Intermediates and Side-Reactions in the Synthesis of Molecular Diphenolatonickel Compounds Containing Trimethylphosphane Ligands

Hans-Friedrich Klein*[a], Attila Dal[a], Thomas Jung[a], Ulrich Flörke[b], and Hans-Jürgen Haupt[b]

Institut für Anorganische Chemie der Technischen Universität Darmstadt[a],
Petersenstraße 18, D-64285 Darmstadt, Germany

Anorganische und Analytische Chemie der Universität/GH Paderborn[b],
Warburger Straße 100, D-33095 Paderborn, Germany

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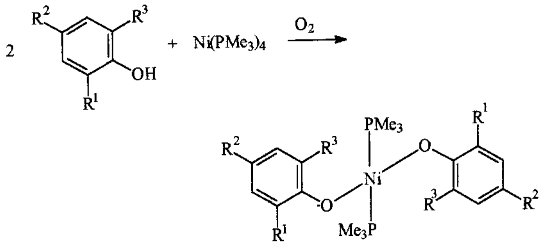
Admission of molecular oxygen to a solution containing $Ni(PMe_3)_4$ and substituted phenols (ArOH) affords bisphenolatonickel compounds *trans*-$Ni(OAr)_2(PMe_3)_2$ [ArOH = 2-chlorophenol (**1**), 2-bromophenol (**2**), 2,4,6-trichlorophenol (**3**)]. In the absence of dioxygen the phenols reversibly protonate the nickel complex to form ionic compounds $[NiH(PMe_3)_4]^+ Y^-$ containing hydrogen-bonded anions Y = $[H_2(2\text{-Cl–}C_6H_4O)_3]$ (**4**), $[H(2\text{-OH–}C_6H_4COO)_2]$ (**5**). As a side-reaction, formal insertion of nickel to give 2-hydroxyphenylnickel compounds $Ni(Ar')X(PMe_3)_3$ [Ar′ = 2-OH–C_6H_4; X = Br (**6**), I (**7**)], *trans*-$Ni(Ar')Cl(PMe_3)_2$ [Ar′ = 2-OH–3,5-Cl_2–C_6H_2 (**8**)] and *trans*-$Ni(OAr)Cl(PMe_3)_2$ [Ar = 2,4,6-Cl_3–C_6H_2 (**9**)] is observed. An X-ray crystal structure determination of **1** shows a *trans* square planar arrangement of donor atoms, that of **6** shows a distorted square pyramid, while **4** contains tetrahedral nickel cations with a delocalized hydrogen atom and triphenolate anions $H_2(ArO)_3^-$.

Introduction

Steric protection is the key feature in the synthesis of molecular diphenolato-bis(trimethylphosphane) nickel compounds starting from substituted phenols, $Ni(PMe_3)_4$, and dioxygen.[1] Prior to the admission of dioxygen the colour of the pale yellow solution is observed to deepen depending on the phenol and on solvent polarity. In our first attempts to isolate a reaction intermediate we recovered mixtures of the starting materials. However, the introduction of halide substituents into the phenols led to the crystallization, in high yields, of ionic compounds containing the hydridotetrakis(trimethylphosphane)nickel cation and hydrogen-bonded oligophenolate anions. Under these conditions we also observed formation of arylnickel complexes in a side-reaction and investigated the factors supporting formation of Ni−C bonds.

Results and Discussion

From pale yellow solutions containing $Ni(PMe_3)_4$ and 2-halogenophenol (except 2-iodophenol, see below) in ether at −78 °C a yellow solid precipitated. Upon admission of dioxygen the precipitate dissolved to fom a red solution according to an overall Eq. 1.



(1)

	R¹	R²	R³
1	Cl	H	H
2	Br	H	H
3	Cl	Cl	Cl

The diphenolatonickel complexes **1**−**3** are red or brown solids that are stable in air for several hours. Recrystallization from pentane or ether afforded dark red crystals that can be dried in vacuo without loss of phosphane ligands. Infrared spectra contain fingerprint absorptions of diphenolatonickel complexes and do not show νOH bands. The proton resonance of the trimethylphosphane groups is a singlet, indicating fast exchange of ligands, and no paramagnetic shift or line broadening is observed. Physical and spectroscopic data are thus in accordance with molecular compounds in a low-spin state and square planar coordination of nickel.[1] When compared with 2-*tert*-butyl-substituted diphenolatonickel complexes no significant downfield shift of the 6-H proton resonance signal is detected and hence no steric congestion in the coordination plane is indicated. Indeed, freely oriented 2-chlorophenolato groups are apparent in the molecular structure of complex **1** (Figure 1).

