Syntheses and Structures of Molecular Diphenolatonickel Compounds Containing Trimethylphosphane Ligands

Hans-Friedrich Klein*[a], Attila Dal[a], Thomas Jung[a], Siegmar Braun[b], Caroline Röhr[c], Ulrich Flörke[d], and Hans-Jürgen Haupt[d]

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

Institut für Organische Chemie der Technischen Universität Darmstadt[b],
Petersenstraße 22, D-64285 Darmstadt, Germany

Institut für Anorganische Chemie der Universität Freiburg[c],
Albertstraße 21, D-79104 Freiburg, Germany

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

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The reaction of substituted phenols and dioxygen with $Ni(PMe_3)_4$ yields the low-spin tetracoordinate diphenolatonickel compounds $Ni(OAr)_2(PMe_3)_2$ [ArOH = 2-*tert*-butylphenol (**1**), 2-*tert*-butyl-4-methylphenol (**2**), 2-*tert*-butyl-6-methylphenol (**3**), 2,4-di(*tert*-butyl)phenol (**4**), 2-*tert*-butyl-4-methoxophenol (**5**), 2-chloro-4-*tert*-butylphenol (**6**), 2-isopropylphenol (**7**), 3-*tert*-butylphenol (**8**)]. As is revealed by variable temperature ^1H- and ^{13}C-NMR spectroscopy the complexes constitute a mixture of two isomers, each of which can be observed separately at lower temperatures when interconversion is slower. An additional 6-carbaldehyde function transforms the phenolate into a chelating ligand, giving rise to a high-spin hexacoordinate compound $Ni(OAr)_2(PMe_3)_2$ (**9**). X-ray crystal-structure determinations of **2** and **3** show a *trans* square-planar structure, and that of **9** shows a *trans* octahedral arrangement of donor atoms P_2O_4. Bulky substituents in the 3- or 4-position, or non-demanding substituents in the 2-position, are less effective in stabilizing molecular diphenolatonickel complexes.

Many low-valent metal compounds, if combined with a proton source and dioxygen, form an oxidizing system. Examples are Fentons reagent, Bartons Gif systems and the Wacker process. Peroxometal complexes are believed to be key intermediates in these reactions.[1] Strongly reducing phosphane complexes of zerovalent nickel are known to form peroxo species according to Eq. 1. In exceptional cases these may be isolated, e.g. with space-filling tricyclohexylphosphane ligands.[2]

$$Ni(PR_3)_4 + O_2 \rightarrow (R_3P)_2NiO_2 \rightarrow Ni + 2\ R_3P{=}O \qquad (1)$$

With the small trimethylphosphane the peroxo intermediate is explosive, and for this reason even small crystals of $Ni(PMe_3)_4$ crackle upon contact with air. Using mol-equivalent amounts of oxygen in solution the system becomes a mild oxidant. On this basis we have developed a new synthesis of molecular diphenolatonickel complexes containing trimethylphosphane ligands.

Conventionally, but not conveniently, unsolvated diphenolatonickel compounds may be prepared in an anhydrous medium as insoluble coordination polymers. Methods using $NiCl_2$ and sodium or lithium phenolates usually afford products which pertinaciously occlude halide impurities.

Some *ortho*-substituted phenols form diphenolatonickel dihydrates that can be converted into anhydrous compounds. These materials cannot be dissolved without reaction.[3] However, with nitrogen donor atoms in a suitable configuration numerous soluble chelate complexes, e. g. with 8-hydroxoquinolines or salicylaldimines, have been shown to exist as molecular compounds with square-planar coordination at the nickel atom. These complexes usually do not accommodate additional phosphane ligands.

In this contribution a novel method of synthesis is described which smoothly affords crystalline diphenolatobis(trimethylphosphane)nickel compounds starting from substituted phenols, $Ni(PMe_3)_4$, and dioxygen.

Results and Discussion

Pale-yellow solutions of $Ni(PMe_3)_4$ and two mol-equivalents of a phenol in hydrocarbon or ether solvents turn dark-red when treated with one mol-equivalent of dioxygen[4] according to Eq. 2. One of the trimethylphosphanes serves as a co-reductant, in this respect resembling the natural methane monooxygenase system.[5]

Using sterically shielding 2-*tert*-butylphenols, mononuclear diphenolatonickel complexes containing trimethylphosphane are obtained in good to excellent yields. Separation from moist trimethylphosphane oxide[6] is conveniently achieved by filtration, and trace impurities can be sublimed from the product in vacuo at 20°C.

