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Syntheses and Properties of the First Octahedral Diorganonickel(IV) Compounds

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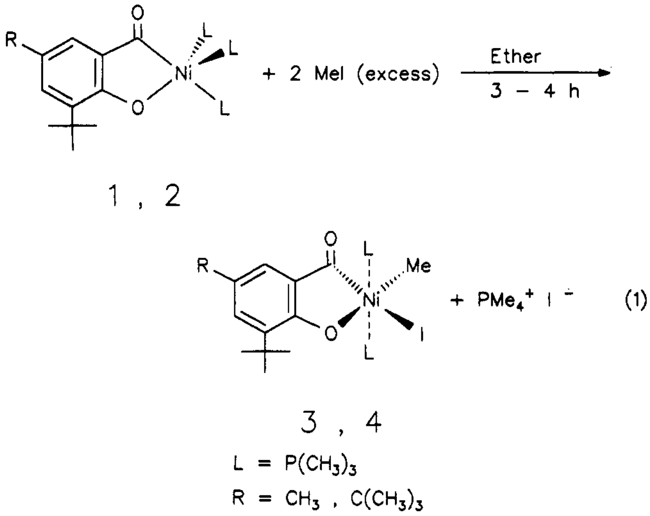
Summary: Iodomethane oxidatively substitutes trimethylphosphine in $Ni(\overset{\sqcap}{OC}{=}O)(PMe_3)_3$ ($\overset{\sqcap}{OC}{=}O$ *= 3-tert-butyl-5-methyl-2-oxobenzoyl (1), 3,5-di-tert-butyl-2-oxobenzoyl (2)) to afford the complexes mer-trans-*$Ni(Me)I(\overset{\sqcap}{OC}{=}O)(PMe_3)_2$ *(3 and 4, respectively). Both compounds undergo a regioselective C,C-coupling reaction in solution and in the crystal state, caused by thermal activation.*

C,C-coupling reactions are effectively catalyzed by organophosphine-supported nickel(II) complexes.[1] In systems where neither spontaneous reduction to nickel(0) nor radicals are indicated, the mechanism, which usually consists of an addition/elimination reaction sequence, requires the presence of nickel(IV) intermediates. Such schemes have been previously proposed[2] but have become rare, in recent times, because no organonickel(IV) compound has actually been observed. Currently most mechanistic considerations avoid the topic[3] and concentrate on radical pathways involving well-established diorganonickel(III) intermediates,[4] although to date no such species has been isolated.[5] On the other hand, chelating diphosphines have long been known to stabilize octahedral nickel(IV) halide complexes, e.g. $\{Ni[1,2\text{-}(PMe_2)_2C_6H_4]_2Cl_2\}(ClO_4)_2$,[6] as generated in concentrated nitric acid. In this communication we describe a simple oxidative substitution reaction of 18-electron acylnickel phenolates[7] by iodomethane under mild conditions which affords the title compounds in good yield.

The cyclic acylnickel phenolates 1 and 2[7] are, when reacted with excess iodomethane, transformed into tetramethylphosphonium iodide and the novel complexes 3 and 4[8] according to eq 1. Elemental composition and spectroscopic data[9] are only compatible with a nickel atom surrounded by a pair of *trans* trimethylphosphine ligands and four different anionic functions: two from the unchanged chelating acylphenolato dianion and the oxidatively added iodo and methyl ligands in mutually *cis* positions. The resulting ligand field accommodates a low-spin d^6 metal center, and ligand proton resonance signals are shifted in a way to be expected in a higher oxidation state.



1 , 2

3 , 4

L = $P(CH_3)_3$
R = CH_3 , $C(CH_3)_3$

From ether, 3 crystallizes as orange prisms (**3a**) and orange platelets (**3b**) that can be handled in air for 10 min without apparent change. The orange solid of 4, as

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[•] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

(1) Parshall, G.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992; Chapter 7.4.

(2) (a) Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5908. (b) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1975; Vol. II, p 269. (c) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7262.

(3) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 738.

(4) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547.

(5) In contrast, organonickel(III) dihalides have been characterized: van de Kuil, L. A.; Luitjes, H.; Grove, D. M.; Zwikker, J. W.; van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468 and references cited therein.

(6) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3136.

(7) Klein, H.-F.; Bickelhaupt, A.; Hammerschmitt, B. *Organometallics*, in press.