The nickel atom resides at a crystallographic centre of symmetry, and the P−Ni−O angles attain almost ideal values because there is no steric strain, unlike in the case of 2-*tert*-butyl-substituted analogs in which the angle P−Ni−O is opened up by $CH_3−CH_3$ repulsion of trimethylphosphanes with bulky substituents R^1 and R^2 (Table 1). In two

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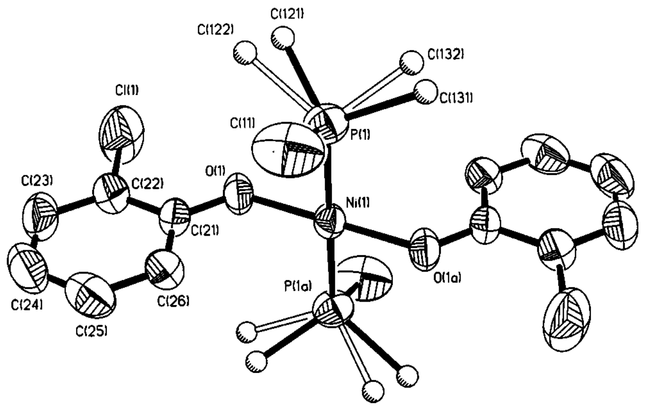
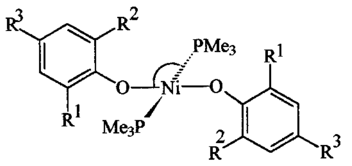
Figure 1. Molecular structure of **2** (ORTEP plot without hydrogen atoms)[a]



[a] Principal bond lengths [Å] and angles [°]: Ni−O1 1.857(3), Ni−P1 2.233(2), O1−C21 1.320(5), C21−C26 1.394(6), C25−C26 1.378(7); O1−Ni−P1 90.37(12), O1−Ni−P1a 89.63(12), C21−O1−Ni 122.7(3)

Table 1. Distortion by PCH_3-CCH_3 repulsion in diphenolato-nickel complexes



	R^1	R^2	R^3	Ni−P [Å]	O−Ni−P [°]
1	Cl	H	H	2.233(2)	90.37(12)
[a]	$C(CH_3)_3$	H	CH_3	2.233(2)	94.08(12)
[a]	$C(CH_3)_3$	CH_3	H	2.268(2)	98.55(12)

[a] Ref.[1]

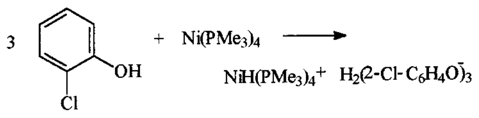
structures where R^2 = H the bond distances Ni−P are equal within experimental error while a significant elongation is found in the third.

Ion Pair Intermediates

The exclusion of dioxygen from the reaction mixture induces precipitation of a yellow solid by 2-chlorophenol in 85% yield according to Eq. 2.

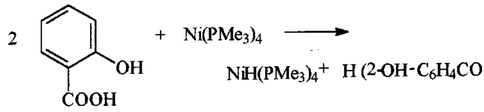
Recrystallization from toluene gives pale yellow needles in low yield, and solid **4** under argon at 20°C decomposes within two weeks. The crystalline solid may be stored for several months at −20°C and, on rapid heating, decomposes above 162°C.

The use of salicylic acid leads to the formation of a crystalline precipitate according to Eq. 3. Solid **5** may be stored under argon at 20°C for several weeks and in solution is thermally more stable than **4**. The infrared spectra of nujol mulls of **4** and **5** in the region 3000−1600 cm^{-1} contain several broad bands, and a broad absorption at 1950 cm^{-1} is assigned to an Ni−H vibration. A deuterated sample, **4D**, obtained by reaction according to Eq. 1 using 2-$Cl-C_6H_4-OD$ displayed the expected bathochromic shift of bands, which coincided within a multitude of bands in the fingerprint region. In the NMR experiment freshly prepared samples of **4** in CD_3CN or of **5** in $[D_6]$THF gave a resonance at δ = −17.2, which is typical for cationic NiH species. After 30 min the signal of **4**, which was not detected in $[D_6]$THF, gave way to broad resonances of unknown paramagnetic species while that of **5** persisted for some hours.



