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# Synthesis and characterisation of 3-aza-7-phosphabicyclo[3.3.1]nonan-9-ones

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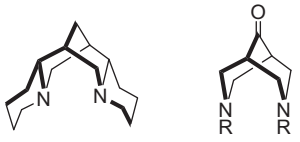
ABSTRACT

Novel 3-aza-7-phosphabicyclo[3.3.1]nonan-9-ones have been synthesised via the Mannich reaction of a phosphorinanone, a primary amine and formaldehyde. The new phosphorus–nitrogen (PN) compounds are rigid and adopt a twin-chair conformation both in solution and the solid states. The coordination properties of the PN compounds were explored and a stable platinum complex was synthesised in which the PN ligand was bonded through both donor atoms.



The rigid bicyclo[3.3.1]nonan-9-one framework occurs in many polycyclic alkaloids such as sparteine (**1**, shown is the structure of α-isosparteine) and in the synthetic bispidinone derivatives **2**. Since sparteine has known medical and chemical applications,[1] the simplified bispidinones have also been extensively investigated for potential biological activity and as bidentate ligands for transition metals.[1–5]




**1** **2**

Bispidinones were first reported by Mannich and Mohs in 1930.[6] In general, they can be easily prepared by the Mannich condensation reaction of a ketone with acidic α-C–H protons, an aldehyde and a primary amine in a protic solvent (Scheme 1). The reaction intermediate is a piperidinone which can either be isolated or condensed further with 2 equiv of aldehyde and 1 equiv of a primary amine to produce the diazabicyclo[3.3.1]nonan-9-one. In total, four Mannich condensations are required to yield the final bispidinone.

Replacement of one of the nitrogen atoms in bispidinone compounds with a heteroatom leads to 3-aza-7-heterobicyclo[3.3.1]nonan-9-ones. Oxygen,[7] sulfur[8,9] and selenium[10] analogues have been prepared by the Mannich reaction starting from the respective 4-heterocyclohexanones. These bispidinone analogues have been used for conformational studies and were tested for potential biological activity due to their antiarrhythmic and analgesic properties.

To date, bispidinone derivatives containing both phosphorus and nitrogen atoms are not known. Such compounds are attractive synthetic targets as the combination of the rigid and highly preorganised bicyclic backbone and the different features associated with each donor atom are expected to provide unique properties to the resultant phosphorus–nitrogen (PN) derivatives as chelating ligands in transition metal complexes. Furthermore, the possibility of substitution at the 1/5, 2/4 and 6/8 positions of the bicyclic ring offers unique opportunities to fine-tune the steric environment around the metal centre. Herein, we report the synthesis and spectroscopic and structural data of the first examples of 3-aza-7-phosphabicyclo[3.3.1]nonan-9-ones.

The bispidinone synthetic method is not chemically viable to prepare the analogous PN compounds as there is no equivalent for the iminium ion, which is the reactive species in the Mannich reaction,[11,12] in phosphorus chemistry due to the weakness of P=C bonds. Thus, a different route was developed using the phosphorus analogues of piperidinones, known as 4-phosphorinanones, to obtain the new bispidinone derivatives.

The condensation of dimethyl 1,3-acetonedicarboxylate (**3**) with *p*-dimethylaminobenzaldehyde produced the α,β-unsaturated carbonyl compound **4** (Scheme 2). Subsequently, the *P*-Michael[13] reaction of **4** with bis(hydroxymethyl)phenylphosphine in pyridine

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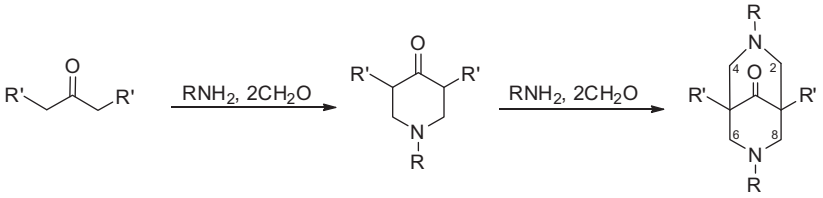


