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Note

Methylnickel compounds containing trimethylphosphine and salicylaldiminato(*N:O*) ligands

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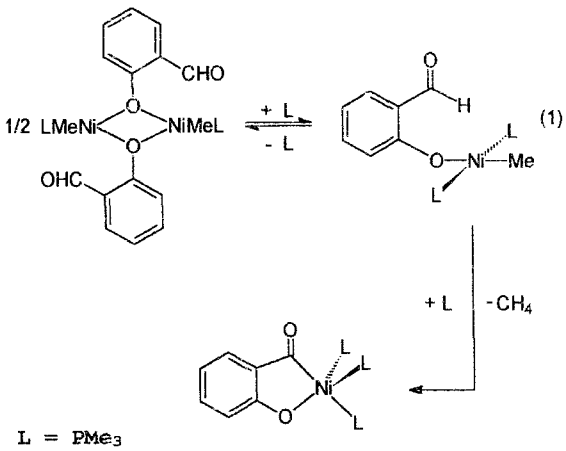
Abstract

Methyl(salicylaldiminato[*N:O*])nickel complexes $NiMe(2\text{-}O\text{-}C_6H_4\text{-}CH{=}NR)PMe_3$ (R = Me, Ph, $CHMe_2$, n-Bu, $CH_2CH(OMe)_2$, CH_2CF_3) have been prepared from $[NiMe(OMe)(PMe_3)]_2$ and the corresponding salicylaldimine. The diamagnetic methylnickel compounds contain the well known six-membered chelate ring and are unreactive towards excess trimethylphosphine. Steric demand of the N-substituent ($R = CMe_3$) causes ring opening and ligand dismutation reactions at the nickel center.

Keywords: Nickel complexes; Methyl complexes; Salicylaldiminato-(*N:O*) complexes; Chelate complexes

1. Introduction

Dinuclear methylnickel compounds containing the phenolate function of salicylaldehyde as μ^2-bridging ligand undergo a trimethylphosphine induced fragmentation reaction [1] according to Eq. (1).



We have introduced the isoelectronic Schiff base ligands under similar conditions and report here on their reactions which are more in line with classic chelating properties.

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2. Experimental

2.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Microanalysis of **7** was carried out under inert gas by Dornis and Kolbe, Microanalytical Laboratory, Mülheim, Germany; other compounds were analyzed in air by combustion. $[NiMe(OMe)(PMe_3)]_2$ [2] and salicylaldimines $2\text{-}OH\text{-}C_6H_4\text{-}CH{=}NR$ ($R = Me$, Ph, $CHMe_2$, n-Bu, $CH_2CH(OMe)_2$, CH_2CF_3) [3] ($R = CMe_3$) [4] were prepared according to published procedures. IR spectra (4000–400 cm^{-1}) as obtained from nujol mulls between KBr windows were recorded on a Perkin-Elmer type 397 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker WM 300 spectrometer at 297 K from samples dissolved in THF-d_8. Melting points as determined in capillaries under argon are uncorrected.

2.2. Procedures

2.2.1. Synthesis of salicylaldiminato-NiMe(PMe3) (1–6)

$[NiMe(OMe)L]_2$ ($L = PMe_3$) in 70 ml of THF are combined with 2 mole equiv. amounts of the salicylaldimine. After 3 h at 20 °C the change of color from yellow-brown to orange is complete. The volatiles are removed in vacuo and the residue is extracted with 50 ml of pentane over a glass-sinter disc (G 3). Crystallization at −27 °C, washing with cold pentane and drying in vacuo yields analytically pure material (Table 1).

Table 1
Scales and yields of preparations of compounds **1–6**

	R	[NiMe(OMe)L]$_2$	2-OH-C$_6$H$_4$-CH=NR	Yield	Crystal habitus m.p. (decomp.)
1	Me	520 mg	390 mg	470 mg	dark brown needles
		1.44 mmol	2.88 mmol	58%	66–68 °C
2	Ph	350 mg	380 mg	450 mg	dark red plates
		0.97 mmol	1.93 mmol	63%	103–105 °C
3	CHMe$_2$	350 mg	320 mg	220 mg	red-brown needles
		0.97 mmol	1.96 mmol	36%	(>101 °C)
4	n-Bu	480 mg	480 mg	370 mg	red-brown needles
		1.33 mmol	2.71 mmol	43%	(>42 °C)
5	CH$_2$CH(OMe)$_2$	360 mg	420 mg	430 mg	gold-brown plates
		1.00 mmol	2.01 mmol	60%	64–65 °C
6	CH$_2$CF$_3$	480 mg	540 mg	520 mg	red-brown needles
		1.33 mmol	2.66 mmol	56%	(>67 °C)