(2)

4



(3)

5

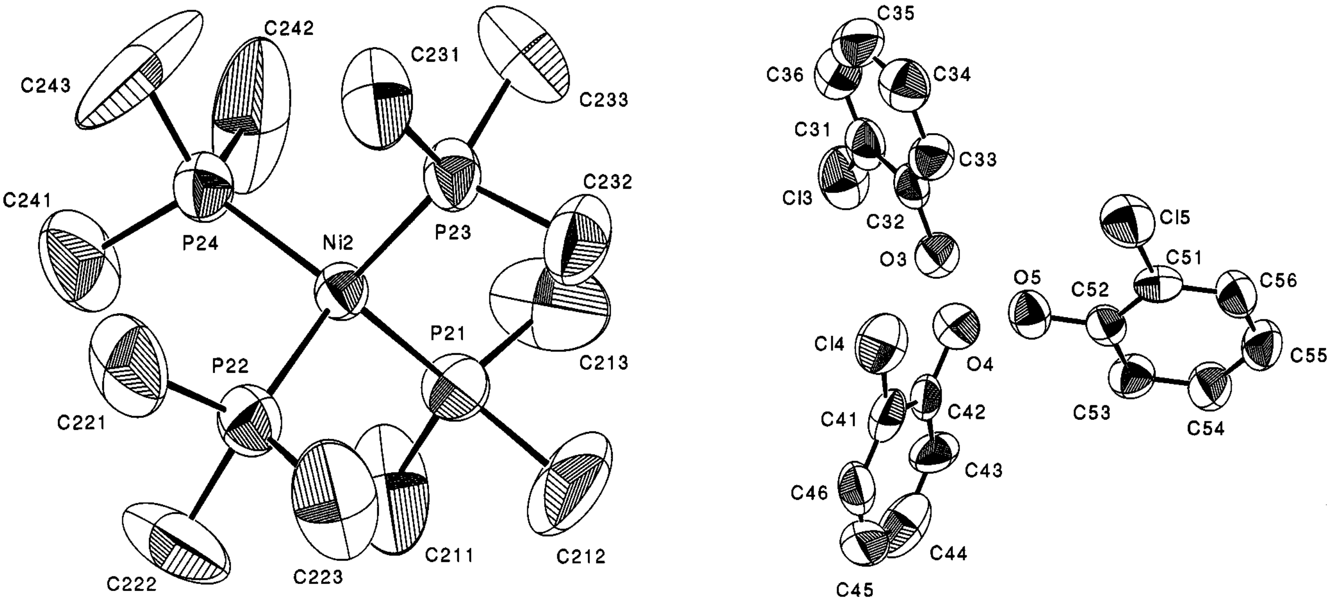
A pale yellow prismatic single crystal of **4** was subjected to an X-ray diffraction experiment. The lattice of **4** consists of separate nickel cations and triphenolate anions with no bonding contacts between the units. The molecular structure of one of the two metal complex cations in the cell is shown on the left hand side of Figure 2. The frame of heavy atoms, NiP_4, appears as an almost ideal tetrahedron with Ni−P distances in the range 2.213(3)−2.236(3) Å (average 2.224 Å) and angles P−Ni−P in the range 105.93(13)−112.60(14)°.

The two anions in the cell consist of three 2-chlorophenolate entities, each arranged with their anionic O atoms in an approximate equilateral triangle with distances O1−O6 = 2.56(1), O2−O6 = 2.53(1), and O1−O2 = 4.26(1) Å (not depicted) or O3−O5 = 2.53(1), O4−O5 = 2.56(1), and O3−O4 = 4.06(1) Å (Figure 2), respectively, which imply two in-plane hydrogen bridges at angles O1−O6−O2 = 112.9(5)° or O3−O5−O4 = 105.9(5)°, respectively. The phenyl rings are oriented roughly perpendicular to that plane with an up-up-down orientation of the 2-chloro substituents. These structural features are in accordance with the presence of a triphenolate anion, which has been previously observed with *para*-cresolates and a ruthenium complex counterion.[2]

Although the structure of the tetrahedral cation $Ni(PMe_3)_4^+$ in $\{Ni(PMe_3)_4][BPh_4]$[3] displays significantly shorter Ni−P bond distances [2.213(3)−2.221(3) Å, average 2.216 Å], the presence of an additional hydrogen atom in **4** appears questionable based solely on structural parameters. Therefore experiments were designed in order to test the presence of the NiH^+ moiety.