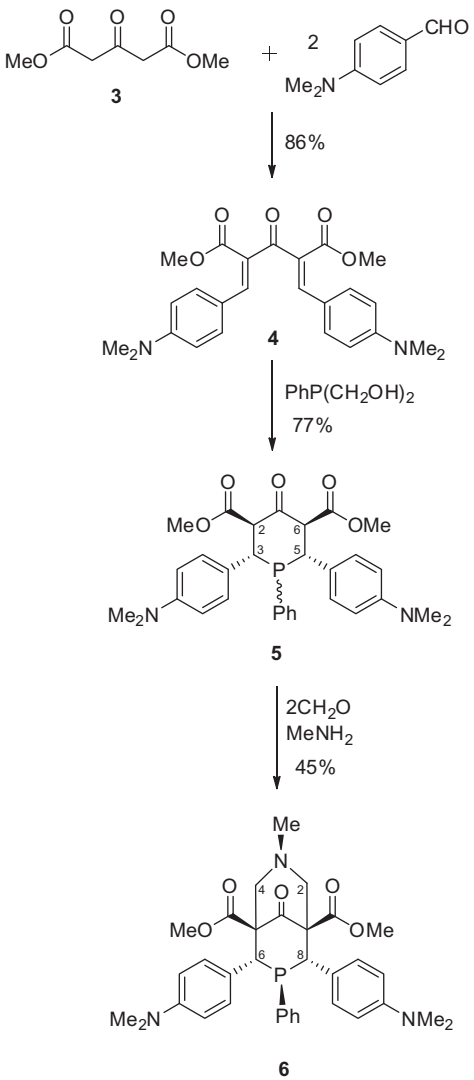

**Scheme 1.** General synthesis of bispidinones.

under reflux yielded a complex reaction mixture containing several phosphorinanone isomers, from which **5** was isolated as an air-stable solid.[14]

Phosphorinanone **5** displayed characteristically simple $^{1}H$ and $^{13}C$ NMR spectra owing to the presence of a plane of symmetry. The pairs of equivalent protons H3/H5 and H2/H6 appeared as doublets of doublets at 3.79 and 4.24 ppm, respectively, with large diaxial coupling constants. This indicated that the bulky carbomethoxy and dimethylaminophenyl groups were in equatorial positions. The orientation of the phenyl group on phosphorus could not be determined in compound **5**. However, in previous conformational analysis work on six-membered phosphacycles, axial Ph-P orientations have been determined.[15–17] The $^{31}P$ NMR spectrum of **5** showed one resonance at −6.9 ppm.

The Mannich reaction of phosphorinanone **5** with methylamine and 2 equiv of formaldehyde in ethanol produced the air-stable bicyclic PN compound **6** (Scheme 2).[18] The $^{1}H$ NMR spectrum of **6** implied symmetrical positions for the carbomethoxy and dimethylaminophenyl substituents, and for H6/8 and H2/4. The $^{31}P$ NMR spectrum showed a single resonance at −15.1 ppm, and the IR spectrum was dominated by two carbonyl stretches at 1722 and 1744 $cm^{-1}$ corresponding to the ketone and ester groups, respectively.

Crystals of PN compound **6** were obtained from diethyl ether and dichloromethane. The X-ray crystal structure shows a mirror symmetrical chair–chair conformation with the carbomethoxy, dimethylaminophenyl, Me and Ph substituents in equatorial sites (Fig. 1). This observation is in agreement with the structure in solution. The solid state crystal structure also shows that PN compound **6** is similar to the bispidinones as the intramolecular distance between the phosphorus and nitrogen donor atoms is