2.2.2. Analyses and spectroscopic characterization of compounds 1–6

1: *Anal.* Calc. for $C_{12}H_{20}NNiOP$ (284.0): C, 50.75; H, 7.10; N, 4.93. Found: C, 50.72; H, 7.03; N, 4.92%.

IR (Nujol, ν(C=N), cm^{-1}): 1595 vs. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −1.00 (s, 3H); δ(PCH_3) 1.24 (d, 9H, ^2J(PH) = 9.9 Hz); δ(NCH_3) 3.22 (s, 3H); δ(CH) 6.31 (ddd, 1H, ^3J(HH) = 6.9 and 7.9 Hz, ^4J(HH) = 1.1 Hz); δ(CH) 6.50 (dd, 1H, ^3J(HH) = 8.9 Hz, ^4J(HH) = 0.8 Hz); δ(CH) 7.02 (m, 2H); δ(CH=N) 8.02 (s, 1H). ^{13}C NMR (75.4 MHz, THF-d$_8$, 297 K): δ(NiCH$_3$) −17.54 (s, broad); δ(PCH$_3$) 12.83 (d, ^1J(PC) = 27.4 Hz); δ(NCH$_3$) 50.22; δ(CH) 113.2, 122.3, 133.1, 134.1; δ(C) 120.4; δ(CH=N) 165.9; δ(C–O) 167.2.

2: *Anal.* Calc. for $C_{17}H_{22}NNiOP$ (346.0): C, 59.00; H, 6.70; N, 4.05. Found: C, 58.96; H, 6.33; N, 4.03%.

IR (Nujol, ν(C=N), cm^{-1}): 1595 s, 1585 s. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −1.44 (s, 3H); δ(PCH_3) 1.25 (d, 9H, ^2J(PH) = 9.9 Hz); δ(CH) 6.37 (ddd, 1H, ^3J(HH) = 6.9 and 7.9 Hz, ^4J(HH) = 1.1 Hz); δ(CH) 6.59 (dd, 1H, ^3J(HH) = 8.9 Hz, ^4J(HH) = 0.7 Hz); δ(CH) 7.11 (m, 5H); δ(CH) 7.29 (m, 2H); δ(CH=N) 8.06 (s, 1H). ^{13}C NMR (75.4 MHz, THF-d$_8$, 297 K): δ(NiCH$_3$) −13.53 (s); δ(PCH$_3$) 12.82 (d, ^1J(PC) = 27.9 Hz); δ(CH) 113.8, 123.0, 125.0, 125.7, 129.0, 134.1, 134.9; δ(C) 120.2, 155.6; δ(CH=N) 165.8; δ(C–O) 168.0.

3: *Anal.* Calc. for $C_{14}H_{24}NNiOP$ (312.0): C, 53.89; H, 7.75; N, 4.49. Found: C, 53.77; H, 7.73; N, 4.48%.

IR (Nujol, ν(C=N), cm^{-1}): 1598 vs. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −1.11 (s, 3H); δ(PCH_3) 1.23 (d, 9H, ^2J(PH) = 9.9 Hz); δ(CH(CH_3)$_2$ 1.28 (d, 6H, ^3J(HH) = 6.7 Hz); δ(CH(CH$_3$)$_2$ 3.92 (sept. 1H, ^3J(HH) = 6.7 Hz); δ(CH) 6.31 (t, 1H, ^3J(HH) = 6.8 Hz); δ(CH) 6.48 (d, 1H, ^3J(HH) = 8.5 Hz); δ(CH) 7.04 (m, 2H); δ(CH=N) 8.05 (s, 1H). ^{13}C NMR (75.4 MHz, THF-d$_8$, 297 K): δ(NiCH$_3$) −17.49 (s); δ(PCH$_3$) 12.66 (d, ^1J(PC) = 28.0 Hz); δ(CH(CH$_3$)$_2$ 24.4; δ(CH(CH$_3$)$_2$ 52.48; δ(CH) 113.1, 122.3, 133.2, 134.2; δ(C) 121.4; δ(CH=N) 161.2; δ(C–O) 166.8.