(8) **Synthesis of 3:** A 1.68-g (3.52-mmol) amount of Ni(3-*tert*-butyl-5-methyl-2-oxobenzoyl)$(PMe_3)_3$ (1) in 80 mL of ether at −70 °C was condensed in vacuo with 2.50 g (17.6 mmol) of iodomethane. The intensely red mixture was stirred at 20 °C for 3 h under 1 bar of argon. An orange solid was removed by filtration through a sintered-glass disk (G 4), and the resulting brownish yellow solution was kept at 4 °C. A total of 630 mg of orange crystals was isolated by decanting, washing with small amount of cold ether, and drying in vacuo. The orange solid was extracted with 50 mL of ether, leaving insoluble $PMe_4^+I^-$ on the sinter. Cooling this solution gave a second crop of orange crystals, which were combined with those previously obtained (900 mg, 1.65 mmol, 47% total yield); dec pt >92 °C. **Synthesis of 4:** A 2.54-g (4.93-mmol) amount of Ni(3,5-di-*tert*-butyl-2-oxobenzoyl)$(PMe_3)_3$ (2) in 40 mL of ether at −70 °C was condensed in vacuo with 3.50 g (24.7 mmol) of iodomethane. After the mixture was stirred at 20 °C for 2 h, a white solid ($PMe_4^+I^-$; IR) was removed by filtration. The yellow-brown solution was kept at −27 °C and deposited 340 mg of a light brown solid (0.58 mmol, yield 12%), which was isolated as above. The compound slowly decomposed at 20 °C.

(9) **3:** Anal. Calcd for $C_{19}H_{35}INiO_2P_2$ (mol wt 543.0): C, 42.03; H, 6.50; P, 11.41. Found: C, 41.80; H, 6.53; P, 11.20. IR (Nujol, 2700–1600 cm^{-1}): 1705 vs ($\nu(C{=}O)$). ^1H NMR (300 MHz, 1,4-dioxane-d_8, 297 K): $\delta(NiCH_3)$ 1.16 (t, 3 H, $^3J(PH) = 8.2$ Hz); $\delta[C(CH_3)_3]$ 1.38 (s, 9 H); $\delta(PCH_3)$ 1.46 (pseudotriplet, 18 H, $|^2J(PH) + {}^4J(PH)| = 8.4$ Hz); $\delta(CCH_3)$ 2.13 (s, 3 H); $\delta(CH)$ 6.82 (s, 1 H), 7.02 (s, 1 H). $^{13}C\{^1H\}$ NMR (75.4 MHz, THF-d_8, 248 K): $\delta(PCH_3)$ 13.88 (pseudotriplet, $|^1J(PC) + {}^3J(PC)| = 34.0$ Hz); $\delta(CCH_3)$ 20.46; $\delta(NiCH_3)$ 20.93 (t, $^2J(PC) = 11.0$ Hz); $\delta[C(CH_3)_3]$ 30.18; $\delta[C(CH_3)_3]$ 35.34; $\delta(CH)$ 123.41, 134.69; $\delta(C)$ 124.17, 140.85. $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, 198 K): δ 13.30 (s). MS (FD, 0–12 mA; m/e(^{58}Ni) (%)): 542 (20), M. **4:** IR (Nujol, 2700–1600 cm^{-1}): 1705 vs ($\nu(C{=}O)$). ^1H NMR (300 MHz, THF-d_8, 223 K): $\delta(NiCH_3)$ 1.15 (t, 3 H, $^3J(PH) = 8.2$ Hz); $\delta[C(CH_3)_3]$ 1.27 (s, 9 H), 1.45 (s, 9 H); $\delta(PCH_3)$ 1.53 (pseudotriplet, 18 Hz, $|^2J(PH) + {}^4J(PH)| = 8.4$ Hz); $\delta(CH)$ 7.02 (d, 1 H, $^3J(HH) = 2.2$ Hz), 7.36 (d, 1 H, $^3J(HH) = 2.2$ Hz. ^{13}C NMR (75.4 MHz, THF-d_8, 223 K): $\delta(PCH_3)$ 13.94 (pseudotriplet, $|^1J(PC) + {}^3J(PC)| = 33.9$ Hz); $\delta(NiCH_3)$ 21.28 (t, $^2J(PC) = 11.4$ Hz); $\delta[C(CH_3)_3]$ 30.39, 31.93; $\delta[C(CH_3)_3]$ 34.90, 35.87; $\delta(C)$ 118.87, 137.65, 140.58; $\delta(CH)$ 119.64, 131.39; $\delta(C{-}O)$ 178.42; $\delta(C{=}O)$ 212.77 (t, $^2J(PC) = 7.8$ Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, 198 K): δ 13.33 (s).

