen atoms in a square-based plane and the Ni and P atoms lined up in a perpendicular C_2 axis. The trimethylphosphine is seen in rotational disorder. The distance Ni$-$P = 232.8(1) pm exceeds the mean value expected for nickel(II) (220 $\pm$ 2 pm). When compared with chemical properties of **12**, such elongation does not yet indicate an incipient dissociation of trimethylphosphine. Bond lengths and angles in the planar six-membered chelate rings resemble those of acac ligands[23] while in a transoid arrangement containing a distinctly longer Ni$-$O bond of the keto function as opposed to a normal phenolato-*O* bond to nickel.

Molecular Structures of 19 and 19a. As a reference compound for **19** (Figure 5) *trans*-bromo(phenyl)-bis(trimethylphosphine)nickel (**19a**) (Figure 6) was synthesized which shows little steric congestion. Both phenylnickel complexes adopt a *trans*-square planar configuration with rotational orientations of the phenyl rings perpendicular to the coordination plane, which is

typical for phenylnickel compounds.[24−28] The ester function of **19** remains uncoordinated pointing away from the metal as well as away from that of the next molecule. Bond lengths and angles around the nickel atom (Tables 3 and 4) are as expected.

Octahedral Bis(acylphenolato)nickel(IV) Compounds. Oxidation of acylphenolato complexes **1−5** using iodine, diiodomethane, or 1,2-diiodoethane results in a ligand dismutation reaction (eqs 7 and 8).
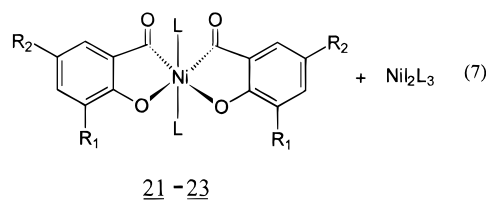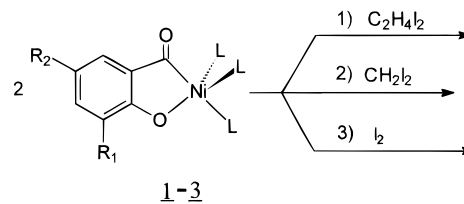
R_1	R_2	method	
$C(CH_3)_3$	CH_3	1 - 3	$\underline{21}$[a]
$C(CH_3)_3$	$C(CH_3)_3$	1, 3	$\underline{22}$[b]
OCH_3	H	1	$\underline{23}$[b]
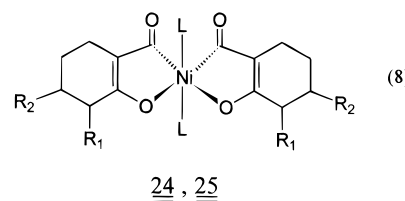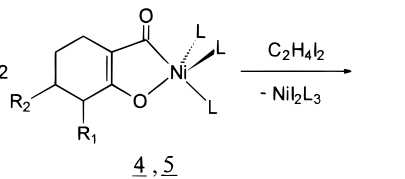
R_1	R_2	
Benzo		$\underline{24}$[b]
H	H	$\underline{25}$[b]

L = PMe$_3$

[a]   reference [3]

[b]   this work

Mole equivalent amounts of NiI$_2$(PMe$_3$)$_3$ are separated by fractional crystallization from ether or, more conve-

(23) Barnett, D. L.; Krüger, C. *J. Organomet. Chem.* **1972**, *42*, 169.

(24) Churchill, M. R.; Kalra, K.-L.; Veidis, M. V. *Inorg. Chem.* **1973**, *12*, 1656.
(25) Carmona, E.; Gonzales, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1981**, 777.
(26) Xu, D.; Kai, Y.; Miki, K.; Nashiwaki, K.; Wada, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1459.
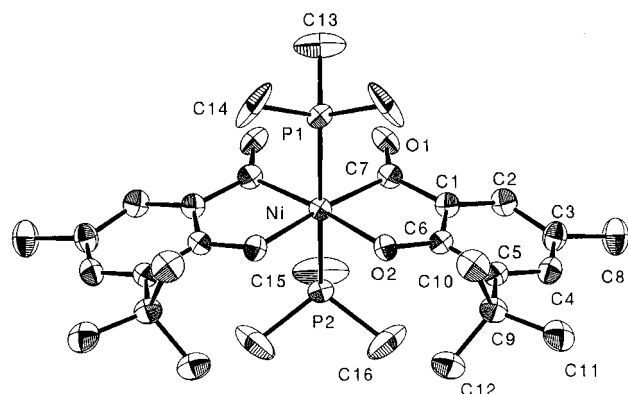(27) Chen, J.; Kai, Y.; Wada, M.; Kumazoe, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2802.
(28) Sturge, K.; Hunter, A. D.; McDonald, R.; Santasiero, B. D. *Organometallics* **1992**, *11*, 3056.