No reaction of **4** or **5** was observed with cyclopentene or carbon dioxide as substrates for an insertion into a metal hydride function. While **4** and **5** failed to protonate trimethylphosphane, action of strong base (NaH, K, or MeLi) on a suspension of **4** or **5** in pentane at −78°C liberated the

Figure 2. Molecular structure of **4** (ORTEP plot without hydrogen atoms)[a]



[a] Principal bond lengths [Å] and angles [°]: Ni2−P21 2.223(3), Ni2−P22 2.228(3), Ni2−P23 2.220(4), Ni2−P24 2.236(3), O3−O5 2.53 (1), O4−O5 2.56(1), O3−O4 4.06(1), O3−C32 1.357(9), Cl3−C31 1.733(9), O4−C42 1.354(9), Cl4−C41 1.745(8), O5−C52 1.367(8), Cl5−C51 1.717(7); P21−Ni2−P22 108.52(13), P21−Ni2−P23 108.33(13), P21−Ni2−P24 112.60(14), P22−Ni2−P23 110.5(2), P22−Ni2−P24 106.82(13), P23−Ni2−P24 110.08(14), O3−O5−O4 105.9(5).

expected volume of gas, and quantitative amounts of $Ni(PMe_3)_4$ were recovered (Eq. 4).

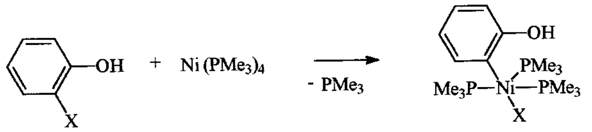
$$\mathbf{5} \xrightarrow{\substack{\text{a) } + 2\,NaH,\ -2\,H_2 \\ \text{b) } + 2\,K,\ -H_2 \\ \text{c) } + 2\,LiCH_3,\ -2\,CH_4}} Ni(PMe_3)_4 \qquad (4)$$

$$\mathbf{5} \xrightarrow{+ 2\,CO,\ -2\,PMe_3} Ni(CO)_2(PMe_3)_2 \qquad (5)$$

Protonation of $Ni(PMe_3)_4$ by the phenolic acids was reversed in **4** and **5** under 1 bar CO according to Eq. 5. Thus all successful reactions of **4** and **5** point to the presence of an NiH function exhibiting protic reactivity.

Insertion Reactions

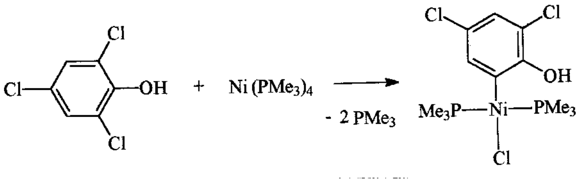
The exclusion of oxygen from the mixtures of $Ni(PMe_3)_4$ and 2-bromo- and 2-iodophenol led to oxidative addition reactions of C−X bonds according to Eq. 6.



(6)

6: X = Br
7: X = I

The pentacoordinate 2-hydroxyphenylnickel complexes **6** and **7** were obtained from ether as red crystals that are air-sensitive and under argon decompose above 100°C. 2-Chlorophenol does not react under these conditions. Additional activation in 2,4,6-trichlorophenol affords a square planar complex according to Eq. 7. The yellow crystals of **8** are stable in air for several hours and under argon decompose above 102°C. Sharp infrared absorptions at 3204 cm^{-1} (**6**), 3264 cm^{-1} (**7**), and at 3264 cm^{-1} (**8**) indicate the presence of an OH group, which is supported by broad proton resonances at δ = 6.7 (**6**), δ = 7.6 (**7**), and δ = 6.1 (**8**).



(7)

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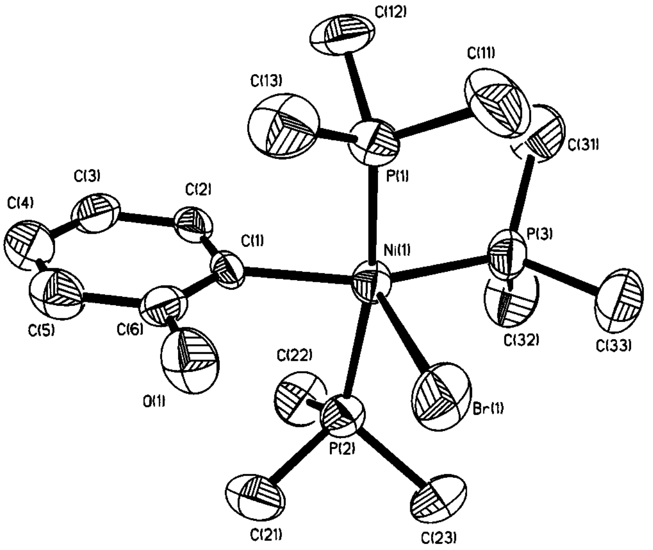
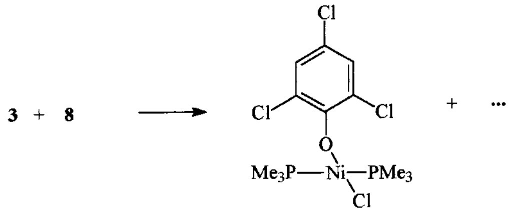
The molecular structure of **6** (Figure 3) shows a pentacoordinate nickel atom in an approximately square pyramidal surrounding of atoms ($CBrP_3$). The axial distance [Ni−Br = 2.805(2) Å] is considerably longer than the equatorial distances in $NiBr_2(PMe_3)_3$ (Ni−Br = 2.426−2.580 Å).[4] There are two short Ni−P distances in the *trans*-PNiP unit and a longer one roughly opposite to the Ni−C bond reflecting a considerable *trans*-influence. A sizeable *trans*-effect is believed to operate and cause exchange of chloride and phenolato ligands involving **8** and **3** under conditions where both oxidation and insertion reactions occur concurrently according to Eq. 8.