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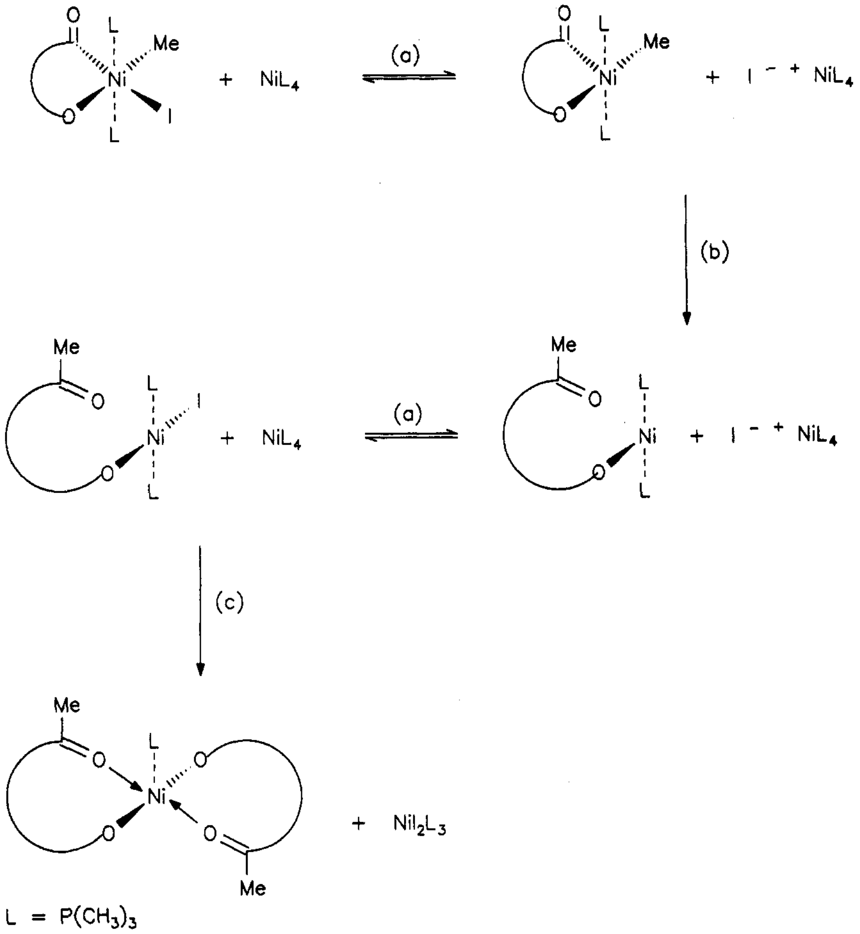
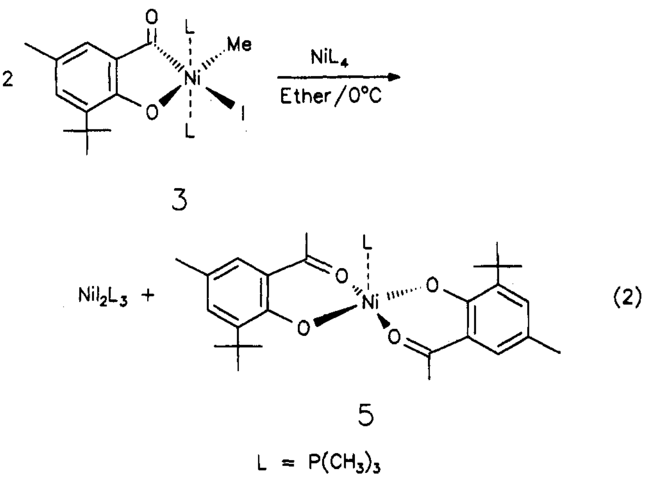
Scheme 1. Mechanistic Consideration of C,C-Coupling



obtained from pentane, exhibits similar properties. If air is admitted to ether solutions of **3**, the oxidation of phosphine ligands eventually affords trimethylphosphine oxide and a number of dark-colored products, of which $NiI_2(PMe)_3$[10] is one. Under 1 bar of CO there is no reaction prior to thermal decomposition.

Crystals of **3a,b** under argon after 4 weeks at 22 °C gradually turn dark blue, retaining the shining crystal surface. Strong infrared absorptions at 1650 and 1630 cm^{-1} (ν(C=O)) indicate the presence of coordinated acetyl groups originating from a reductive C,C-coupling reaction of acyl and methylnickel functions.[11]

In solution catalytic amounts of $Ni(PMe_3)_4$ accelerate the transformation according to eq 2,[12] which affords the novel bis(2-acetylphenolato)nickel complex **5**,[13] although trimethylphosphine alone under the same conditions has no effect.