**Scheme 2.** Synthesis of 3-aza-7-phosphabicyclo[3.3.1]nonan-9-one derivative **6**.

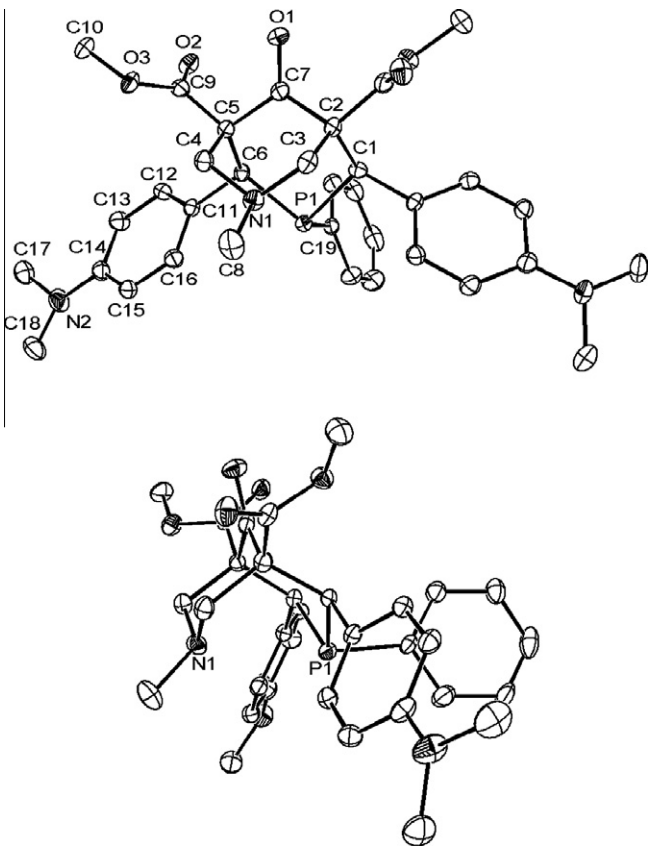
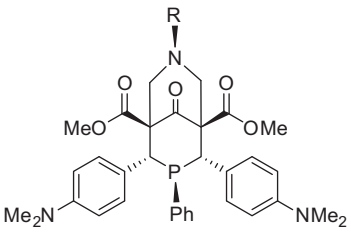



**Figure 1.** ORTEP diagrams of PN compound **6** (30% thermal ellipsoids). Hydrogen atoms omitted for clarity.

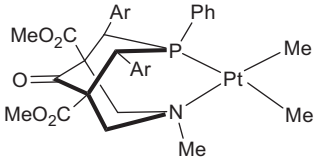
2.9 Å, which is the same as the average N–N distance in bispidinone compounds.[1]

Similarly, phosphorinanone **5** was reacted with ethylamine or isobutylamine and formaldehyde via the Mannich reaction to yield the new PN analogues **7** and **8**. The spectroscopic data[19] of **7** and **8** were very similar to **6** as they adopted a mirror symmetrical chair–chair conformation in solution.



**7** R = $CH_2CH_3$ 36% yield
**8** R = $CH_2CH(CH_3)_2$ 60% yield

PN ligand **6** was reacted with [$PtMe_2$(1,5-hexadiene)] to form the square planar complex [$PtMe_2$(**6**)] (**9**).[20] The $^{31}P$ NMR spectrum showed a single resonance at 14.6 ppm with $^{195}Pt$ satellites of 2036 Hz. The $^{1}H$ NMR spectrum of **9** was simple indicating that the coordinated PN ligand retained its plane of symmetry upon coordination to platinum.



**9** (Ar = *p*-$C_6H_4N(Me)_2$)

The NMR signals for the methyl groups in **9** were differentiated as a result of being *trans* to the different donor atoms: the methyl group *trans* to phosphorus resonated at 1.35 ppm in the $^{1}H$ NMR spectrum, while the methyl *trans* to nitrogen appeared at 1.43 ppm. Both signals were doublets with $J_{PH}$ values of 7.5 Hz. The *trans*-effect of P and N was much more pronounced in the $^{13}C$ NMR chemical shifts of the methyl groups: the methyl *trans* to phosphorus resonated at 11.2 ppm as a doublet ($J_{PC}$ = 114.6 Hz) with $^{195}Pt$ satellites of 727 Hz, whereas the methyl group *trans* to nitrogen appeared at −20.9 ppm as a doublet ($J_{PC}$ = 3.7 Hz) with a slightly larger $^{195}Pt$ coupling constant of 787 Hz. The above NMR data confirm that PN ligand **6** is bonded to platinum via both donor atoms, hence maintaining its chair–chair conformation.

