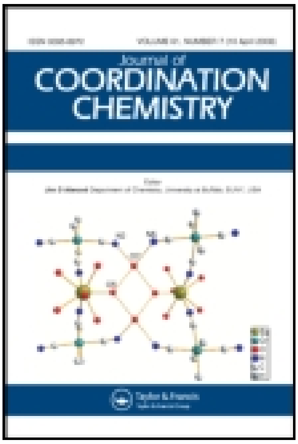

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Synthesis and characterization of nickel(II) maltolate complexes containing ancillary bisphosphine ligands

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Synthesis and characterization of nickel(II) maltolate complexes containing ancillary bisphosphine ligands

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Cationic nickel(II) complexes containing chelating *O*,*O*′-donor maltolate or ethyl maltolate ligands in conjunction with bidentate bisphosphine ligands $Ph_2P(CH_2)_nPPh_2$ were prepared by a one-pot reaction starting from nickel(II) acetate, bisphosphine, maltol (or ethyl maltol), and trimethylamine, and isolated as their tetraphenylborate salts. An X-ray structure determination of $[Ni(maltolate)(Ph_2PCH_2CH_2PPh_2)]BPh_4$ shows that the maltolate ligand binds asymmetrically to the (slightly distorted) square-planar nickel(II) center. The simplicity of the synthetic method was extended to the synthesis of the known platinum(II) maltolate complex $[Pt(maltolate)(PPh_3)_2]BPh_4$ which was obtained in high purity.

Keywords: Nickel complexes; Maltol complexes; Phosphine ligands; X-ray crystal structure

1. Introduction

Maltol (3-hydroxy-2-methyl-4-pyrone) (**1a**) (the compounds are defined in scheme 1) is a naturally occurring, non-toxic substance, approved for use as a food additive, and together with its analog ethyl maltol (3-hydroxy-2-ethyl-4-pyrone) (**1b**), has been used to form a wide range of coordination complexes. The ligands bind as bidentate chelating ligands through the keto group and the deprotonated OH, forming a five-membered chelate ring system. The coordination chemistry of such hydroxypyranone ligands and related derivatives has been the subject of a recent comprehensive review [1]. Maltolate complexes have attracted particular interest for their medicinal potential; for example aluminum tris(maltolate) has been used to investigate aluminum transport to the brain [2], the corresponding complex of gallium shows promise in cancer chemotherapy [3–5], and bis(ethylmaltolato)oxovanadium(IV) has undergone clinical trials for diabetes treatment [6–8].

Relatively few maltolato complexes are known in group 10 chemistry. For example, the octahedral nickel(II) complex $[Ni(maltolato)_2(H_2O)_2]$ (**2**) has been known for some time [9–11], and in a recent report [12] was prepared by the reaction of nickel(II) acetate with maltol in the presence of NaOH, the complex being characterized by an X-ray

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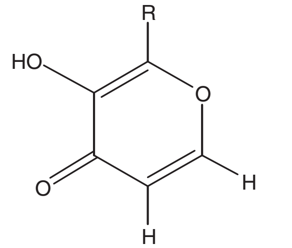
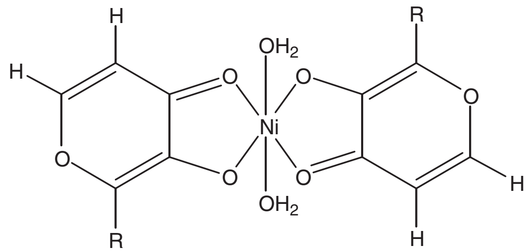


