

Tetramethylphosphorinones as Functional Alternatives to Di-*tert*-butylphosphino Substituents in Ligand Design

James D. Nobbs,^{a*} Kai Bin Jonathan Chan,^{ab} Sigit Sugiarto,^a Choon Boon Cheong,^a Min Jean Chua,^a Cun Wang,^a Ludger Paul Stubbs,^a Han Vinh Huynh^{b*} and Martin van Meurs^a

^aInstitute of Sustainability for Chemicals, Energy and Environment (ISCE²), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833, Republic of Singapore. ^bDepartment of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, Singapore 117543, Republic of Singapore.

KEYWORDS

phosphorinone ligands · bulky phosphines · ligand design · methoxycarbonylation · homogeneous catalysis · palladium

ABSTRACT

Bulky phosphino substituents such as ^tBu₂P are key components of ligands in homogeneous catalysis, yet few options exist to tune their electronic properties while retaining comparable steric environments. Here we report the synthesis of oxo-tetramethylphosphinane (**oxo-TMPhos**), a 2° phosphorinone scaffold that incorporates a γ -ketone substituent into the tetramethylphosphinane framework. The ketone handle enables broad derivatization, including reduction, amination, and C–C bond formation, while the 2° phosphine can be used to construct a variety of ligands. Systematic donor strength evaluation using the Huynh Electronic Parameter (HEP) confirmed that phosphorinones are weaker donors than tetramethylphosphinane (**TMPhos**) and ^tBu₂PH, reflecting the electron-withdrawing C=O substituent. From this scaffold we prepared a series of phosphorinone ligands, including Buchwald type, bidentate phosphines with propyl (**BPP**) or butyl (**BPB**) linkers, bulky PCP and PNP pincer ligands, and a new scalable route to bis(2,2,6,6-phosphorin-4-one)-*o*-xylene (**BPX**). In Pd-catalyzed isomerizing methoxycarbonylation of 4-octene, **BPP** delivered over an order of magnitude higher turnover numbers (TONs) than the corresponding di-*tert*-butylphosphino analogue. It could be applied across a broad substrate scope, including internal, branched, cyclic, and styrenic alkenes. This work highlights phosphorinones as a practical and tunable alternative to classical bulky alkylphosphines, with significant potential for applications in homogeneous catalysis.

INTRODUCTION

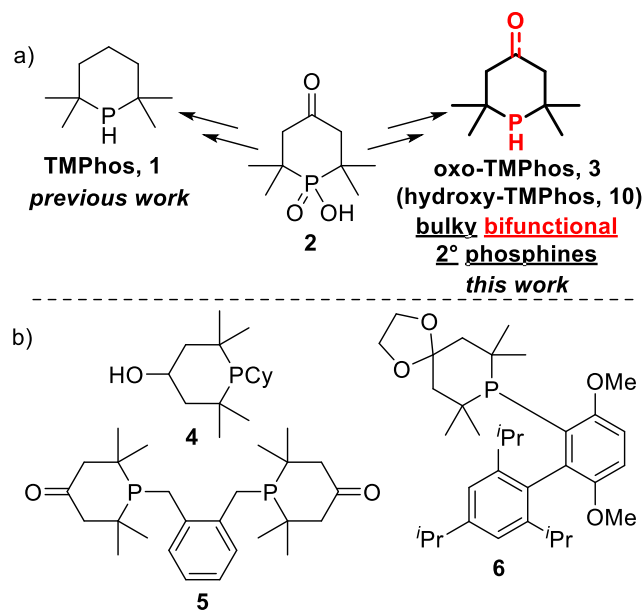


Figure 1. Bulky γ -functionalized phosphinanes. a) 2° phosphinanes obtained from the corresponding phosphorinic acid, **2**. b) Functionalized phosphinanes used in catalysis.

Bulky phosphino substituents such as ^tBu₂P are important components of ligands in many homogeneous catalysts, stabilizing coordinative unsaturation and promoting catalytic pathways.¹⁻³ Recently, we reported a multigram synthesis of 2,2,6,6-tetramethylphosphinane, (**TMPhos, 1**, Figure 1a), a cyclic analogue of ^tBu₂PH derived from the corresponding phosphaninic acid precursor (**2**).⁴ While both **TMPhos** and ^tBu₂PH give rise to sterically bulky ligands, they lack additional functional groups, limiting the ability to fine-tune electronic properties and access further ligand derivatives. In contrast, phosphorinones such as **3**, possess a distinct electronic environment compared to their parent phosphinanes and offer bifunctionality, enabling further modifications to adjust electronics, solubility, and other properties.⁵ γ -Substituted phosphinanes have proven to be effective ligands in homogeneous catalysis (Figure 1b). For example, ligand **4** promotes Ni-catalyzed Kumada coupling reactions under mild conditions.⁶ Bis(phosphorinone) **5** is a highly active and selective ligand for the Pd catalyzed isomerizing methoxycarbonylation of alkenes,⁷⁻⁹ while biaryl phosphorinane **6** enables challenging C–N and C–O cross coupling reactions of pharmaceutical intermediates.¹⁰