In conclusion, novel phosphorus–nitrogen derivatives of the bispidinones were synthesised by the Mannich reaction of phosphorinanone **5** with primary amines and formaldehyde. The new bicyclic PN compounds adopted a rigid chair–chair conformation both in solution and solid states. This conformation is favourable as it presets a bidentate capability for such PN compounds to serve as chelating ligands for transition metals.

## Supplementary data

The synthesis and characterisation data for compound **4** are supplied, as well as the synthetic methods for compounds **7** and **8**. The crystallographic parameters and a summary of bond distances and angles for compound **6** are also included. CCDC 838817 contains the supplementary crystallographic data for compound **6**. This information can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.12.031.

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14. *Preparation of 4-phenyl-2,6-di(carbomethoxy)-3,5-bis(p-dimethylaminophenyl)-4-phosphacyclohexanone (**5**)*:
Compound **4** (0.10 g, 0.23 mmol) and bis(hydroxymethyl)phenylphosphine (0.03 $cm^3$, 0.23 mmol) were heated under reflux for 4 h in pyridine (10 $cm^3$) under an inert atmosphere. After 30 min, a white solid (shown to be paraformaldehyde) deposited in the condenser. The solvent was removed *in vacuo* to give a red oil, which was taken up in EtOH and kept at 5 °C. The title compound precipitated as an orange solid. This was filtered and recrystallised from EtOH (0.10 g, 77%); mp 154–156.9 °C. IR (KBr) $\nu_{max}$ 1740, 1642, 1629, 1610 $cm^{-1}$; $^{1}H$ NMR $\delta$ (300 MHz, $CDCl_3$): 2.85 (s, 12H, $NMe_2$), 3.57 (s, 6H, OMe), 3.79 (dd, $J_{HH}$ = 112.8 Hz, $J_{PH}$ = 6.6 Hz, 2H, PCH), 4.24 (dd, $J_{HH}$ = 13.4 Hz, $J_{PH}$ = 5.7 Hz, 2H, PCCH), 6.48 (d, $J_{HH}$ = 8.0 Hz, 4H, *m*-H), 6.92 (d, $J_{HH}$ = 8.0, 4H, *o*-H), 7.14–7.34 (m, 5H, $C_6H_5$); $^{13}C$ NMR $\delta$ (75 MHz, $CDCl_3$): 40.5 (s, $NMe_2$), 45.4 (d, $J_{PC}$ = 19.2 Hz, PCH), 52.6 (s, OMe), 64.5 (m, P**C**H), 112.1 (s, Ar), 120.4 (s, Ar), 125.9 (d, $J_{PC}$ = 34.8 Hz, Ar), 127.7 (d, $J_{PC}$ = 9.2 Hz, Ar), 130.0 (s, Ar), 132.4 (d, $J_{PC}$ = 8.6 Hz, Ar), 133.0 (d, $J_{PC}$ = 6.4 Hz, Ar), 150.1 (s, Ar), 169.2 (d, $J_{PC}$ = 10.3 Hz, COO), 202.7 (s, CO); $^{31}P$ NMR $\delta$ (121 MHz; $CDCl_3$): −6.9; HRMS calcd for $C_{31}H_{36}N_2O_5P$ $[M+H]^+$: *m*/*z* = 547.2362; found: 547.2365; Anal. calcd for $C_{31}H_{35}N_2O_5P$: C, 68.1; H, 6.5; N, 5.1; P, 5.7; found: C, 68.4; H, 6.7; N, 5.2; P, 5.8.