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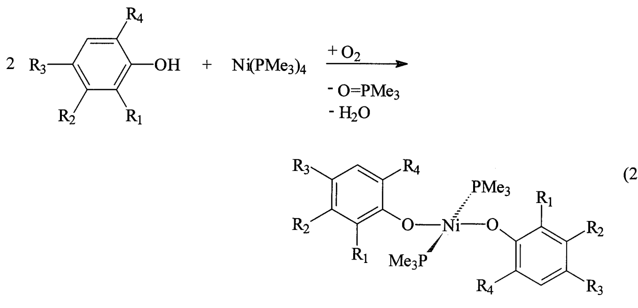


(2)

	1	2	3	4	5	6	7	8	9
R_1	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*i*Pr	H	*t*Bu
R_2	H	H	H	H	H	H	H	*t*Bu	H
R_3	H	Me	H	*t*Bu	OMe	Cl	H	H	Me
R_4	H	H	Me	H	H	H	H	H	CHO
Yield [%]	52	78	86[a]	70	54	48	11	8	83

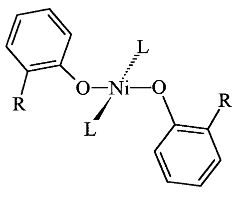
[a] Yield of crude product.

Recrystallization from pentane or ether affords red crystals that can be dried in vacuo without loss of phosphane ligands. While coordination of substoichiometric amounts of triorganophosphanes by diphenolatonickel polymers has been noticed,[7] to the best of our knowledge the molecular trimethylphosphane complexes **1**−**8** constitute a novel type of compound. The 2-*tert*-butyl groups not only prevent formation of coordination polymers by steric shielding but also enhance the reactivity of the phenolic function, when compared with the unsubstituted phenol. In a sluggish reaction with $Ni(PMe_3)_4$ and oxygen this parent phenol gives low yields of insoluble material which, according to the infrared data, appears to be a mixture of nickel oxide and diphenolatonickel containing residual trimethylphosphane ligands.

To investigate the limits of steric demand, the size and positions of phenolic substituents were varied.

Steric Protection of the Phenolate Function

Reducing the size of the substituent in 2-position induces loss of trimethylphosphane while forming insoluble coordination polymers at the expense of molecular diphenolatonickel compounds. This tendency increases from R = CMe_3 to R = H. Moving the protecting *tert*-butyl group to the 3- or 4-position dramatically reduces the yields of molecular complexes.

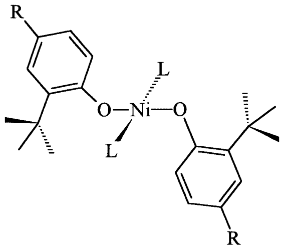


L = $P(CH_3)_3$

R	CMe_3	$CHMe_2$	2,4,6-Me_3	H
Yield [%]	52	11	0	0

R	2-CMe_3	3-CMe_3	4-CMe_3
Yield [%]	52	8	0

Neither steric nor electronic changes in the 4-position can affect the reasonably constant yields of bis(2-*tert*-butylphenolato)bis(trimethylphosphane)nickel compounds.



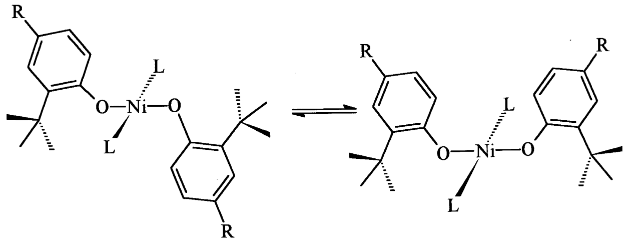
L = $P(CH_3)_3$

R	CMe_3	Me	H	OMe	Cl
Yield [%]	70	78	52	54	48

Thus, the stability of molecular diphenolatonickel complexes containing trimethylphosphane appears to be controlled by the size of the phenolic substituent in 2-position.

NMR Spectroscopy

For steric reasons an optimum configuration of the bis(2-*tert*-butylphenolato)nickel complexes **2** and **3** in solution is likely to be the same as that in the solids, and is characterized by CMe_3 groups pointing away from the plane of coordination (Figures 1 and 2). In the crystal a *transoid* arrangement of CMe_3 substituents (A) is favored, while in solution a second minimum of energy is populated through rotation of phenolato ligands (B), as shown by dynamic ^1H-NMR spectroscopy.



A B

L = $P(CH_3)_3$

The room-temperature ^1H-NMR spectra (300 MHz) of the complexes **1**, **2**, **4**, **5**, and **7** (Table 1) show a broad one-proton signal at $\delta_H \approx 9 \pm 0.5$, whereas the other protons of the benzene ring show clearly resolved multiplets, e.g. for **2** a doublet of 1.9 Hz for the signal at $\delta_H = 6.65$ and a double doublet of 7.7 and 1.9 Hz for that at $\delta_H = 6.90$. From an analysis and comparison of the NMR data the broad high-frequency signal has to be assigned to 6-H, which is deshielded by the nearby nickel atom. On cooling the solution (e.g. **2** was cooled to 233 K) two clearly resolved doublets are observed for 6-H at $\delta_H = 9.21$ and 8.63 in an intensity ratio of about 2:1 with $J_{6\text{-H},5\text{-H}} = 7.8$ Hz for both signals. Line separations, albeit amounting to only a few Hz (ca. 0.01 ppm), can be seen also for the other protons, an exception being the 4-CH_3 protons. An H,H-COSY spectrum proves that the signals of 5-H of both species overlap at $\delta_H = 6.90$ and those of the 3-H atoms at $\delta_H = 6.65$. On the other hand, when heating a solution of **2** in