4: *Anal.* Calc. for $C_{15}H_{26}NNiOP$ (326.0): C, 55.26; H, 8.04; N, 4.30. Found: C, 54.11; H, 7.80; N, 4.26% (handled in moist air).

IR (Nujol, ν(C=N), cm^{-1}): 1600 vs. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −1.06 (s, 3H); δ(CH_3) 0.95 (t, 3H, ^3J(HH) = 7.4 Hz); δ(PCH_3) 1.21 (d, 9H, ^2J(PH) = 9.8 Hz); δ(CH_2) 1.35 (sext, 2H, ^3J(HH) = 7.4 Hz); δ(CH_2) 1.72 (quint, 2H, ^3J(HH) = 7.4 Hz); δ(NCH_2) 3.35 (t, 2H, ^3J(HH) = 7.4 Hz); δ(CH) 6.31 (ddd, 1H, ^3J(HH) = 6.8 and 7.9 Hz, ^4J(HH) = 1.0 Hz); δ(CH) 6.48 (d, 1H, ^3J(HH) = 8.7 Hz); δ(CH) 7.02 (m, 2H); δ(CH=N) 7.95 (s, 1H). ^{13}C NMR (75.4 MHz, THF-d$_8$, 297 K): δ(NiCH$_3$) −9.09 (s); δ(PCH$_3$) 12.79 (d, ^1J(PC) = 29.1 Hz); δ(CH$_3$) 23.40; δ(CH$_2$) 30.02, 45.11, 69.78; δ(CH) 122.3, 131.3, 142.3, 143.2; δ(C) 129.8; δ(CH=N) 174.0; δ(C–O) 176.2.

5: *Anal.* Calc. for $C_{15}H_{26}NNiO_3P$ (358.0): C, 50.32; H, 7.32; N, 3.91. Found: C, 49.37; H, 7.06; N, 3.89% (handled in moist air).

IR (Nujol, ν(C=N), cm^{-1}): 1592 s, 1578 s. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −1.05 (s, 3H); δ(PCH_3) 1.25 (d, 9H, ^2J(PH) = 9.8 Hz); δ(OCH_3) 3.35 (s, 6H); δ(NCH_2) 3.50 (d, 2H, ^3J(HH) = 5.0 Hz); δ(CH(OCH$_3$)$_2$) 4.73 (t, 1H, ^3J(HH) = 5.0 Hz); δ(CH) 6.33 (ddd, 1H, ^3J(HH) = 6.9 and 7.8 Hz, ^4J(HH) = 1.1 Hz); δ(CH) 6.50 (dd, 1H, ^3J(HH) = 8.5 Hz, ^4J(HH) = 0.7 Hz); δ(CH) 7.04 (m, 2H); δ(CH=N) 7.96 (s, 1H). ^{13}C NMR (75.4 MHz, THF-d$_8$, 297 K): δ(NiCH$_3$) −19.15 (s); δ(PCH$_3$) 10.93 (d, ^1J(PC) = 27.7 Hz); δ(OCH$_3$) 52.76; δ(NCH$_2$) 61.03; δ(CH(OCH$_3$)$_2$) 104.01; δ(CH) 111.5, 120.6, 131.6, 132.8; δ(C) 118.8; δ(CH=N) 165.9; δ(C–O) 165.5.

6: *Anal.* Calc. for $C_{13}H_{19}F_3NNiOP$ (351.0): C, 44.36; H, 5.44; N, 4.00. Found: C, 44.36; H, 5.39; N, 3.93%.