1a maltol, R = Me
1b ethylmaltol, R = Et



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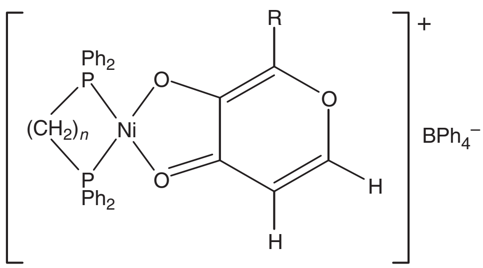
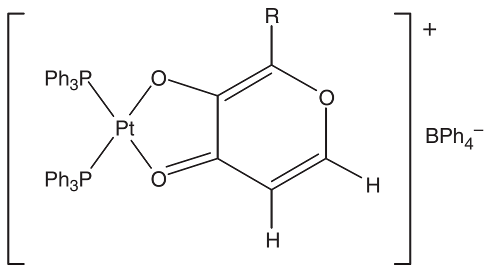


3a, *n* = 2, R = Me
3b, *n* = 3, R = Me
3c, *n* = 2, R = Et
3d, *n* = 3, R = Et



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Scheme 1. Maltol and nickel and platinum maltolate complexes described herein.

diffraction study. The stabilities of the complexes of divalent metal ions (including Ni^{2+}) with maltol had been previously studied [13]. In this article, we describe the synthesis of some new nickel(II) complexes containing maltolate and ethyl maltolate ligands with ancillary bis(phosphine) ligands, dppe [1,2-bis (diphenylphosphino)ethane] or dppp [1,3-bis(diphenylphosphino)propane]. Related cationic palladium(II) and platinum(II) complexes of maltolate with ancillary nitrogen-donor [14–17] or PPh_3 ligands [18] are known.

2. Results and discussion

A selection of mixed-ligand complexes **3a–3d** containing either maltolate or ethylmaltolate and either dppe or dppp were prepared by a one-pot reaction of nickel(II) acetate with the phosphine and maltol or ethylmaltol in the presence of trimethylamine. The resulting cationic products were isolated in moderate to good yield by the addition of excess $NaBPh_4$, yielding yellow-orange to orange products which give good microanalytical data. The complexes are slightly soluble in methanol, but soluble in dichloromethane and chloroform.