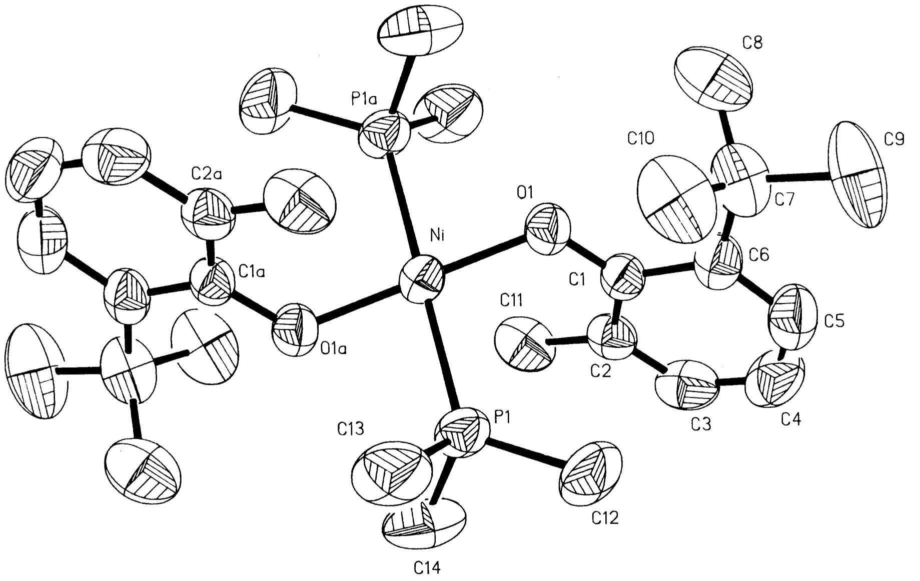


Figure 2. Molecular structure of **3** (ORTEP plot without hydrogen atoms)[a]

[a] Selected bond lengths [Å] and angles [°]: Ni−O1 1.861(3), Ni−P1 2.268(2), O1−C1 1.331(6), C2−C11 1.495(7), C6−C7 1.535(8); O1−Ni−P1 98.6(1), O1−Ni−P1a 81.5(1), C1−O1−Ni 127.3(3).

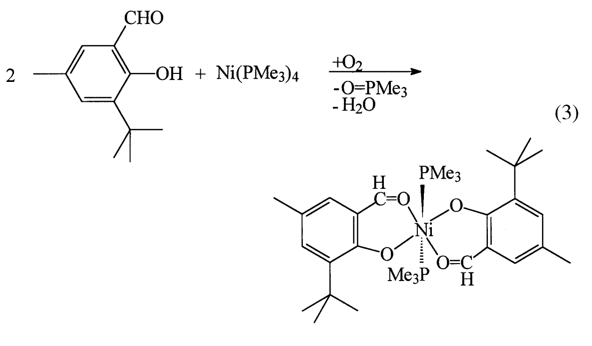
[D$_8$]toluene to 373 K, one doublet at $\delta_H = 9.07$ with $J = 7.8$ Hz appears.

Analogous results are obtained from the ^{13}C-NMR spectra (Table 2), e.g. that of **2**. At 305 K one set of signals is obtained, the one at $\delta_C = 123.0$ exhibiting some line broadening; according to 2D-H,C correlation it has to be attributed to C-6. At 233 K two sets of signals in a ratio of about 2:1 are observed for most C atoms, exceptions being those of C-3 and of both types of CMe$_3$ under the routine measurement conditions applied.

From these results it has to be concluded that there is a mixture of two rotamers, A and B, which can be observed separately when interconversion is slow on the NMR time scale.

Coordination Number 6

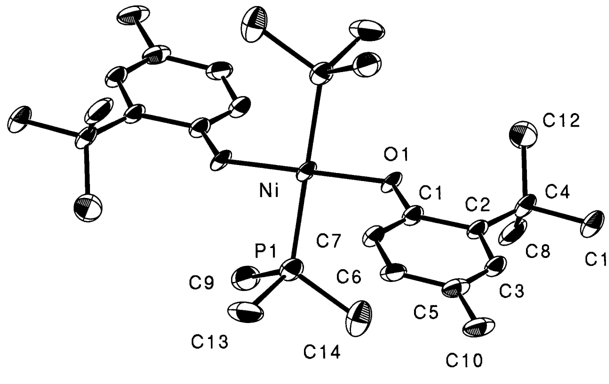
In a suitable conformation an aldehyde or ketone function can serve as additional O-donor ligand. This chelating property has been previously observed in equilibria of ligand dissociation involving pentacoordinate species which are formed in a ligand dismutation reaction from iodo(phenolato)nickel precursors.[8]



(3)

Trimethylphosphane is smoothly added to produce hexacoordinate **9** according to Eq. 3. Involvement of both aldehyde groups is evident from a bathochromic coordination shift of the ν(C=O) bands. Both types of diphenolatonickel complexes have been characterized by single-crystal X-ray diffraction.