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18. *Preparation of 1,5-di(carbomethoxy)-6,8-bis(p-dimethylaminophenyl)-3-methyl-7-phenyl-3-aza-7-phosphabicyclo[3.3.1]nonan-9-one (**6**)*:
Phosphorinanone **5** (0.10 g, 0.18 mmol), methylamine (0.02 $cm^3$, 0.18 mmol) and formaldehyde (0.03 $cm^3$, 0.36 mmol) were combined in EtOH (35 $cm^3$). The red reaction mixture was heated under reflux for 1 d under an inert atmosphere. The title compound precipitated from the reaction mixture as it cooled down to room temperature as a pale-yellow solid (0.05 g, 45%); mp 145–149 °C. IR (KBr) $\nu_{max}$ 1744, 1722, 1709, 1646 $cm^{-1}$; $^{1}H$ NMR $\delta$ (300 MHz, $CDCl_3$): 2.67 (s, 3H, NMe), 2.83 (d, $J_{HH}$ = 11.7 Hz, 2H, $CH_2$), 2.90 (s, 12H, $NMe_2$), 3.57 (d, $J_{HH}$ = 12.6 Hz, 2H, $CH_2$), 3.67 (s, 6H, OMe), 4.14 (d, $J_{PH}$ = 6.2 Hz, 2H, PCH), 6.60 (d, $J_{HH}$ = 8.8 Hz, 4H, *m*-H), 7.09 (m, 2H, $PC_6H_5$), 7.17 (m, 3H, $PC_6H_5$), 7.30 (d, $J_{HH}$ = 8.5 Hz, 4H, *o*-H); $^{13}C$ NMR $\delta$ (75 MHz, $CDCl_3$): 40.6 (s, $NMe_2$), 44.5 (s, NMe), 47.4 (d, $J_{PC}$ = 19.7 Hz, PCH), 52.3 (s, OMe), 60.4 (s, $CH_2$), 65.7 (d, $J_{PC}$ = 2.8 Hz, PCH**C**), 112.4 (s, Ar), 125.2 (d, $J_{PC}$ = 17.5 Hz, Ar), 128.2 (d, $J_{PC}$ = 5.3 Hz, Ar), 128.6 (s, Ar), 131.6 (d, $J_{PC}$ = 19.5 Hz, Ar), 132.1 (d, $J_{PC}$ = 13.4 Hz, Ar), 141.2 (d, $J_{PC}$ = 33.1 Hz, Ar), 149.9 (s, Ar), 169.5 (d, $J_{PC}$ = 3.6 Hz, COO), 205.2 (s, CO); $^{31}P$ NMR $\delta$ (121 MHz; $CDCl_3$): −15.1; HRMS calcd for $C_{34}H_{41}N_3O_5P$ $[M+H]^+$: *m*/*z* = 602.2784; found: 602.2785; Anal. calcd for $C_{34}H_{40}N_3O_5P$: C, 67.9; H, 6.7; N, 7.0; P, 5.2; found: C, 66.8; H, 6.9; N, 6.7; P, 5.3.
19. *Spectral data for compound **7**:*
IR (KBr) $\nu_{max}$ 1743, 1725, 1707, 1611 $cm^{-1}$; $^{1}H$ NMR $\delta$ (500 MHz, $CDCl_3$): 1.41 (t, $J_{HH}$ = 7.1 Hz, 3H, $NCH_2CH_3$), 2.85 (d, $J_{HH}$ = 11.2 Hz, 2H, $CH_2$), 2.90 (s, 12H, $NMe_2$), 2.95 (q, $J_{HH}$ = 7.1 Hz, 2H, $NCH_2CH_3$), 3.62 (d, $J_{HH}$ = 11.2 Hz, 2H, $CH_2$), 3.68 (s, 6H, OMe), 4.14 (d, $J_{PH}$ = 5.6 Hz, 2H, PCH), 6.61 (d, $J_{HH}$ = 6.8 Hz, 4H, *m*-H), 7.09 (m, 2H, $PC_6H_5$), 7.16 (m, 3H, $PC_6H_5$), 7.33 (d, $J_{HH}$ = 7.3 Hz, 4H, *o*-H); $^{13}C$ NMR $\delta$