Table 4. Characteristic Spectroscopic Data for 2-Acylphenolato Complexes of Ni^{II} (1, 2) and Ni^{IV} (6, 7, 20, 21)

|	1	2	6	7	21	22
			IR Data (cm^{-1})			
ν(C=O)	1595 s	1600 vs	1705 vs	1745 w	1700 vs	1745 m
	1575 vs	1570 vs		1700 vs		1715 vs
			^{1}H NMR Data			
δ(NiCH_3) (ppm)			1.16 t	1.15 t		
^3J(PH) (Hz)			8.2	8.2		
			^{13}C NMR Data			
δ(C=O) (ppm)	230.3 s	230.3 s	207.7	212.8 t	211.7 t	212.3 t
			209.3^a			
^2J(PC) (Hz)				7.8	10.5	10.6
			^{31}P NMR Data			
δ(P) (ppm)	−18.5	−17.7	10.4	10.5	7.0	7.1

^{a} See Figure 2.

Figure 7. Molecular structure of **21**.

niently, are dissolved in acetone and aqueous HCl, while the nickel(IV) compounds **21**−**25** are precipitated. The raw products are recrystallized from ether or toluene affording air-stable crystals. Thermal stability is excellent as shown by sublimation of **22** (130 °C, 8 mbar) with only slight decomposition. **25** decomposes at 0 °C and was characterized by spectroscopy. Infrared absorptions (1725−1700 cm^{-1}, ν(C=O)) are shifted by 110 cm^{-1} to higher wavenumbers as compared with those of the nickel(II) educts. ^{31}P NMR singlet resonances experience low-field shifts of about 25 ppm which is of the same order as for **6**−**10**. Mass spectra (FD) contain M$^+$ at highest intensities with correct isotopic distribution. All data are thus in accord with a low-spin d^6 configuration of nickel valence electrons in an octahedral ligand field. As characteristic features, a *cisoidal* arrangement of the chelating ligands in an equatorial plane and two axial trimethylphosphines (Figure 7) have been established by an X-ray crystal structure determination of **21**.[3]

Conclusions

Chelating 2-acylphenolato ligands show the unusual property of stabilizing nickel to carbon σ-bonds in high as well as in normal oxidation states of the metal (Scheme 2). Bond distances and angles of the chelate rings are not sensitive enough to indicate a change in oxidation state, while infrared data (ν(C=O)) and NMR chemical shifts show new regions which are characteristic for low-spin d^6 compounds of nickel (Table 4). The stability of diacylnickel(IV) compounds **21**−**25** toward aqueous mineral acids and less pronounced oxidizing properties, when compared with K$_2$NiF$_6$, appears to be a consequence of the reduced polarity of the Ni−C bond.

Scheme 2. Reactions and Reactivities of (Acylphenolato)nickel(II) and -nickel(IV) Compounds
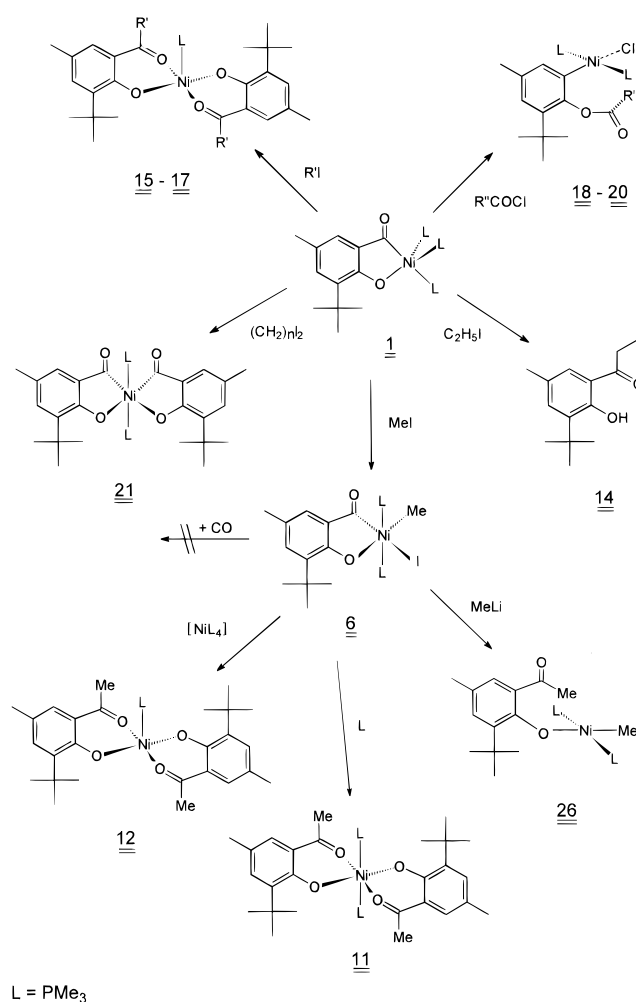
L = PMe$_3$

Supporting Information Available: Tables of atomic coordinates and displacement parameters for compounds **16**, **19**, and **19a** (4 pages). Ordering information is given on any current masthead page.

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