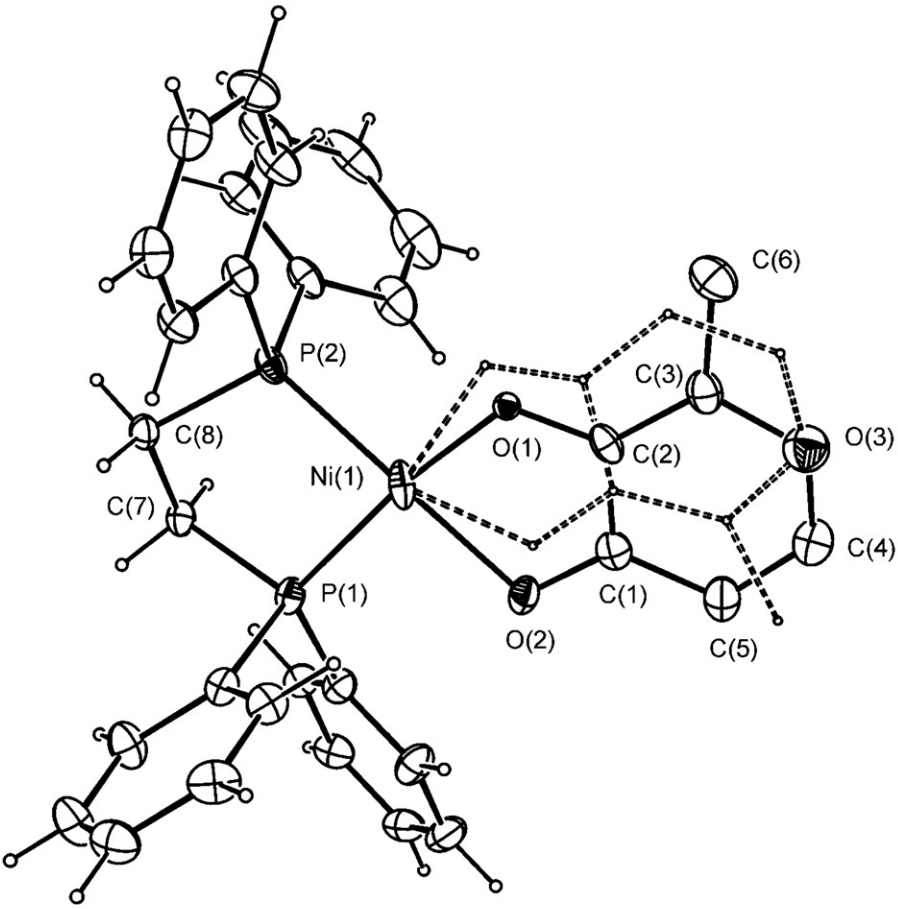

Figure 1. Structure of the cation of [Ni(maltolate)(dppe)]BPh_4 (**1a**) showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level. The dotted line shows the disordered component of the maltolate ligand.

The crystals of complex **3a** suitable for an X-ray structure determination were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the complex, and the structure was determined in order to provide comparative data with the known nickel(II) bis-maltolate complex **2**. The molecular structure of the cation is shown in figure 1 together with the atom numbering scheme, while table 1 gives selected bond lengths and angles for the core of the cation. The maltolate ligand is disordered over two equivalent overlapping orientations in a 2 : 1 ratio. The orientation of the minor component is indicated in figure 1 by the dotted lines; the major effect of this disorder is the increased uncertainty in bond parameters of those atoms of the maltolate ligand most remote from the nickel atom, specifically the bonds involving the pyranyl oxygen O(3).

The binding of the maltolate ligand in **3a** is somewhat asymmetric; the P(2)–Ni(1)–O(1) bond angle is 96.81(13)°, while P(1)–Ni(1)–O(2) is 90.5(11)°. The Ni–O bond distances are also different, with Ni(1)–O(1) 1.817(3) Å (from the C–O "single" bond),

Table 1. Selected bond lengths (Å) and angles (°) for [Ni(maltolate)(dppe)]BPh_4 (**1a**).

Ni(1)–O(1)	1.817(3)	Ni(1)–O(2)	1.995(3)
Ni(1)–P(2)	2.1471(8)	Ni(1)–P(1)	2.1497(8)
O(1)–C(2)	1.369(6)	O(2)–C(1)	1.265(5)
O(3)–C(4)	1.319(13)	O(3)–C(3)	1.390(11)
C(1)–C(2)	1.419(7)	C(1)–C(5)	1.447(7)
C(2)–C(3)	1.368(6)	C(3)–C(6)	1.470(7)
C(4)–C(5)	1.346(7)	–	–
O(1)–Ni(1)–O(2)	87.26(16)	O(1)–Ni(1)–P(2)	96.81(13)
O(2)–Ni(1)–P(1)	90.51(11)	P(2)–Ni(1)–P(1)	86.09(3)
O(2)–Ni(1)–P(2)	171.33(9)	O(1)–Ni(1)–P(1)	174.52(11)
C(2)–O(1)–Ni(1)	109.3(3)	C(1)–O(2)–Ni(1)	107.7(3)
O(2)–C(1)–C(2)	117.3(4)	O(1)–C(2)–C(1)	117.4(4)

and 1.995(3) Å (from the C=O "double" bond). Ni–O bond distances in related cationic β-diketonate complexes of nickel(II) that also contain dppe, namely [Ni(CH_3COCH $COCH_3$)(dppe)]$^+X^-$ [X = BF_4, 1.866(2) and 1.869(2) Å; X = ClO_4, 1.875(3) and 1.865(3) Å] [19] are similar to the average Ni–O distance in **3a**. However, the Ni–O bond lengths in **2** [2.039(1) and 2.052(1) Å] are considerably longer due to the octahedral coordination geometry of nickel in this complex. The asymmetry in the Ni–O bond lengths of **3a** is not reflected in Ni–P distances which are very similar to each other [Ni(1)–P(2) 2.1471(8) Å, Ni(1)–P(1) 2.1497(8) Å].