(125 MHz, $CDCl_3$): 11.5 (s, $NCH_2CH_3$), 40.4 (s, $NMe_2$), 46.9 (d, $J_{PC}$ = 20.1 Hz, PCH), 51.1 (s, $CH_2$), 52.0 (s, OMe), 57.5 (s, $NCH_2CH_3$), 65.6 (d, $J_{PC}$ = 3.3 Hz, PCHC), 112.2 (s, Ar), 125.0 (d, $J_{PC}$ = 17.4 Hz, Ar), 127.9 (d, $J_{PC}$ = 5.1 Hz, Ar), 128.2 (s, Ar), 131.2 (d, $J_{PC}$ = 19.4 Hz, Ar), 131.8 (d, $J_{PC}$ = 13.4 Hz, Ar), 149.7 (d, $J_{PC}$ = 1.7 Hz, Ar), 169.4 (d, $J_{PC}$ = 3.3 Hz, COO), 205.2 (s, CO); $^{31}$P NMR $\delta$ (121 MHz; $CDCl_3$): −16.2.

HRMS calcd for $C_{35}H_{43}N_3O_5P$ $[M+H]^+$: $m/z$ = 616.2940; found: 616.2941; Anal. calcd for $(C_{35}H_{42}N_3O_5P)_3.CDCl_3$: C, 64.7; H, 6.6; N, 6.4; P, 4.7; found: C, 64.3; H, 6.7; N, 6.5; P, 5.0.

*Spectral data for compound **8**:*

IR (KBr) $\nu_{max}$ 1744, 1709, 1621, 1519 $cm^{-1}$; $^1$H NMR $\delta$ (300 MHz, $CDCl_3$): 1.32 (d, $J_{HH}$ = 6.4 Hz, 6H, $NCH_2CH(CH_3)_2$), 2.18 (m, 1H, $NCH_2CH(CH_3)_2$), 2.47 (d, $J_{HH}$ = 6.8 Hz, 2H, $NCH_2CH(CH_3)_2$), 2.76 (d, $J_{HH}$ = 12.4 Hz, 2H, $CH_2$), 2.90 (s, 12 H, $NMe_2$), 3.64 (m, 2H, $CH_2$), 3.67 (s, 6H, OMe), 4.13 (d, $J_{PH}$ = 5.2 Hz, 2H, PCH), 6.59 (d, $J_{HH}$ = 7.1 Hz, 4H, *m*-H), 7.08 (m, 2H, $PC_6H_5$), 7.16 (m, 3H, $PC_6H_5$), 7.30 (d, $J_{HH}$ = 8.3 Hz, 4H, *o*-H); $^{13}$C NMR $\delta$ (75 MHz, $CDCl_3$): 22.2 (s, $NCH_2CH(CH_3)_2$), 22.3 (s, $NCH_2CH(CH_3)_2$), 26.4 (s, $NCH_2CH(CH_3)_2$), 40.8 (s, $NMe_2$), 47.3 (d, $J_{PC}$ = 21.4 Hz, PCH), 52.2 (s, OMe), 59.7 (s, $CH_2$), 65.6 (d, $J_{PC}$ = 3.9 Hz, PCHC), 67.6 (s, $NCH_2CH(CH_3)_2$), 112.5 (br s, Ar), 125.4 (br s, Ar), 128.1 (d, $J_{PC}$ = 5.5 Hz, Ar), 128.6 (s, Ar), 131.6 (d, $J_{PC}$ = 19.6 Hz, Ar), 131.9 (d, $J_{PC}$ = 12.2 Hz, Ar), 149.8 (br s, Ar), 169.6 (d, $J_{PC}$ = 3.7 Hz, COO), 205.5 (s, CO); $^{31}$P NMR $\delta$ (121 MHz; $CDCl_3$): −16.1.