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



[a] Selected bond lengths [Å] and angles [°]: Ni−O1 1.868(3), Ni−P1 2.233(1), O1−C1 1.355(6), C1−C7 1.382(8), C6−C7 1.402(8); O1−Ni−P1 94.1(1), O1−Ni−P1′ 85.9(1), C1−O1−Ni 120.6(3).

Molecular Structures of 2, 3, and 9

Single crystals were obtained from pentane solutions at −20°C. Figures 1−3 give the atom numberings and the principal bond lengths and angles.

In all three molecular structures the nickel atom lies on a crystallographic inversion center. Bond lengths show significant deviations only between the hexacoordinate species **9** and the two square-planar complexes. Thus, in **9** the

Table 1. Dynamic ^{1}H-NMR spectra ([D$_8$]THF) of compounds **1**, **2**, **4**, **5**, and **8**[a]

Comp. T [K]	PCH$_3$	CCH$_3$	R	2-H	3-H	4-H	5-H	6-H
1 293	0.95 18 H s (br.)	1.22 18 H s	–	–	6.78 2 H d, J = 7.4	6.32 2 H t, J = 7.4	7.09 2 H t, J = 7.4	9.15 1 H s (br.)
1a 233	– 0.92 18 H s (br.)	– 1.20 18 H s			6.78 2 H s (br.)	6.33 2 H s (br.)	7.11 2 H s (br.)	8.75 0.7 H d, J = 6.7
1b 233								9.34 1.3 H d, J = 7.4
2 305	0.95 18 H s (br.)	1.22 18 H s	2.17 6 H s	–	6.65 2 H d, J = 1.3	–	6.90 2 H dd, J = 6.5/1.3	8.99 2 H s (br.)
2a 233	0.92 18 H t', N = 8.0	1.20 18 H s	2.17 6 H s	–	6.63 2 H s (br.)	–	6.90 2 H m	8.63 0.7 H d, J = 8.0
2b 233	0.94 t', N = 8.0	1.21 s	2.18 s					9.21 1.3 H d, J = 8.0
4 305	0.93 18 H t'', N = 6.3	1.23 18 H s	1.25 18 H s	–	6.89 2 H d, J = 2.5	–	6.90 2 H dd, J = 8.1/2.5	9.00 2 H s (br.)
4a 233	0.92 18 H t', N = 8.2	1.23 18 H s	1.25 18 H s	–	6.87 2 H t, J = 3.0	–	7.14 2 H m	8.82 1 H d, J = 8.1
4b 233								9.18 1 H d, J = 8.0
5 305	0.94 18 H t', N = 6.4	1.21 18 H s	3.57 6 H s	–	6.48 2 H d, J = 3.1	–	6.69 2 H dd, J = 8.4/3.1	9.01 1 H s (br.)
8 305	0.96 18 H s (br.)	1.27 18 H s	–	7.75 2 H s	–	6.45 2 H d, J = 7.0	7.06 2 H m	7.21 2 H d, J = 6.7

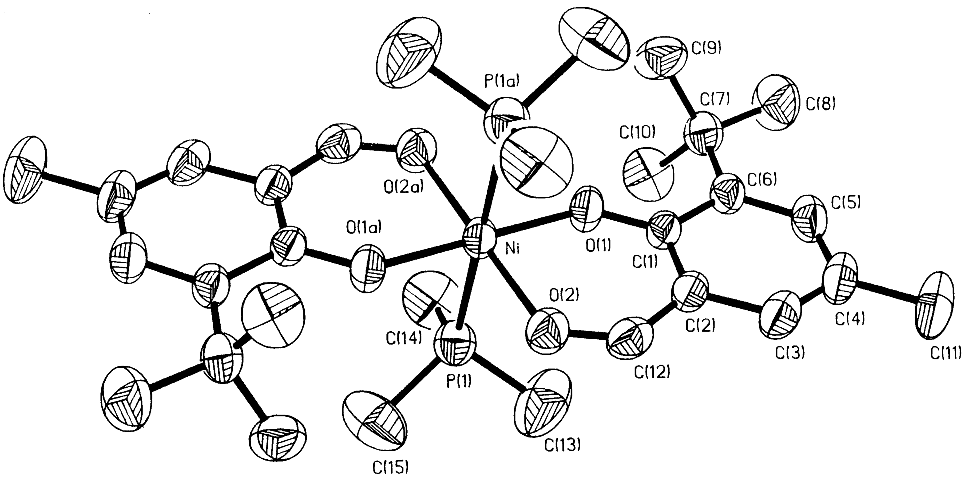
[a] t' = virtual triplet with N as distance of outer lines.

