

## Synthesis and Structure of Octahedral Nickel(IV) Complexes Containing Two Chelating Acylphenolato Ligands

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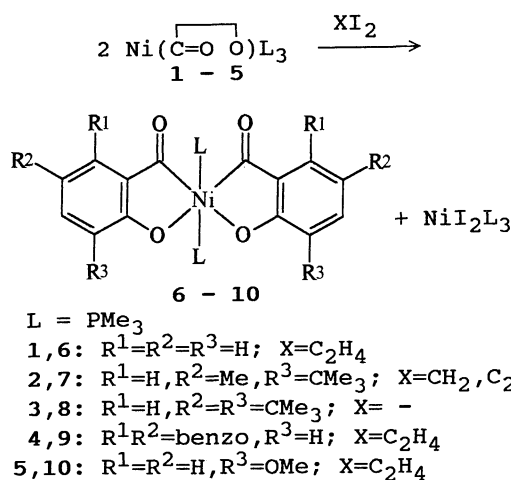
2-Acylphenolato complexes  $\text{Ni}(\overline{\text{C}=\text{O}}\text{O})(\text{PMe}_3)_3$  can be oxidized using iodine or diiodoalkanes at ambient conditions to afford low-spin  $d^6$  complexes  $\text{Ni}(\overline{\text{C}=\text{O}}\text{O})_2(\text{PMe}_3)_2$ . The molecular structure of the 5-*tert*-butyl-3-methyl derivative contains two axial trimethylphosphines and a *cisoidal* arrangement of two acylphenolato dianions in equatorial positions.

When compared with the diamine Schiff bases of salicylaldehyde as ancient ligands for transition metals<sup>1</sup> the corresponding oxo ligand derivatives have received less attention. Neither of these chelate systems has been considered for stabilizing unusual high oxidation states of metals. Recently salicylaldehyde, by reaction with methyl-nickel compounds, has been transformed into a chelating acylphenolato ligand<sup>2</sup> which was found to support an oxidative addition of iodomethane to a nickel(II) complex. The existence of stable diorganonickel(IV) compounds sheds new light on C,C-coupling and cross-coupling reactions<sup>3</sup> as catalyzed by nickel(II) complexes.

Crystals of *trans-mer*- $\text{Ni}(\overline{\text{C}=\text{O}}\text{O})\text{MeIL}_2$  ( $\text{L} = \text{PMe}_3$ ) have been isolated which are reluctant to undergo a clean reductive elimination but slowly decompose at room temperature to give a mixture of products. However, selective C,C-coupling reactions can be induced by catalytic amounts of  $\text{Ni}(\text{PMe}_3)_4$ <sup>4</sup> at 0 °C. The unexpected thermal stability of organometallic compounds of nickel(IV) has been connected with the presence of a rigid chelate ring spanning a bite angle  $\text{C-Ni-O} = 86 - 87^\circ$  in the nickel(II) precursor<sup>2</sup> as well as in the resulting nickel(IV) complex.<sup>4</sup> In order to test this hypothesis we have synthesized a series of acylphenolatonickel(IV) complexes of the bis(chelate) type expecting an even better thermal stability.

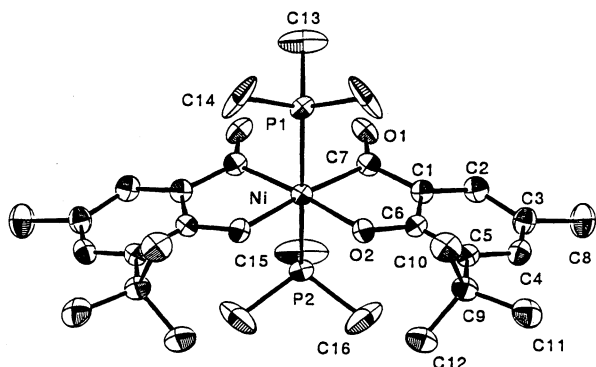
Reaction of  $\text{Ni}(\overline{\text{C}=\text{O}}\text{O})(\text{PMe}_3)_3$  with diiodomethane, diiodoethane or iodine in ether at -70 °C results in oxidation of half of the nickel in a ligand dismutation reaction while the remaining nickel(II) accommodates iodide and phosphine ligands.