While the C=O bond lengths of **2** and **3a** are the same [complex **2** 1.266(2) Å; complex **3a** C(1)–O(2) 1.265(5) Å], the C(2)–O(1) single bond of **3a** [1.369(6) Å] is longer than the corresponding bond distance of 1.333(2) Å in **2**. The bite angle of the maltolate ligand of **3a** [87.26(16)°] is less acute than the ligand in **2** [82.40(5)°], which reflects the longer Ni–O bond distances in **2**.

A further point of difference between the two structures concerns the conformation of the maltolate ligands. In **2** these are planar, but in **3a** there is a slight puckering of the nickel–maltolate moiety, as defined by an angle of 9.50° between the O(1)–Ni(1)–O(2) coordination plane, and the plane of the pyranyl ring (defined by atoms C(1), C(2), C(3), C(4), C(5), and O(3)). There is also a slight distortion from regular square-planar geometry at the nickel centre, with an angle of 9.46° between the O(1)–Ni(1)–O(2) and P(1)–Ni(1)–P(2) planes. The τ_4 parameter [20] of the complex is 0.100, which indicates that the distortion from perfect square-planar geometry is relatively small. The other bond parameters of the maltolate ligand of **3a** are similar (given the uncertainty arising from the disorder) to those of **2**.

The ethylmaltolate complex **3c** has been characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ 56.3 and 54.7 ppm due to the two inequivalent PPh_2 groups of dppe, showing $^2J(PP)$ coupling of 80 Hz. The ^1H NMR spectrum of **3c** shows characteristic resonances of the ethyl group in the form of a quartet at δ 2.69 [$^3J(HH)$ 7.6], and corresponding triplet at δ 1.12. The dppe CH_2 protons appear as a broad multiplet at δ 1.78 and a broad singlet at δ 1.54. The maltolate CH proton adjacent to the C=O group appears as a doublet at δ 6.57 [$^3J(HH)$ 5.0 Hz], while the other CH proton is superimposed on the multitude of signals from the phenyl rings. The dppp complexes gave broad ^{31}P NMR spectra, for example for the maltolate complex **3b**, which gave two broad peaks at δ 12.7 and 9.9.

The complexes **3a–d** were also characterized by positive-ion ESI MS, with all complexes giving strong $[M]^+$ cations at the expected *m*/*z* values (refer Section 3), and with good agreement between observed and calculated isotope patterns. For the dppe complexes **3a** and **3c**, an additional unidentified ion at *m*/*z* 905 was observed, while for the dppp complexes **3b** and **3d** an additional ion was observed at *m*/*z* 933. The mass difference (28 *m*/*z*) suggests two phosphine ligands (differing in total by two CH_2 groups), and the isotope pattern suggests the presence of two Ni centers, but we have been unable to provide a sensible assignment for these ions.