Table 2. Dynamic ^{13}C-NMR spectra ([D$_8$]THF) of compounds **1**, **2**, **4**, **5**, and **8**

Comp. T [K]	PCH$_3$	$C\mathit{C}H_3$	$\mathit{C}CH_3$	R	C-1	C-2	C-3	C-4	C-5	C-6
1 305	10.8 t', N = 22	28.4	33.6	–	164.2	138.1	125.4	112.4	123.8	121.5
2 305	10.9 t', N = 23	28.5	33.5	19.1 (Me)	162.1	137.6	124.9	120.3	125.5	121.1
2a 233	10.3 t', N = 23	28.1	33.3	19.1 (Me)	161.2	137.0	124.7	119.8	125.4	120.4
2b 233	10.6 t', N = 23				161.6	137.1		119.9	125.5	121.1
4 305	10. 8 t' (br.)	28.5	32.6	30.5 (Me) 33.8 ($\mathit{C}Me_3$)	161.7	134.1	120.8	136.9	121,5	120.8
5 305	10.8 t', N = 23	28.2	33.7	53.8 (OMe)	158.0	138.2	108.9	148.3	112.0	120.3
8 305	9.7 t', N = 24	29.9	33.2	–	165.0	111.4	150.2	109.9	116.4	126.8

Ni−O distances of 1.995(2) and 2.060(2) Å, which are as expected for octahedral complexes of nickel,[9] exceed those of **2** and **3** by more than 10 pm. Also the large Ni−P distances of 2.482(1) Å are due to octahedral coordination in

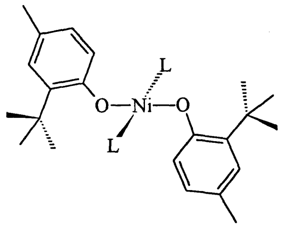
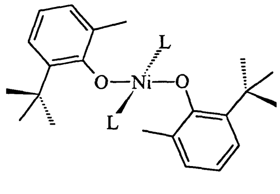
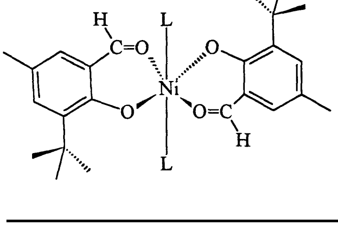
Figure 3. Molecular structure of **9** (ORTEP plot without hydrogen atoms)[a]



[a] Selected bond lengths [Å] and angles [°]: Ni−O1 1995(2), Ni−O2 2.060(2), Ni−P1 2.482(1), O1−C1 1.289(2), O2−C12 1.245(3), C4−C11 1.522(3), C6−C7 1.531(4); O1−Ni−P1 87.2(1), O1a−Ni−P1 92.8(1), O2−Ni−P1 89.9(1), O2a−Ni−P1 90.1(1), C1−O1−Ni 130.1(2), C12−O2−Ni 123.9(2).

the 20-electron complex **9** and are similar to those of octahedral nickel(IV) complexes[10] (18 electrons). The diamagnetic square-planar complexes **2** and **3** exhibit shorter Ni−O and Ni−P bond lengths. While Ni−P distances are as expected for 16-electron (trimethylphosphane)nickel complexes[11][12] the Ni−O distances of *trans*-bis(trimethylphosphane)nickel diphenolates are unprecedented as far as we are aware. When compared with a pentacoordinate tripyridinebis(2,4,6-trichlorophenolato)nickel(II)[13] [Ni−O = 2.014(4) Å] Ni−O distances such as 1.868(3) Å for **2** and 1.861(3) Å for **3** are considerably shorter. There is no structural indication for magnetic shielding of the aromatic 6-H nucleus by a close approach to the metal atom (see NMR Spectroscopy) because the calculated distance Ni−H(7) = 2.627 Å seems too large for such interaction. Similarly, in the 6-methyl-substituted compound **3** the distance between the 6-alkyl group and the nickel atom is beyond the radius of interaction.

Table 3. Distortions of square-planar geometries at nickel centres; L = $P(CH_3)_3$

formula	angles
	α=Ni-O-C(1)=120.6(3)° β=P(1)-Ni-O(1)=85.92(12)° γ=P(1a)-Ni-O(1)=94.08(12)°
	α=Ni-O-C(1)=127.3(3)° β=P(1)-Ni-O(1)=81.45(12)° γ=P(1a)-Ni-O(1)=98.55(12)°
	α=Ni-O-C(1)=130.1(2)° β=P(1)-Ni-O(1a)=92.8(1)° γ=P(1)-Ni-O(1)=97.2(1)°

Indeed, the substituent in 6-position points away from the nickel atom. While the angle α = 120.6(3)° in **2** (see Table 3) this angle in **3** is augmented by 6.7°. The sterically demanding 2-*tert*-butyl-6-methylphenolato ligand causes contraction of angles β from 85.92(12)°in **2** to 81.45(12)° in **3**. An even larger angle α in **9** is due to incorporation in the 6-membered chelate ring which also affects angles β and γ.