Separation and isolation of the products



is facilitated by the stability and low solubility of the nickel(IV) complexes 7, 8 and 10 in aqueous mineral acids. This is another surprising property of the Ni-C(O) group, because so far all compounds  $\text{Ni}(\overline{\text{C}=\text{O}}\text{O})(\text{PMe}_3)_3$  under same conditions smoothly yield the salicylaldehyde derivatives  $\overline{\text{C}=\text{O}}\text{OH}$ .

In a typical synthesis 2 (740 mg,  $1.55 \times 10^{-3}$  mol) in ether (70 ml) at -70 °C is reacted with iodine (400 mg,  $1.58 \times 10^{-3}$  mol). After 12 h at 20 °C the dark green mixture is evaporated to dryness, and the residue is dissolved in acetone (5 ml). 1 M aqueous HCl (50 ml) is added in order to precipitate a yellow solid which is filtered and washed with water. This is dissolved in ether (50 ml) and dried over  $\text{Na}_2\text{SO}_4$ . At -30 °C orange needles of 7 are formed and isolated by decantation and drying in vacuo (270 mg, 29% based on Ni). This material can be handled in air for more than 10 min, dec. pt. (1 bar Ar) > 225 °C.<sup>5</sup> The mass spectra contain the peaks of parent ions with highest intensities, and 8 (dec. pt. > 168 °C) can be sublimed in vacuo at 8 mbar/130 °C with only slight decomposition. The C=O stretching frequencies are observed as strong bands in the region 1700 - 1725  $\text{cm}^{-1}$  which is characteristic for acylnickel(IV) compounds<sup>4</sup> when compared with those of the nickel(II) educts (1590 - 1610  $\text{cm}^{-1}$ ). Likewise, <sup>31</sup>P-NMR shifts between 7 and 8



**Figure 1.** ORTEP drawing of **7**. Selected bond distances (Å) and angles (deg): Ni-C7 1.967(4), Ni-O2 2.004(3), Ni-P1 2.266(3), Ni-P2 2.296(3), C7-O1 1.222(4), C1-C7 1.463(5), C6-O2 1.307(4); O2-Ni-C7 85.9(1), Ni-C7-C1 107.4(2), Ni-C7-O1 125.8(3), O1-C7-C1 126.7(3), Ni-O2-C6 111.0(2).

ppm are indicative of a low-spin  $d^6$  configuration of metal valence electrons.

An X-ray crystal structure analysis was carried out on single crystals of **7** (from ether).<sup>6</sup> The molecular units (Figure 1) are less symmetric than expected from ligand symmetries. There is a single mirror plane containing the Ni and the P atoms, but the chelate rings are no longer planar as in the educt complex **2**.<sup>2</sup> In the coordination plane there is a bending of the phenyl rings by an angle of  $15.6^\circ$  about the O1C7O2 axes away from the closer P1 atom and towards the more distant P2 atom. This is believed to be caused by packing forces rather than by non-innocent behavior of the chelating ligands, because a similar bending is observed in one of the structures of dimorphous  $\text{Ni}(\overline{\text{C}=\text{O}}\text{O})\text{MeI}(\text{PMe}_3)_2$  and is absent in the other.<sup>4</sup> The *cisoidal* arrangement in **7** appears to avoid two acyl functions exerting their strong *trans* influence on each other.