Using the same synthetic method, the platinum(II) triphenylphosphine complex **4** was prepared as a white solid in 89% yield starting from *cis*-$[PtCl_2(PPh_3)_2]$. This complex has been previously prepared by the reaction of the dioxygen complex $[Pt(\eta^2–O_2)(PPh_3)_2]$ with maltol under a nitrogen atmosphere [18], but the product in this case was obtained as a yellow solid, the color of which may be due to impurities. Although ^{31}P NMR data for **4** were not reported previously, the $^{31}P\{^1H\}$ NMR spectrum of **4** revealed a highly pure Pt complex, giving two doublets at δ 9.0 and 5.1 showing coupling to ^{195}Pt with $^1J(PtP)$ values of 3908 and 3563 Hz, respectively, consistent with PPh_3 ligands *trans* to different oxygen-donors of the maltolate ligand. The phosphine at δ 5.1 is assigned as the one *trans* to the deprotonated maltol hydroxyl donor, because related catecholate and dioxolene complexes of platinum(II) show similar $^1J(PtP)$ coupling constants, for example $[Pt(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2]$ (3613 Hz) [21]. The phosphine at δ 9.0 is accordingly *trans* to the putative C=O donor of the maltolate ligand; its value of $^1J(PtP)$ (3908 Hz) is also comparable with values of 3931 and 3932 Hz for the acetone complexes *cis*-$[Pt(OCMe_2)_2L_2](ClO_4)_2$ ($L = PMePh_2$ or $L_2 =$ dppe) [22]. The positive-ion ESI MS of **4** shows a single dominant ion at *m*/*z* 844.245 for the parent cation, together with a minor fragment ion at *m*/*z* 718 due to the cyclometallated PPh_3 species $[Pt(C_6H_4PPh_2)(PPh_3)]^+$, this being commonly observed in the MS of Pt-PPh_3 complexes [23].

In conclusion, we have synthesized the first examples of nickel(II) complexes containing maltolate and phosphine ligands, including an X-ray structure determination on one complex. The simplicity of our synthetic method, validated in the synthesis of the known platinum(II) derivative $[Pt(maltolate)(PPh_3)_2]BPh_4$ in high yield and purity, suggests it could find use in the synthesis of maltolate complexes of other metals, which is currently under investigation.

3. Experimental

Maltol (3-hydroxy-2-methyl-4-pyrone, Aldrich), ethyl maltol (2-ethyl-3-hydroxy-4*H*-pyran-4-one, Aldrich), nickel(II) acetate tetrahydrate (BDH), sodium tetraphenylborate (BDH) and aqueous trimethylamine (BDH, 25–30% w/v), 1,2-bis(diphenylphosphino)ethane (dppe, Aldrich) and 1,3-bis(diphenylphosphino)propane (dppp, Aldrich) were used as supplied. The complex *cis*-$[PtCl_2(PPh_3)_2]$ was prepared by the reaction of $[PtCl_2(COD)]$ [24] (COD = cyclo-octa-1,5-diene) with 2 mole equivalents of PPh_3 in CH_2Cl_2 solution.

ESI MS were recorded on a Bruker MicrOTOF instrument, calibrated using a solution of sodium formate. The samples of isolated products were prepared for analysis by dissolution in a few drops of dichloromethane followed by dilution with methanol and centrifugation. Ion assignment was based on a comparison of experimental and theoretical [25] isotope patterns. NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC300P instrument. Elemental analyses were obtained from the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

3.1. *Synthesis of [Ni(maltolate)(dppe)]BPh$_4$ (3a)*

A mixture of $Ni(OAc)_2 \cdot 4H_2O$ (200 mg, 0.804 mmol) and dppe (320 mg, 0.804 mmol) in methanol (25 mL) was stirred with gentle warming for 5 min to give a clear yellow solution. Maltol (220 mg, 1.74 mmol) was added, giving a more orange solution. Aqueous trimethylamine (10 drops) was added, and the mixture warmed to around 60°C, giving an orange solution. After filtration to remove a small quantity of insoluble material, solid $NaBPh_4$ (300 mg, 0.88 mmol) was added to the filtrate to give a yellow-orange precipitate. After cooling to room temperature, the product was filtered, washed with cold methanol (5 mL), and dried under vacuum to give **3a** (377 mg, 52%). Found (%): C, 74.85; H, 5.56; N, 0.00. $C_{56}H_{49}BNiO_3P_2$ (M_r 901.01) requires (%): C, 74.58; H, 5.48; N, 0.00. ESI MS m/z 581.145 (Calcd 581.094), [**3a** – BPh_4]$^+$. $^{31}P\{^1H\}$ NMR, δ 57.4 [d, $^2J(PP)$ 81], 55.8 [d, $^2J(PP)$ 81]. ^1H NMR, δ 7.75–6.80 (m, Ph, and CH of maltolate), 6.53 [d, CH of maltolate, $^3J(HH)$ 5], 2.30 (s, CH_3 of maltolate), 1.79 (m, br, CH_2 of dppe), 1.52 (s, br, CH_2 of dppe).