A mixed phenolato-chloro compound (**9**) was found to crystallize from the mixture as violet crystals that are air-stable and melt at 162−164°C. The spectroscopic data support a *trans* square-planar coordination geometry of nickel,

Figure 3. Molecular structure of **6** (ORTEP plot without hydrogen atoms)[a]



[a] Principal bond lengths [Å] and angles [°]: Ni–C1 2.004(8), Ni–P1 2.196(3), Ni–P2 2.196(3), Ni–P3 2.245(3), Ni–Br 2.805(2), O1–C6 1.370(10); C1–Ni–P1 85.1(3), C1–Ni–P2 84.7(2), C1–Ni–P3 150.6(3), P1–Ni–P2 167.88(11), P1–Ni–P3 96.07(11), P2–Ni–P3 96.03(11), C1–Ni–Br 108.9(3), P1–Ni–Br 88.99(9), P2–Ni–Br 88.14(8), P3–Ni–Br 100.52(8), C6–C1–Ni 124.3(7), C1–C6–O1 125.5(8).



(8)

9

and 2,4,6-trichlorophenol is recovered from the reaction with concentrated hydrochloric acid.

Conclusion

Molecular diphenolatobis(trimethylphosphane)nickel complexes can be prepared in high yields starting from substituted phenols, $Ni(PMe_3)_4$, and dioxygen, if halide substituents in the 2-position of the phenolato ligand prevent condensation reactions. Hydrido(trimethylphosphane)nickel cations and oligomeric hydrogen phenolate counterions are observed as ion-pair intermediates. Single bromide and iodide or multiple chloride substituents in the absence of dioxygen give rise to insertion reactions that, with the exception of iodophenols, are usually dominated by the faster oxidation processes.

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Experimental Section

General Procedures and Materials: All air-sensitive and volatile materials were handled by standard vacuum techniques and kept under argon. Details have been given elsewhere.[5] $Ni(PMe_3)_4$ was prepared by literature methods,[6] phenols and salicylic acid (Merck-Schuchardt) were used as purchased. Measured volumes of oxygen were admitted to the reaction mixture at −70°C in vacuo.

trans-Di(2-chlorophenolato)bis(trimethylphosphane)nickel (**1**): 830 mg of $Ni(PMe_3)_4$ (2.29 mmol) and 2000 mg of 2-chlorophenol (15.6 mmol) in 70 ml of THF at −78°C were combined with 50 ml of dioxygen. Upon warming, the pale yellow solution turned red/brown. After 72 h at 20°C the volatiles were removed in vacuo and the residue was extracted with pentane over a glass-sinter disc (G3). Crystallization at −20°C afforded dark red rhombs. Yield 575 mg (54% based on nickel), m.p. 179–181°C. – IR (Nujol): $\tilde{\nu}$ = 1577 cm^{-1} (C=C), 1033 (C–O), 949 ρ(PCH_3). – ^1H NMR ([D_8]toluene): δ = 0.98 [s(br), 18 H, $P(CH_3)_3$], 6.31 (t, *J* = 7.2 Hz, 2 H, 4-H), 6.95 (d, *J* = 7.4 Hz, 2 H, 6-H), 7.03 (t, *J* = 7.4 Hz, 2 H, 5-H), 8.15 (m, 2 H, 3-H). – ^{13}C NMR ([D_8]THF): δ = 9.39 [s(br), $P(CH_3)_3$], 112.98 (s, C-6), 120.47(s, C-4), 123.26 (s, C-2), 126.11, 127.63 (C-3, C-5), 160.21 (s, C-1). – $C_{18}H_{26}Cl_2NiO_2P_2$ (466.0): calcd. C 45.40, H 5.62, P 13.33; found C 45.99, H 5.54, P 14.78.