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#### References and Notes

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- 4 H.-F. Klein, A. Bickelhaupt, T. Jung, G. Cordier, *Organometallics*, **13**, 2557 (1994).
- 5 Data for **6**:  $^1\text{H}$  NMR (300 MHz,  $\text{D}_8\text{-THF}$ )  $\delta/\text{ppm}$  0.99 (virtual triplet,  $|^4J(\text{PH}) + ^2J(\text{PH})| = 9.4$  Hz, 18H,  $\text{PCH}_3$ ), 6.31 (ddd,  $^3J = 7.3$  and  $7.3$  Hz,  $^4J = 0.8$  Hz, 2H, CH), 6.77 (d,  $^3J = 8.5$  Hz, 2H, CH), 7.20 (m, 4H, CH).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{D}_8\text{-THF}$ )  $\delta/\text{ppm}$  10.87 (virtual triplet,  $|^3J(\text{PC}) + ^1J(\text{PC})| = 30.0$  Hz,  $\text{PCH}_3$ ), 114.2, 121.6, 125.1, 136.8 (CH).  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{D}_8\text{-THF}$ )  $\delta/\text{ppm}$  7.79 (s). MS (FD, 0 - 20 mA,  $^{58}\text{Ni}$ )  $m/z$  450 (100,  $\text{M}^+$ ). IR (nujol) 1722 vs ( $\nu\text{C}=\text{O}$ ).

Data for **7**:  $^1\text{H}$  NMR (300 MHz,  $\text{D}_8\text{-THF}$ )  $\delta/\text{ppm}$  0.96 (virtual triplet,  $|^4J(\text{PH}) + ^2J(\text{PH})| = 9.4$  Hz, 18H,  $\text{PCH}_3$ ), 1.49 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 2.15 (s, 6H,  $\text{CCH}_3$ ), 6.85 (s, 2H, CH), 7.05 (d,  $^4J = 2.0$  Hz, 2H, CH).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{D}_8\text{-THF}$ )  $\delta/\text{ppm}$  10.79 (virtual triplet,  $|^3J(\text{PC}) + ^1J(\text{PC})| = 29.4$  Hz,  $\text{PCH}_3$ ), 20.74 ( $\text{CCH}_3$ ), 29.69 ( $\text{C}(\text{CH}_3)_3$ ), 35.61 ( $\text{C}(\text{CH}_3)_3$ ) 122.3 (CH), 122.6 (C), 123.8 (C), 134.0 (CH), 140.7 (C), 175.6 (C-O), 211.7 (t,  $^2J(\text{PC}) = 10.5$  Hz, C=O).  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{D}_8\text{-THF}$ )  $\delta/\text{ppm}$  7.04 (s). MS (FD, 0 - 15 mA,  $^{58}\text{Ni}$ )  $m/z$  590 (100,  $\text{M}^+$ ). IR (nujol) 1700vs ( $\nu\text{C}=\text{O}$ ). Anal. Found: C, 61.57; H, 7.82. Calcd. for  $\text{C}_{30}\text{H}_{46}\text{NiO}_4\text{P}_2$  (591.3): C, 60.93; H, 7.84.

- 6 Crystallographic data for complex **7**:  $\text{C}_{30}\text{H}_{46}\text{NiO}_4\text{P}_2$ ,  $M = 591.3$ , orthorhombic, space group  $\text{Cmca}$ ,  $a = 20.736(8)$  Å,  $b = 9.94(2)$  Å,  $c = 32.04(3)$  Å,  $V = 6601(13)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.19$  gcm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 0.714$  mm<sup>-1</sup>. The structure was solved by statistic methods (SHELXS-86) and refined by standard methods (SHELXL-93). All non-hydrogen atoms were refined anisotropically with hydrogen atoms fixed in calculated positions. 2949 unique reflections were collected by  $\omega$ -2 $\theta$  scan in the range  $2.5^\circ \leq 2\theta \leq 50.1^\circ$ . Final  $R$  indices for all data converged at  $R_1 = 0.0647$ ,  $wR_2 = 0.1935$ ,  $\text{GOF} = 1.119$ .