3.2. *Synthesis of [Ni(maltolate)(dppp)]BPh$_4$ (3b)*

$Ni(OAc)_2 \cdot 4H_2O$ (200 mg, 0.804 mmol) and dppp (332 mg, 0.806 mmol) in methanol (30 mL) was stirred with gentle warming for 5 min to give a clear orange solution. Maltol (220 mg, 1.74 mmol) was added, giving a lighter orange solution, followed by 10 drops of aqueous trimethylamine. After briefly warming to 60°C the solution was filtered and $NaBPh_4$ (300 mg, 0.88 mmol) was added to the filtrate, giving an orange precipitate. Water (4 mL) was added to assist precipitation. After cooling to room temperature the solid was filtered, washed with water (2 × 10 mL), then with 1 : 1 methanol–water (10 mL), and dried under vacuum to give **3b** as an orange solid (463 mg, 63%). Found (%): C, 74.75; H, 5.65; N, 0.00. $C_{57}H_{51}BNiO_3P_2$ (M_r 915.02) requires (%): C, 74.75; H, 5.62; N, 0.00. ESI MS m/z 595.162 (Calcd 595.110), [**3b**–BPh_4]$^+$. $^{31}P\{^1H\}$ NMR, δ 12.7 and 9.9 (br).

3.3. *Synthesis of [Ni(Et-maltolate)(dppe)]BPh$_4$ (3c)*

Following the procedure for **3a**, $Ni(OAc)_2 \cdot 4H_2O$ (200 mg, 0.804 mmol) with dppe (320 mg, 0.804 mmol) in methanol (25 mL), with ethyl maltol (250 mg, 1.78 mmol), aqueous trimethylamine (10 drops), and $NaBPh_4$ (300 mg, 0.88 mmol) gave a yellow-orange precipitate. After cooling to room temperature, water (3 mL) was added to assist precipitation. The product was filtered, washed with water (2 × 10 mL), then with 1 : 1 methanol–water (10 mL), and dried under vacuum to give **3c** (531 mg, 72%) as a deep yellow solid. Found (%): C, 74.68; H, 5.39; N, 0.00. $C_{57}H_{51}BNiO_3P_2$ (M_r 915.02) requires (%): C, 74.75; H, 5.62; N, 0.00. ESI MS m/z 595.163 (Calcd 595.110), [**3c**–BPh_4]$^+$. $^{31}P\{^1H\}$ NMR, δ 56.3 [d, $^2J(PP)$ 80], 54.7 [d, $^2J(PP)$ 80]. ^1H NMR, δ 7.73–6.78 (m, Ph, and CH of Et-maltolate), 6.57 [CH of Et-maltolate, $^3J(HH)$ 5.0 Hz], 2.69 [q, CH_2 of Et-maltolate, $^3J(HH)$ 7.6], 1.78 (m, br, CH_2 of dppe), 1.54 (s, br, CH_2 of dppe), 1.12 [t, CH_3 of Et-maltolate, $^3J(HH)$ 7.5].