IR (Nujol, ν(C=N), cm^{-1}): 1598 vs, 1580 vs. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −1.07 (s, 3H); δ(PCH_3) 1.26 (d, 9H, ^2J(PH) = 10.2 Hz); δ(CH_2CF_3) 4.03 (quart, 2H, ^3J(FH) = 9.2 Hz); δ(CH) 6.35 (ddd, 1H, ^3J(HH) = 6.7 and 8.2 Hz, ^4J(HH) = 1.0 Hz); δ(CH) 6.52 (dd, 1H, ^3J(HH) = 9.0 Hz, ^4J(HH) = 0.8 Hz); δ(CH) 7.08 (m, 2H); δ(CH=N) 8.13 (m, 1H). ^{13}C NMR (75.4 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −16.44 (d, ^2J(PC) = 44.6 Hz); δ(PCH_3) 12.72 (d, ^1J(PC) = 28.9 Hz); δ(CH_2CF_3) 57.84 (quart, ^2J(FC) = 30.2 Hz); δ(CH) 113.9, 123.1, 134.6, 135.3; δ(C) 120.3, 123.8, 127.5; δ(CH=N) 171.0; δ(C–O) 168.4.

2.2.3. Synthesis of methyl(N-tert-butylsalicylaldiminato-[N:O])(trimethylphosphine)nickel (7)

To 350 mg (0.97 mmol) [NiMe(OMe)(PMe$_3$)]$_2$ in 50 ml of ether at −70 °C are added 350 mg (1.98 mmol) of *N*-tert-butylsalicylaldimine. Within 15 min the solution turns orange. Removing the volatiles at 0 °C in vacuo followed by extraction of the residue with 50 ml of pentane and workup as above affords 380 mg of orange–brown needles (60%), decomp. > 78 °C.

Anal. Calc. for $C_{15}H_{26}$NNiOP (326.0): C, 55.26; H, 8.04; N, 4.30. Found: C, 54.83; H, 7.68; N, 4.49%.

IR (Nujol, ν(C=N), cm^{-1}): 1592 vs.

2.2.4. Synthesis of methyl(N-tert-butylsalicylaldiminato)-bis(trimethylphosphine)nickel (8)

370 mg (1.02 mmol) [NiMe(OMe)(PMe$_3$)]$_2$ and 370 mg (2.09 mmol) of *N*-tert-butylsalicylaldimine in 70 ml of ether at 0 °C form an orange solution. After 30 min, 860 mg (11.3 mmol) PMe$_3$ are added in vacuo causing a yellow–brown precipitation. This is dissolved by briefly warming up and filtering. At −27 °C 360 mg of yellow–brown needles are obtained (44%), decomp. > 131 °C.

Anal. Calc. for $C_{18}H_{35}NNiOP_2$ (402.1): C, 53.76; H, 8.77; N, 3.48. Found: C, 53.98; H, 8.80; N, 3.49%.

IR (Nujol, ν(C=N), cm^{-1}): 1612 m, 1572 vs. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −1.15 (s, 3H); δ(PCH_3) 1.07 (d, 18H, ^2J(PH) = 6.3 Hz); δ(C(CH_3)$_3$ 1.27 (s, 9H); δ(CH) 6.22 (t, 1H, ^3J(HH) = 7.3 Hz); δ(CH) 6.94 (ddd, 1H, ^3J(HH) = 7.5 and 7.1 Hz, ^4J(HH) = 2.0 Hz); δ(CH) 7.18 (d, 1H, ^3J(HH) = 7.5 Hz); δ(CH) 7.49 (dd, 1H, ^3J(HH) = 7.6 Hz, ^4J(HH) = 1.9 Hz); δ(CH=N) 8.77 (s, 1H). ^{13}C NMR (75.4 MHz, THF-d$_8$, 297 K): δ(NiCH_3) −21.26 (s); δ(PCH_3) 13.15 (d, ^1J(PC) = 16.5 Hz); δ(C(CH_3)$_3$ 31.11; δ(NC(CH_3)$_3$ 57.38; δ(CH) 112.5, 121.9, 128.5, 131.7; δ(C) 127.4; δ(CH=N) 155.7; δ(C–O) 170.2.