Conclusion

Molecular diphenolatobis(trimethylphosphane)nickel complexes can be prepared by convenient methods in high yields, if bulky substituents in the 2-position of the phenolato ligand prevent condensation reactions between metal centers. By dynamic NMR spectroscopy 2-*tert*-butyl groups are shown to hinder rotation of phenolato ligands around Ni−O bonds. X-ray crystallography reveals the nickel atoms to be surrounded by a meridian of two phenolato and two trimethylphosphane donors in mutual *trans* positions. These structures have been filed as the first reported for diamagnetic diphenolatonickel compounds. The five-membered chelate rings are all planar and show similar dimensions and the expected increase in bond lengths at the nickel atom as going from square-planar to octahedral coordination. Although in **9** the Ni−P distance represents an extremely long bond [2.482(1) Å], crystals of this compound do not release trimethylphosphane at 20°C in vacuo. Further investigation of properties of (trimethylphosphane)nickel diphenolates are in progress in order to better understand the role of chelating phenols as active catalysts in olefin oligomerization reactions.[14]

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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.[8] Ni(PMe$_3$)$_4$ was prepared by literature methods,[15] phenols (Merck-Schuchardt) were used as purchased. Measured volumes of oxygen were admitted to the reaction mixture at −70°C and in vacuo.

Bis(2-tert-butylphenolato)bis(trimethylphosphane)nickel (**1**): 510 mg of Ni(PMe$_3$)$_4$ (1.37 mmol) and 414 mg of 2-*tert*-butylphenol (2.74 mmol) in 60 ml of THF were combined with 25 ml of dioxygen (1.04 mmol). Upon warming the light yellow solution turned dark-red. After 16 h at 20°C, the volatiles were removed in vacuo and the residue extracted with 50 ml of pentane through a glass-sinter disc (G3). Crystallization at −20°C afforded dark-red rhombs. Yield 362 mg (52% based on nickel), m.p. 184−186°C. − IR (Nujol): $\tilde{\nu}$ = 1574 cm^{-1} (C=C), 1044 (C−O), 944 [ρ(PCH$_3$)]. − $C_{26}H_{44}NiO_2P_2$ (509.3): calcd. C 61.32, H 8.71, P 12.16; found C 61.15, H 9.04, P 12.21.

Bis(2-tert-butyl-4-methylphenolato)bis(trimethylphosphane)nickel (**2**): 500 mg of Ni(PMe$_3$)$_4$ (1.37 mmol) and 452 mg of 2-*tert*-butyl-4-methylphenol (2.74 mmol) in 50 ml of THF at −70°C were combined with 33 ml of dioxygen (1.37 mmol). After warming the mixture to 20°C, the volatile components were removed in vacuo and the residue extracted with 60 ml of pentane. Keeping the dark-red solution at −20°C for 30 h afforded red-brown cubes. Yield 572 mg (78% based on nickel), m.p. 133−135°C. − IR (Nujol): $\tilde{\nu}$ = 1596 cm^{-1} (C=C), 1019 (C−O), 943 [ρ(PCH$_3$)]. − $C_{28}H_{48}NiO_2P_2$ (537.3): calcd. C 62.59, H 9.00, P 11.53: found C 62.96, H 9.48. P 11.78.

Bis(2-tert-butyl-6-methylphenolato)bis(trimethylphosphane)nickel (**3**): 870 mg of Ni(PMe$_3$)$_4$ (2.40 mmol) and 787 mg of 2-*tert*-butyl-6-methylphenol (4.80 mmol) in 50 ml of THF at −70°C were combined with 50 ml of dioxygen (2.08 mmol). After warming to 20°C, the light-yellow solution turned red-brown and was stirred for a further16 h. The volatiles were removed in vacuo, and the residue extracted with 50 ml of pentane. The crude product was collected as a brown oil (1110 mg, 86%) and used for spectroscopic measurements. Crystallization from 5 ml of pentane at −27°C starting with 900 mg of crude material afforded 260 mg of red-brown crystals (20%), m.p. 169−171°C. − IR (Nujol): $\tilde{\nu}$ = 1581 cm^{-1} (C=C), 950 [ρ(PCH$_3$)]. − ^{1}H NMR ([D$_8$]THF): δ = 0.61 [s (br.), 18 H, P(CH$_3$)$_3$], 1.30 (s, 6 H, CH$_3$), 1.50 [s, 18 H, C(CH$_3$)$_3$], 6.54 (t, *J* = 7.3 Hz, 1 H, 4-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(*C*H$_3$)$_3$], 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).

Bis(2,4-di-tert-butylphenolato)bis(trimethylphosphane)nickel (**4**): 1350 mg of Ni(PMe$_3$)$_4$ (3.72 mmol) and 1530 mg of 2,4-di-*tert*-butylphenol (7.44 mmol) in 70 ml of THF at −70°C were combined with 90 ml of dioxygen (3.74 mmol). Upon warming to 20°C the yellow solution turned dark-red. After 16 h at 20°C, the volatiles were removed in vacuo and trimethylphosphane oxide sublimed from the residue at 30°C/0.1 mbar. Extraction with 60 ml of pentane and crystallization at −20°C afforded dark-red crystals. Yield 1620 mg (70% based on nickel), m.p. 169−171°C. − IR (Nujol): $\tilde{\nu}$ = 1591 cm^{-1} (C=C), 1016 (C−O), 942 [ρ(PCH$_3$)]. − $C_{34}H_{60}NiO_2P_2$ (621.5): calcd. C 65.71, H 9.73, P 9.97; found C 65.78, H 9.65, P 10.03.