trans-Di(2-bromophenolato)bis(trimethylphosphane)nickel (**2**): 720 mg of $Ni(PMe_3)_4$ (1.98 mmol) and 1000 mg of 2-bromophenol (5.78 mmol) in 60 ml of THF at −78°C were combined with 50 ml of dioxygen. Upon warming, the pale yellow solution turned dark red. After 16 h at 20°C the volatiles were removed in vacuo and the residue was washed with 50 ml of ether and extracted with THF over a glass-sinter disc (G3). Crystallization at −20°C afforded dark red rhombs. Yield 640 mg (58% based on nickel), m.p. 175–177°C. – IR (Nujol): $\tilde{\nu}$ = 1571 cm^{-1} (C=C), 1021(C–O), 948 ρ(PCH_3). – ^1H NMR ([D_8]toluene): δ = 1.08 [s(br), 18 H, $P(CH_3)_3$], 6.26–8.26 (m, 8 H). – $C_{18}H_{26}Br_2NiO_2P_2$ (554.9): calcd. C 38.96, H 4.72, P 11.16; found C 39.06, H 4.46, P 11.30.

trans-Bis(2,4,6-trichlorophenolato)bis(trimethylphosphane)nickel (**3**): 700 mg of $Ni(PMe_3)_4$ (1.93 mmol) and 761 mg of 2,4,6-trichlorophenol (3.86 mmol) in 80 ml of THF at −78°C were combined with 50 ml of dioxygen. After stirring the mixture at 20°C for 16 h the volatile components were removed in vacuo and the dark brown residue was washed with pentane and extracted with ether to afford dark brown crystals. Yield 650 mg (56% based on nickel), m.p. 176–178°C. – IR (Nujol): $\tilde{\nu}$ = 1564 cm^{-1} (C=C), 1071 (C–O), 948 ρ(PCH_3). – ^1H NMR ([D_8]THF): δ = 1.64 [s(br), 18 H, $P(CH_3)_3$], 6.90 (m, 4 H). – ^{13}C NMR ([D_8]THF): δ = 13.82 [s(br), $P(CH_3)_3$], 126.44 (s). –$C_{18}H_{22}Cl_6NiO_2P_2$ (603.7): calcd. C 35.81, H 3.67, P 10.26: found C 35.72, H 3.68, P 10.30.

Hydridotetrakis(trimethylphosphane)nickel–Dihydrogentris(2-chlorophenolate) (**4**): 1000 mg of $Ni(PMe_3)_4$ (2.76 mmol) and 1060 mg of 2-chlorophenol (8.28 mmol) were combined in 80 ml of ether at −70°C to give a yellow precipitate. After warming to 20°C the solid was isolated by decantation and drying in vacuo. Yield (1340 mg, 65%). Recrystallization from ether at −27°C afforded 370 mg of yellow crystals (18%), m.p. 162–164°C. – IR (Nujol): $\tilde{\nu}$ = 1950 cm^{-1} (NiH), 1568 (C=C), 1028 (C–O), 940 ρ(PCH_3). – ^1H NMR ([D_8]THF): δ = −17.24 (m, 1 H, NiH), 1.35 [s(br), 36 H, $P(CH_3)_3$], 6.62 (t, *J* = 6.7 Hz, 1 H), 7.00 (m, 2 H, 3-H, 5-H). – ^{13}C NMR ([D_8]toluene): δ = 11.88 [s(br), $P(CH_3)_3$], 20.92 (s, CH_3), 29.94 [$C(CH_3)_3$], 35.21 [s, *C*$(CH_3)_3$], 114.89 (s, C-3), 124.80 (s, C-5), 128.90 (s, C-4), 141.45 (s, C-2), 143.96 (C-6), 163.07 (s, C-1). – $C_{30}H_{47}Cl_3NiO_3P_4$ (748.7): calcd. C 48.13, H 6.87, Cl 14.21, Ni 7.84, P 16.62; found C 47.68, H 6.91, Cl 14.26, Ni 7.87, P 16.44.