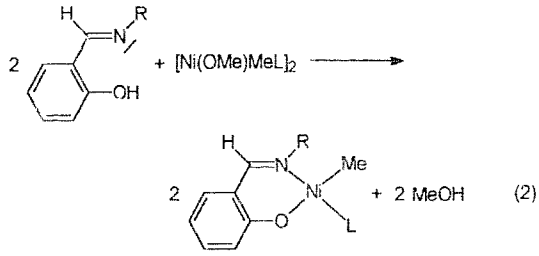
2.2.5. Ligand dismutation reaction of 7 (in situ)

410 mg (1.13 mmol) [NiMe(OMe)(PMe$_3$)]$_2$ and 400 mg (2.26 mmol) of *N*-tert-butylsalicylaldimine in 70 ml of THF after 18 h at 20 °C form a dark red solution. The volatiles are removed in vacuo, and the residue is extracted with 70 ml of pentane. At −27 °C 280 mg of violet–brown needles are obtained (60% based on salicylaldimine), m.p. 199–201 °C.

Anal. Calc. for $C_{22}H_{28}N_2NiO_2$ (411.2): C, 64.26; H, 6.86; N, 6.81. Found: C, 64.19; H, 6.89; N, 6.75%.

3. Results and discussion

Dimeric methyl(trimethylphosphine)nickel methoxide reacts with salicylaldimines according to Eq. (2) liberating methanol and utilizing both the phenolato and the N-donor functions.



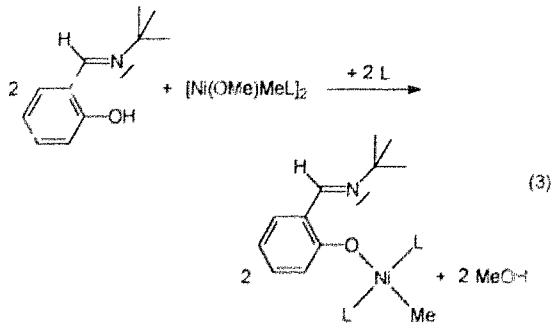
R = Me, Ph, CHMe$_2$, n-C$_4$H$_9$
CMe$_3$, CH$_2$CH(OMe)$_2$, CH$_2$CF$_3$

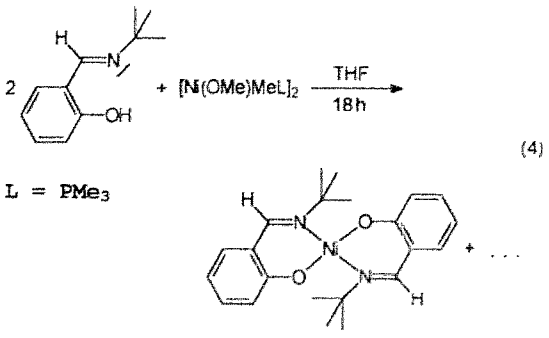
L = PMe$_3$

Mononuclear methylnickel complexes are thus obtained, and in solution there is no indication of dinuclear phenolato-bridged intermediates which would be isoelectronic with the stable product of the salicylaldehyde reaction. The different behavior is explained by the superior donor quality of the nitrogen atom, while ligand conformations of (*O:O*) and (*N:O*) donors should be equally suitable for six-membered chelate rings in square planar metal coordination as exemplified by methyl(trimethylphosphine)nickel β-diketonates [2,5].

Compounds **1–6** cannot be forced to react with trimethylphosphine in the sense of a fragmentation reaction (1b). This could be either due to a low reactivity of the (sp^2)C–H function of Schiff bases when compared with the parent aldehyde or to a high stability of the chelate ring.

The latter possibility was investigated by increasing the size of the N-substituent in the Schiff base until ring opening occurs. With R = CMe$_3$ the reactivity of the primary product **7** according to Eq. (2) is greatly enhanced. Upon contact with air crystals of **7** spontaneously fume and ignite, although solids of **1–6** slowly decompose within weeks at 20 °C. Exclusively with **7** there is a fast uptake of trimethylphosphine according to Eq. (3), while in the absence of the phosphine a ligand dismutation reaction occurs according to Eq. (4).





The bis(phosphine) compound **8** is less air-sensitive than **7** but under argon starts decomposing only above 131 °C. By contrast, solid **7** is thermally labile and in THF at 20 °C yields the ancient tetrahedral bis(salicylaldiminato)nickel complex [4] together with the products expected from the decomposition reaction of *trans*-$NiMe_2(PMe_3)_2$ [6].

The increased reactivity of **7** is best explained by steric constraint as the CMe_3 groups are forced into the plane of coordination. This reactivity does not involve the (sp^2)C–H function of the Schiff base.

Acknowledgements

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