Bis(2-tert-butyl-4-methoxyphenolato)bis(trimethylphosphane)nickel (**5**): 420 mg of Ni(PMe$_3$)$_4$ (1.16 mmol) and 417 mg of 2-*tert*-butyl-4-methoxyphenol (2.74 mmol) in 50 ml of THF at −70°C were combined with 30 ml of dioxygen (1.25 mmol). After warming the solution to 20°C and stirring for 16 h, the volatiles were removed in vacuo. Crystallization from 70 ml of pentane afforded 572 mg of dark-brown crystals (78% based on Ni), m.p. 133−135°C. − IR (Nujol): $\tilde{\nu}$ = 1603 cm^{-1} (C=C), 1018 (C−O), 948 [ρ(PCH$_3$)]. − $C_{28}H_{48}NiO_4P_2$ (569.3): calcd. C 59.07, H 8.50, P 10.88; found C 59.75, H 8.64, P 11.18.

Bis(2-tert-butyl-4-chlorophenolato)bis(trimethylphosphane)nickel (**6**): 770 mg of Ni(PMe$_3$)$_4$ (2.12 mmol) and 787 mg of 2-*tert*-butyl-4-chlorophenol (4.24 mmol) in 50 ml of THF at −70°C were combined with 50 ml of dioxygen (2.08 mmol). After warming up to 20°C, the volatiles were removed in vacuo and the resulting red-brown solid washed with ether (2 × 10 ml) and recrystallized from THF to afford 590 mg of brown-red crystals, m.p. 154−156°C. − IR (Nujol): $\tilde{\nu}$ = 1603 cm^{-1} (C=C), 1018 (C−O), 948 [ρ(PCH$_3$)]. − ^{1}H NMR ([D$_8$]THF): δ = 0.97 [s (br.), 18 H, P(CH$_3$)$_3$], 1.19 [s, 18 H, C(CH$_3$)$_3$], 6.79 [s (br.), 2 H, 3-H], 7.09 (s, 2 H, 5-H). − $C_{26}H_{42}Cl_2NiO_2P_2$ (580.2): calcd. C 53.83, H 7.30, P 10.68; found C 52.97, H 7.40, P 10.88.

Bis(2-isopropylphenolato)bis(trimethylphosphane)nickel(**7**): 620 mg of Ni(PMe$_3$)$_4$ (1.71 mmol) and 465 mg of 2-isopropylphenol (3.42 mmol) in 50 ml of THF at −70°C were combined with 50 ml of dioxygen (2.08 mmol). Stirring at −30°C for 1 h gave a dark red solution. Upon careful removal of volatiles in vacuo at −20°C (within 16 h) and extraction of the residue with 50 ml of pentane a large amount of red oil was obtained from which, after three months, dark-red crystals were deposited. These were isolated by washing with acetone in the cold, yielding 120 mg of red platelets (11% based on Ni), m.p. 109−112°C. − IR (Nujol): $\tilde{\nu}$ = 1591 cm^{-1} (C=C), 1036 (C−O), 948 [ρ(PCH$_3$)]. − ^{1}H NMR ([D$_8$]THF): δ = 0.97 [s, 18 H, P(CH$_3$)$_3$], 1.01 [d, *J* = 7 Hz, 12 H, CH(C*H*$_3$)$_2$], 3.08 [quint, *J* = 7 Hz, 2 H, C*H*(CH$_3$)$_2$], 6.34 (t, *J* = 7 Hz, 2 H, 3-H), 7.05 (m, 4 H, 2-H, 4-H), 8.71 [s (br.), 2 H, 6-H]. − ^{13}C NMR ([D$_8$]THF): δ = 9.79 [t′, *N* = 2 Hz, P(CH$_3$)$_3$], 21.49 [s, CH(*C*H$_3$)$_2$], 25.93 [*C*H(CH$_3$)$_2$], 113.57 (s, C-4), 122.99 (s, C-6), 124.82, 125.09 (s, C-3, C-5); 141.45 (s, C-2), 137.68 (s, C-2), 162.38 (s, C-1). − $C_{33}H_{52}NiO_2P_2$ (617.5): calcd. C 64.19, H 8.49; found C 64.70, H 8.60.

Bis(3-tert-butylphenolato)bis(trimethylphosphane)nickel (**8**): 880 mg of Ni(PMe$_3$)$_4$ (2.42 mmol) and 728 mg of 3-*tert*-butylphenol (4.85 mmol) in 70 ml of THF at −70°C were combined with 50 ml of dioxygen (2.08 mmol). Stirring at −30°C for 1 h gave a dark-red solution. Upon removal of volatiles in vacuo, and extraction of the residue with 50 ml of pentane at −30°C, 520 mg of Ni(PMe$_3$)$_4$ was recovered. A second extraction with 50 ml of pentane at 25°C gave 158 mg of red platelets (15% based on Ni), m.p. 112−117°C. − IR (Nujol): $\tilde{\nu}$ = 3430 cm^{-1} (OH), 1643 [δ(OH)], 1591 (C=C), 1036 (C−O), 948 [ρ(PCH$_3$)]. − $C_{46}H_{72}NiO_4P_2$ (809.7): calcd. C 68.23, H 8.89, P 7.65; found C 67.50, H 9.08, P 7.73.