Hydridotetrakis(trimethylphosphane)nickel–Hydrogendisalicylate (**5**): 1210 mg of $Ni(PMe_3)_4$ (3.33 mmol) and 920 mg of salicylic acid (6.66 mmol) were combined in 70 ml of pentane at −78°C to give a pale yellow precipitate. After warming to 20°C the solid was

Table 2. Crystallographic data of compounds **1**, **4**, and **6**

	1	**4**	**6**
Formula	$C_{18}H_{26}Cl_2NiO_2P_2$	$C_{30}H_{51}Cl_3NiO_3P_4$	$C_{15}H_{32}BrNiOP_3$
Molecular mass	465.9	748.7	459.9
Crystal size [mm]	0.25 × 0.21 × 0.12	0.22 × 0.33 × 0.52	0.28 × 0.20 × 0.18
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/n$	P-1	$Pca2_1$
a [Å]	8.932(3)	12.538(9)	13.633(2)
b [Å]	9.936(3)	12.882(10)	11.925(2)
c [Å]	12.720(3)	29.28(2)	12.962(2)
α [°]	90	100.98(3)	90
β [°]	99.65(2)	90.36(2)	90
γ [°]	90	118.12(6)	90
V [Å^3]	1112.9(6)	4069(5)	2107.3(6)
Z	2	4	4
D_{calc} [g/cm^3]	1.390	1.222	1.450
μ(MoK_α) [mm^{-1}]	1.264	0.857	3.042
Temperature [K]	293(2)	293(2)	293(2)
data coll. range [°]	$5.2 \leq 2\Theta \leq 55$	$2.8 \leq 2\Theta \leq 50$	$4.5 \leq 2\Theta \leq 55$
h	$-11 \leq h \leq 11$	$0 \leq h \leq 14$	$0 \leq h \leq 17$
k	$0 \leq k \leq 12$	$-14 \leq k \leq 13$	$0 \leq k \leq 15$
l	$0 \leq l \leq 16$	$-34 \leq l \leq 34$	$0 \leq l \leq 16$
No. reflect. measured	2690	14880	2544
No. unique reflect.	2580(R_{int} = 0.0463)	14160(R_{int} = 0.0438)	2544
No. parameters refined	120	669	200
R_1 [$F \geq 2\sigma(F)$]	0.0659	0.0873	0.0578
wR_2 [$F \geq 2\sigma(F)$]	0.1246	0.2946	0.0900

isolated by decantation and dried in vacuo. Yield (1650 mg, 78%), m.p. 136−139°C. − IR (Nujol): ṽ = 2612 cm^{-1} (OH), 1950 (NiH), 1032 (C−O), 940 ρ(PCH$_3$). − ^{1}H NMR ([D$_8$]THF): δ = −17.19 (m, 1 H, NiH), 1.36 [s(br), 36 H, P(CH$_3$)$_3$], 6.70 (m, 2 H, 5-H,), 6.81 (m, 2 H, 6-H,), 7.23 (m, 2 H, 4-H), 7.91 (m, 2 H, 3-H), 14.55 (m, 1 H, O−H−O). − $C_{26}H_{48}NiO_6P_4$ (639.3): calcd. C 48.85, H 7.57, P 19.38; found C 48.20, H 7.43, P 19.66.

Bromo(2-hydroxyphenyl)tris(trimethylphosphane)nickel (**6**): 620 mg of Ni(PMe$_3$)$_4$ (1.71 mmol) and 2.0 ml of 2-bromophenol (18.9 mmol) were combined in 60 ml of THF at −78°C. After stirring at 20°C for 72 h the solution attained a deep blue color. The volatiles were removed in vacuo and the resulting dark red solid was washed with two 10-ml portions of ether and recrystallized from THF to afford 160 mg of red crystals (20%), m.p. 108−110°C. − IR (Nujol): ṽ = 3204 cm^{-1} (OH), 1560 (C=C), 1011 (C−O), 951 ρ(PCH$_3$). − ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.07 [s(br), 27 H, P(CH$_3$)$_3$], 6.35 (m, 1 H), 6.67 (s, 1 H), 6.70 (m, 1 H, OH), 6.98 (s, 1 H). − ^{13}C NMR ([D$_8$]THF): δ = 13.78 [s(br), P(CH$_3$)$_3$], 111.36 (s, C-6), 117.96 (s, C-4), 122.25, 134.61 (s, C-3, C-5), 159.87 (s, C-1). − $C_{15}H_{32}BrNiOP_3$ (460.0): calcd. C 39.32, H 7.01, P 20.62; found C 39.17, H 7.01, P 20.20.