3.4. *Synthesis of [Ni(Et-maltolate)(dppp)]BPh₄ (3d)*

Following the procedure for **3b**, $Ni(OAc)_2 \cdot 4H_2O$ (200 mg, 0.804 mmol) with dppp (332 mg, 0.806 mmol) in methanol (30 mL), with ethyl maltol (250 mg, 1.78 mmol), aqueous trimethylamine (10 drops), and $NaBPh_4$ (300 mg, 0.88 mmol) gave an orange precipitate. After cooling to room temperature, water (3 mL) was added to assist precipitation. The product was filtered, washed with water (2 × 10 mL), then with 1 : 1 methanol–water (10 mL), and dried under vacuum to give **3d** (610 mg, 82%) as an orange powder. Found (%): C, 74.96; H, 5.86; N, 0.00. $C_{58}H_{53}BNiO_3P_2$ (M_r 929.04) requires (%): C, 74.92; H, 5.75; N, 0.00. ESI MS *m*/*z* 609.178 (Calcd 609.125), [**3d**–BPh_4]$^+$.

3.5. *Synthesis of [Pt(maltolate)(PPh₃)₂]BPh₄ (4)*

To a suspension of *cis*-[$PtCl_2(PPh_3)_2$] (307 mg, 0.389 mmol) in methanol (30 mL) was added maltol (220 mg, 1.74 mmol) and aqueous trimethylamine (2 mL, excess). The mixture was stirred and heated to reflux for 15 min, whereupon the Pt complex slowly dissolved giving a clear, very pale yellow solution. After filtration to remove a trace of insoluble matter, solid $NaBPh_4$ (250 mg, 0.73 mmol) was added to the filtrate, giving a slightly off-white precipitate that was filtered, washed with water (10 mL), then with 1 : 1 methanol–water (10 mL), and dried under vacuum to give **4** (402 mg, 89%). Found (%): C, 68.28; H, 4.81; N, 0.00. $C_{66}H_{55}BO_3P_2Pt$ (M_r 1163.44) requires (%): C, 68.07; H, 4.76; N, 0.00. ESI MS *m*/*z* 844.245 (Calcd 844.171), [**4** – BPh_4]$^+$. $^{31}P\{^1H\}$ NMR, δ 9.0 [d, $^1J(PtP)$ 3908, $^2J(PP)$ 24], 5.1 [d, $^1J(PtP)$ 3563, $^2J(PP)$ 24]. ^1H NMR, δ 7.47–6.70 (m, Ph and CH of maltolate), 6.25 [CH of maltolate, $^3J(HH)$ 5.0 Hz], 1.99 (s, Me).

3.6. *X-ray structure determination of [Ni(maltolate)(dppe)]BPh₄ (1a)*

The complex crystallizes as red block-like crystals by vapor diffusion of diethyl ether into a dichloromethane solution at room temperature.

X-ray data were collected on a Bruker Apex II CCD diffractometer and were corrected for absorption by a multi-scan method (SADABS) [26]. The structure was solved and refined with SHELX97 [27]. The maltolate ligand was disordered over two equivalent, overlapping orientations in a 0.67 : 0.33 ratio, and the minor component was refined with isotropic temperature factors. H atoms were not included for the disordered ligand. Electron density in a general position in the lattice was modeled as two 0.5 Cl atoms from a disordered CH_2Cl_2 molecule.

3.7. *Crystal data for $C_{56}H_{59}BClNiO_3P_2$*

$M_r = 946.94$; triclinic; space group $P\bar{1}$; $a = 9.5013(4)$ Å; $b = 14.8195(6)$ Å; $c = 16.8470(8)$ Å; $\alpha = 95.959(2)°$; $\beta = 99.641(2)°$; $\gamma = 95.873(2)°$; $V = 2308.59(17)$ Å^3; $Z = 2$; $T = 89(2)$ K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 0.594 mm^{-1}; $d_{calcd} = 1.362$ g cm^{-3}; 56420 reflections collected; 11087 unique ($R_{int} = 0.0533$); giving $R_1 = 0.0546$, $wR_2 = 0.1330$ for data with $[I > 2\sigma(I)]$ and $R_1 = 0.0715$, $wR_2 = 0.1414$ for all data. Residual electron density (e Å^{-3}) max/min: 1.385/−0.959.

Supplementary material

CCDC 802226 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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