HRMS calcd for $C_{37}H_{47}N_3O_5P$ $[M+H]^+$: $m/z$ = 644.3253; found: 644.3257; Anal. calcd for $C_{37}H_{46}N_3O_5P$: C, 69.0; H, 7.2; N, 6.5; P, 4.8; found: C, 68.8; H, 7.3; N, 6.4; P,.5.0.

20. *Preparation of [$PtMe_2$(**6**)] (**9**):*

PN ligand **6** (0.05 g, 0.08 mmol) and [$PtMe_2$(1,5-hexadiene)] (0.02 g, 0.08 mmol) were combined in $CH_2Cl_2$ (5 $cm^3$). The yellow mixture was stirred at room temperature for 1 d. The solvent was evaporated in vacuo to give the title compound as a yellow solid (0.06 g, 86%); mp 230–233 °C. IR (KBr) $\nu_{max}$ 1745, 1735, 1720, 1625 $cm^{-1}$; $^1$H NMR $\delta$ (300 MHz, $C_6D_6$): 1.35 (d, $J_{PH}$ = 7.5 Hz, 3 H, Me *trans* to P), 1.43 (d, $J_{PH}$ = 7.5 Hz, 3 H, Me *trans* to N), 2.34 (s, 3 H, NMe), 2.37 (s, 12 H, $NMe_2$), 2.94 (m, 2 H, $CH_2$), 3.38 (s, 6 H, OMe), 4.32 (d, $J_{HH}$ = 13.4 Hz, 2 H, $CH_2$), 4.44 (d, $J_{PH}$ = 12.1 Hz, 2 H, PCH), 6.50 (d, $J_{HH}$ = 8.4 Hz, 4 H, *m*-H), 6.76 (m, 5H, $PC_6H_5$), 8.61 (d, $J_{HH}$ = 8.4 Hz, 4 H, *o*-H); $^{13}$C NMR $\delta$ (75 MHz, $CDCl_3$): −20.9 (d, $J_{PC}$ = 3.7 Hz, $J_{PtP}$ = 787 Hz, Me *trans* to N), 11.2 (d, $J_{PC}$ = 114.6 Hz, $J_{PtP}$ = 727 Hz, Me *trans* to P), 40.2 (s, $NMe_2$), 45.1 (d, $J_{PC}$ = 19.1 Hz, PCH), 52.2 (s, OMe), 57.3 (s, NMe), 64.1 (d, $J_{PC}$ = 2.0 Hz, $CH_2$), 64.2 (d, $J_{PC}$ = 5.3 Hz, PCH**C**), 111.8 (s, Ar), 120.0 (d, $J_{PC}$ = 2.5 Hz, Ar), 125.6 (d, $J_{PC}$ = 35.1 Hz, Ar), 127.4 (d, $J_{PC}$ = 9.0 Hz, Ar), 129.6 (d, $J_{PC}$ = 1.9 Hz, Ar), 132.1 (d, $J_{PC}$ = 8.6 Hz, Ar), 132.7 (d, $J_{PC}$ = 6.2 Hz, Ar), 149.8 (d, $J_{PC}$ = 0.9 Hz, Ar), 167.8 (d, $J_{PC}$ = 10.3 Hz, COO), 202.3 (d, $J_{PC}$ = 1.5 Hz, CO); $^{31}$P NMR $\delta$ (121 MHz; $C_6D_6$): 14.6 ($J_{PtP}$ = 2036 Hz).

HRMS calcd for $C_{36}H_{45}N_3O_5PPt$ $[M-H]^+$: $m/z$ = 825.2745; found: 825.2761; Anal. calcd for $C_{36}H_{46}N_3O_5PPt$: C, 52.3; H, 5.6; N, 5.1; found: C, 53.7; H, 5.8; N, 4.7.