The role of Ni(0) can be envisaged as single-electron transfer and migration of iodide (a) to generate a pentacoordinate diorganonickel(III) intermediate (Scheme 1), which presumably has a lower barrier for reductive C,C-coupling (b) (as in triorganoplatinum compounds[14]). $Ni(PMe_3)_4$ is regenerated by reverse single-electron and iodide transfer (a), followed by the ligand dismutation reaction (c) expected of a (phenolato)nickel iodide.

The two differently shaped single crystals of **3** were examined by X-ray diffraction[15] and revealed dimorphism. The molecular structures of **3a,b** show the same configuration of the complex (Figure 1) and barely differ in the

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[10] Dahl, O. *Acta Chem. Scand.* **1969**, *23*, 2342.

[11] This transformation is currently under study by solid-state NMR techniques: Kalinowski, H.-O. Giessen University, 1994.

[12] **Catalytic C,C-coupling Reaction of 3**: An 1140-mg (2.10-mmol) amount of **3** and 200 mg (0.55 mmol) of $Ni(PMe_3)_4$ in 50 mL of ether upon warming to 0 °C formed a dark green mixture. After 1 h the volatiles were removed in vacuo, and to recover $Ni(PMe_3)_4$ the residue was first extracted with 30 mL of pentane at −70 °C over a sintered-glass disk. A second extraction with 70 mL of pentane at 20 °C contained the product **5**, and a third extraction with 70 mL of ether dark green needles of $NiI_2(PMe_3)_3$ (350 mg, 0.65 mmol, yield 62% based on iodine). The pentane solution at −27 °C afforded a light brown solid of **5** (270 mg, 0.50 mmol, yield 23% based on nickel).

[13] **5**: Anal. Calcd for $C_{29}H_{43}O_4NiP$ (mol wt 545.3): C, 63.87; H, 7.95; P, 5.68. Found: C, 63.00; H, 7.89; P, 5.49. IR (KBr disk 2700–1570 cm^{-1}): 1620 s, 1580 vs (ν(C=O)); all expected bands of PMe_3 in the region 1400–400 cm^{-1}. MS (FD, 0–15 mA; *m/e*(^{58}Ni) (%)): 468 (100), M − PMe_3; 206 (25), $C_{13}H_{34}O_2$. ^{1}H NMR (300 MHz, THF-d_8, 297 K): broad resonances with large paramagnetic shifts.

[14] Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.

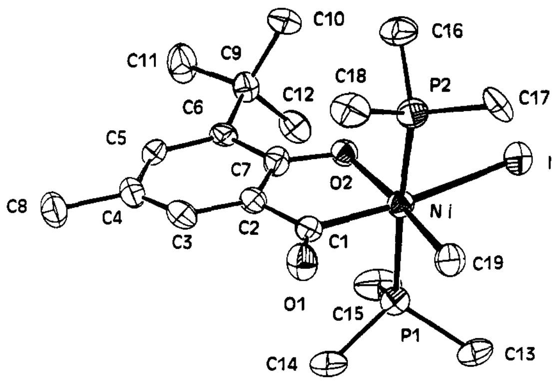

Figure 1. PLATON drawing of the molecular structure of **3**. Selected bond distances (Å) and angles (deg) for **3a** [**3b**]: Ni–I, 2.7613(13) [2.7364(7)]; Ni–P1, 2.242(3) [2.2516(12)]; Ni–P2, 2.240(3) [2.2415(11)]; Ni–O2, 1.960(6) [1.960(3)]; Ni–C1, 1.986(9) [1.965(4)]; Ni–C19, 1.993(9) [1.990(4)]; P–C(average), 1.81(1) [1.82(1)]; O1–C1, 1.197(11) [1.209(5)]; O2–C7, 1.305(10) [1.303(4)]; C1–C2, 1.468(12) [1.469(5)]; C2–C3, 1.388(12) [1.413(5)]; C2–C7, 1.422(12) [1.406(5)]; P1–Ni–P2, 174.28(10) [173.32(4)]; O2–Ni–C1, 86.1(3) [86.39(14)]; O2–Ni–C19, 175.6(3) [176.06(14)]; C1–Ni–C19, 89.6(4) [89.7(2)]; O2–Ni–P2, 92.8(2) [92.94(9)]; C1–Ni–P2, 90.7(3) [90.19(11)]; C19–Ni–P2, 87.7(3) [86.55(12)]; O2–Ni–P1, 92.9(2) [93.33(9)]; C1–Ni–P1, 90.1(3) [87.92(11)]; C19–Ni–P1, 86.7(3) [87.04(12)]; O2–Ni–I, 86.2(2) [87.72(8)]; C1–Ni–I, 172.2(3) [173.90(11)]; C19–Ni–I, 98.1(3) [96.20(12)]; P2–Ni–I, 88.52(7) [91.70(4)]; P1–Ni–I, 91.40(7) [90.85(4)]; C7–O2–Ni, 112.0(5) [111.8(2)]; O1–C1–C2, 128.4(8) [127.9(3)]; O1–C1–Ni, 124.5(7) [125.3(3)]; C2–C1–Ni, 107.1(6) [106.8(3)].