Bis(2-tert-butyl-4-methyl-6-formylphenolato)bis(trimethylphosphane)nickel (**9**): 560 mg of Ni(PMe$_3$)$_4$ (1.54 mmol) and 580 mg of 3-*tert*-butyl-5-methylsalicylaldehyde (3.02 mmol) in 50 ml of THF

Table 4. Crystallographic data of compounds **2**, **3**, and **9**

	2	**3**	**9**
Formula	$C_{28}H_{48}NiO_2P_2$	$C_{28}H_{48}NiO_2P_2$	$C_{30}H_{48}NiO_4P_2$
Molecular mass	537.3	537.3	593.4
Crystal size [mm]	0.24 × 0.29 × 0.35	0.31 × 0.29 × 0.26	0.21 × 0.24 × 0.55
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	8.314(2)	9.857(3)	9.762(2)
b [Å]	9.654(2)	12.867(3)	9.850(2)
c [Å]	11.344(2)	13.136(3)	9.363(2)
α [°]	93.81(2)	90	108.68(1)
β [°]	108.16(2)	110.25(2)	98.10(1)
γ [°]	114.51(2)	90	73.10(1)
V [Å^3]	766.8(3)	1563.1(7)	814.9
Z	1	2	1
$D_{\text{calcd.}}$ [g/cm^3]	1.164	1.142	1.209
μ(Mo-K_α) [mm^{-1}]	0.757	0.743	0.720
T [K]	293(2)	293(2)	293(2)
Data coll. range [°]	$5.5 \leq 2\Theta \leq 45$	$5.4 \leq 2\Theta \leq 55$	$3 \leq 2\Theta \leq 55$
h	$-11 \leq h \leq 11$	$-12 \leq h \leq 12$	$-12 \leq h \leq 12$
k	$-13 \leq k \leq 13$	$0 \leq k \leq 16$	$-12 \leq k \leq 12$
l	$0 \leq l \leq 11$	$0 \leq l \leq 17$	$0 \leq l \leq 12$
No. reflect. measured	2099	3751	7527
No. unique reflect.	1985	3598	3765
No. parameters refined	152	159	170
R_1 [$F \geq 4\sigma(F)$]	0.090	0.075	0.040
wR_2 [$F \geq 4\sigma(F)$][a]	0.251[b]	0.123[b]	0.041[c]

[a] $w = 1/\sigma^2(F) + 0.0001 \cdot F^2$. – [b] Refinement on F. – [c] Refinement on F.

at −70°C were combined with 38 ml of dioxygen (1.58 mmol). Upon warming the solution slowly turned brown. After 24 h at 20°C, the volatiles were removed in vacuo and the residue extracted with 50 ml of pentane. Keeping the solution at 8°C for 70 h afforded yellow-brown crystals. Yield 656 mg (83% based on nickel), m.p. 153–156°C. IR (Nujol): $\tilde{\nu}$ = 1596 cm^{-1} (C=O), 1024 (C–O), 943 [ρ(PCH$_3$)]. – ^{1}H NMR ([D$_8$]toluene): extremely broad signals at δ = 1.1–84.7. – $C_{30}H_{48}NiO_4P_2$ (593.4): calcd. C 60.73, H 8.15, P 10.44; found C 60.76, H 7.97, P 10.41.

Crystal-Structure Analyses: Crystal data are presented in Table 4.

Data Collection. – Complex **2**: A dark-red specimen was sealed under argon in a glass capillary and mounted on a Philips PW 1100 diffractometer. Using graphite-monochromated Mo-K_α radiation lattice parameters were obtained from 25 centered reflections. Intensities were collected (ω scan) and Lp corrections were applied. The structure was solved (SHELX 86) using a full-matrix least-squares refinement (SHELX 93). All non-hydrogen atoms were treated anisotropically, hydrogen atoms were held in idealized fixed positions. – *Complex* **3**: 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. Intensities were collected (ω scan) and Lp and empirical absorption corrections were applied (4 scans). The structure was solved (SHELXS 86) and refined (SHELXL 93). Non-hydrogen atoms were refined anisotropically, hydrogen atoms were fixed in idealized positions. – *Complex* **9**: An orange-brown crystal was sealed and mounted as given for **3**. Lattice parameters were obtained from 25 centered reflections. Intensities were collected and four standard reflections were recorded every 400 measured reflections showing only random intensity fluctuations. Lp corrections and empirical absorption correction were applied (ψ scans, min./max. transmission 0.824/0.868). The structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement was based on F. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were held in calculated positions. Scattering factors and structure refinement: SHELXTL-Plus (G. M. Sheldrick, **1990**).

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 [CCDC-100867 (**2**), -100866(**3**), -100880 (**9**)] 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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