Iodo(2-hydroxyphenyl)tris(trimethylphosphane)nickel (**7**): 1130 mg of Ni(PMe$_3$)$_4$ (3.11 mmol) and 685 mg of 2-iodophenol (3.11 mmol) were combined in 70 ml of THF at −78°C. After stirring at 20°C for 18 h the solution attained a greenish color. The volatiles were removed in vacuo and the resulting dark red solid was recrystallized from ether to afford 1010 mg of red crystals (64%), m.p. 96−98°C. − IR (Nujol): ṽ = 3264 cm^{-1} (OH), 1559 (C=C), 1011 (C−O), 944 ρ(PCH$_3$). − ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.20 [s(br), 27 H, P(CH$_3$)$_3$], 6.37 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1 H, 3-H), 6.55 (dt, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1 H, 4-H), 6.73 (dt, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1 H, 5-H), 7.14 (dd, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1 H, 6-H), 7.60 (m, 1 H, OH). − ^{13}C NMR ([D$_8$]THF): δ = 15.31 [s(br), P(CH$_3$)$_3$], 112.14 (s, C-6), 118.20 (s, C-4), 123.44, 136.84 (s, C-3, C-5), 161.84 (s, C-1). − $C_{15}H_{32}INiOP_3$ (506.9): calcd. C 35.54, H 6.36, P 18.33; found C 35.47, H 6.11, P 18.35.

Chloro(2-hydroxy-3,5-dichlorophenyl)bis(trimethylphosphane)nickel (**8**): 880 mg of Ni(PMe$_3$)$_4$ (2.42 mmol) and 945 mg of 2,4,6-trichlorophenol (4.85 mmol) were combined in 50 ml of THF at −78°C and after warming to 20°C the solution attained an intense yellow color. After 18 h the volatiles were removed in vacuo and the resulting solid was recrystallized from pentane to afford 240 mg of red crystals (24%), m.p. 102−103°C. − IR (Nujol): ṽ = 3486 cm^{-1} (OH), 1552 (C=C), 1063 (C−O), 948 ρ(PCH$_3$). − ^{1}H NMR ([D$_6$]benzene): δ = 0.92 [s(br), 18 H, P(CH$_3$)$_3$], 6.11 (m, 1 H, OH), 7.36 (s, 1 H), 7.42 (s, 1 H). − ^{13}C NMR ([D$_8$]THF): δ = 17.68 [s(br), P(CH$_3$)$_3$], 120.78 (s, CCl), 130.95, 131.84 (s, CH), 132.54 (s, CNi), 162.75 (s, CO). − $C_{12}H_{21}Cl_3NiOP_3$ (408.3): calcd. C 35.30, H 5.18, P 15.17; found C 35.49, H 5.52, P 14.99.

trans-Chloro(2,4,6-trichlorophenolato)bis(trimethylphosphane)-nickel (**9**): 880 mg of Ni(PMe$_3$)$_4$ (2.42 mmol) and 944 mg of 2,4,6-trichlorophenol (4.85 mmol) in 50 ml of THF were combined at −78°C and after warming to 20°C the solution attained an intense yellow color. After stirring for 16 h 50 ml of dioxygen was admitted and a violet coloration was observed. The mixture was stirred for another 3 h, the volatiles were removed in vacuo and the residue extracted with 50 ml of pentane to afford 70 mg of violet crystals (24% based on Ni), m.p. 162−164°C. − IR (Nujol): ṽ = 1564 cm^{-1} (C=C), 1077 (C−O), 948 ρ(PCH$_3$). − ^{1}H NMR ([D$_6$]acetone): δ = 1.57 [m, 18 H, P(CH$_3$)$_3$], 6.88 (s, 2 H). − ^{13}C NMR ([D$_8$] acetone): δ = 10.65 [t′, ^1J(PC) +^3J(PC) = 23.9 Hz, P(CH$_3$)$_3$], 120.94 (s, CH). − $C_{12}H_{20}Cl_4NiOP_2$ (442.8): calcd. C 32.55, H 4.55, P 13.99; found C 32.82, H 4.60, P 14.05.

Crystal Structure Analyses: Crystal data are presented in Table 2.

Data Collection. − Complex **1**: A dark red specimen was sealed under argon in a glass capillary and mounted on a Siemens R3m/V diffractometer. Using graphite-monochromated Mo-K_α radiation, lattice parameters were obtained from 25 centered reflections. ω scan data were collected and Lp and empirical absorption corrections were applied. Structure solution was performed by direct methods, full-matrix least-squares refinement based on F^2. All non-hydrogen atoms were treated anisotropically and hydrogen atoms were fixed at idealized positions. − *Complex* **4**: A yellow specimen (from ether) was sealed under argon in a glass capillary and mounted on a Siemens P4 diffractometer. Data collection, corrections (without ψ-scans), and structure solution and refinement were as for **1**. − *Complex* **6**: A dark red specimen was sealed under argon in a glass capillary and mounted on a Siemens R3m/V diffractometer. Data collection, corrections, and structure solution and refinement as before.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [**1**: CCDC-102020, **4**: CCDC-102094 , **6**: CCDC-102021] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336−033, E-mail: deposit@chemcrys.cam.ac.uk).

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