Table 1. Typical NMR Shifts (ppm) and Couplings (Hz) and Chelate Bond Angles (deg) in Nickel(II) and Nickel(IV) Compounds (298 K)

	1[7]	**2**[7]	**3**	**4**
δ(NiC*H*$_3$)			1.16	1.15
^3J(PH)			8.2	8.2
δ(PC*H*$_3$)	1.27	1.28	1.46	1.53
δ(P*C*H$_3$)	17.5	15.7	13.9	13.9
δ(Ni*C*=O)	230.3	228.5	*a*	212.8
δ(*P*)	−18.5	−17.7	10.4	10.5
Ni–O–C	110.5(2)		112.0(5) 111.8(2)	
Ni–C–O	129.0(4)		124.5(7) 125.3(3)	

[a] Observed in the solid state[11] at 207.7 and 209.3 ppm.

rotational positions of the groups. The molecular units consist of octahedrally coordinated nickel, surrounded by two *trans* trimethylphosphine ligands and a meridional sequence of phenolato, acyl, methyl, and iodo ligands. There are some significant variations in the angles around the nickel center and in the Ni–I and Ni–P1 bond distances (Figure 1). These are believed to be caused by the different packing in **3a** and **3b**. Generally, bond distances and angles do not differ from those expected for Ni(II) in any substantial detail. C,C-coupling between *cis* positions (C–Ni–C = 89.7° (**3a**) and 89.2° (**3b**)) is expected to proceed smoothly from a high formal oxidation state of IV to the most stable one of II.

The unexpected thermal stability of **3** and **4** requires an examination of innocence or noninnocence of the ligands involved. Single-electron oxidation of any of the ligands should dramatically affect all NMR signals and is therefore ruled out. Two-electron oxidation could only involve the chelating acylphenolato ligand. As there are no significant differences in spectroscopic and structural data (Table 1) and the metal chelate ring is planar in all three structures, we see no indication of an oxidation-state ambiguity in these first diorganonickel(IV) compounds **3** and **4**. The acylphenolato ligands appear to form rigid chelate rings in Ni(IV) as well as in Ni(II) complexes, which lends additional stability to the octahedral frame of donor atoms in **3** and **4**. This rigidity has been recently observed with neutral 1,2-bis(phenylimino) ligands in triorganopalladium(IV)[16,17] and -platinum(IV) complexes.[17]

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the Deutsche Forschungsgemeinschaft.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates and isotropic thermal parameters, and selected bond distances and angles for **3a,b** (5 pages). Ordering information is given on any current masthead page.

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(15) Crystal data for dimorphic **3**, $C_{19}H_{35}INiO_2P_2$ (M_r = 543.0): **3a**, orange prisms, orthorhombic, space group *Pbca*, a = 14.033(2) Å, b = 15.627(3) Å, c = 21.408(3) Å, V = 4694.6 Å^3, Z = 8, d_{calc} = 1.537 g/cm^3, μ = 2.288 mm^{-1}; **3b**, orange plates, monoclinic, space group $P2_1/c$, a = 11.524(1) Å, b = 15.904(1) Å, c = 13.462(6) Å, β = 100.25(2)°, V = 2427.8 Å^3, Z = 4, d_{calc} = 1.486 g/cm^3, μ = 2.212 mm^{-1}. Data collection and refinement details: Siemens P4 diffractometer, Mo Kα (λ = 0.710 73 Å) radiation, graphite monochromator, 153(2) K, ω–2θ scanning technique. For **3a** 3629 and for **3b** 6516 unique refections with 2.8° < 2θ < 50° and 4.0° < 2θ < 60°, respectively, were collected and 3018 and 5871, respectively, were considered observed. Values for **3a** (R = 0.050, R_w = 0.1454, GOF = 0.965) and for **3b** (R = 0.052, R_w = 0.1480, GOF = 0.995) are based on those reflections with $F^2 > 4\sigma(F^2)$.

(16) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83.

(17) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.