Current synthetic approaches to phosphorinone ligands typically rely on condensation of primary phosphines with phorone, necessitating laborious preparation of individual primary phosphines – many of which are pyrophoric, highly malodorous, and toxic.¹¹⁻¹² To overcome these limitations, we recognized the benefits of developing a secondary (2°) phosphinane scaffold bearing a γ -ketone group for further derivatization. Herein, we describe a practical synthesis of a bulky 2° phosphorinone, denoted **oxo-TMPhos (3)**. The corresponding nitrogen analogue triacetoneamine is widely used across chemical and pharmaceutical applications;¹³⁻¹⁴ however, its phosphorus counterpart has remained underexplored due to the lack of a scalable synthetic route.

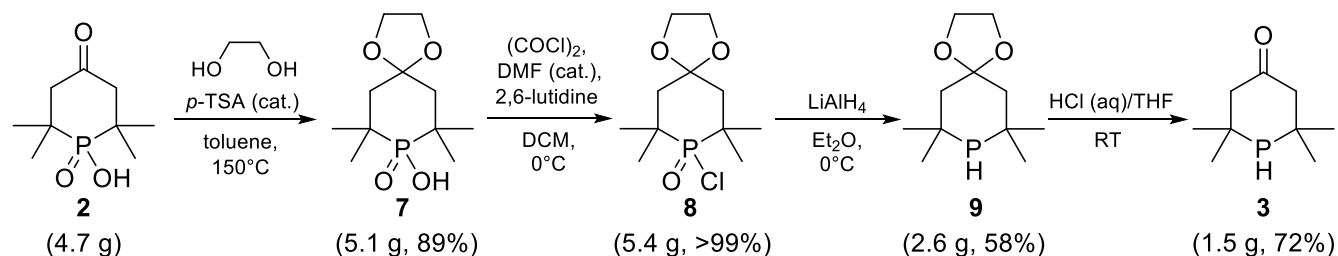
RESULTS AND DISCUSSION

Synthesis of secondary phosphines and their derivatives

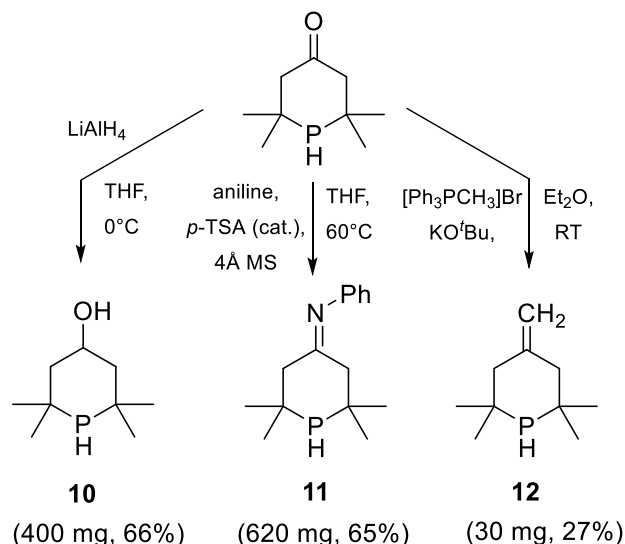
The only reported route to **3** was *via* a Li-mediated cleavage of the Ph–P bond in phenyl phosphorinone which resulted in very low overall yields (<5%) due to competing cleavage of the P–C_{alkyl} bond.¹⁵⁻¹⁶ Our route starts from 2,2,6,6-tetramethylphosphorininc acid (**2**, Figure 2a), which can be obtained on a multigram (>10 g) scale from *in situ* generated bis(trimethylsilyl)phosphonite, (Me₃SiO)₂PH, and phorone.⁴ Ketone protection of **2** furnished ketal-phosphaninic acid (**7**) in 89% yield, which served as the starting point for phosphine derivatization. While the reduction of dialkyl phosphinic acids to their corresponding (2°) phosphines has been shown with silanes,¹⁷⁻¹⁸ our attempts to reduce **2** or **7** with PhSiH₃ or LiAlH₄ resulted in very low conversions (<10% by ³¹P NMR). However, conversion of **7** to phosphonyl chloride (**8**) followed by subsequent reduction gave compound **9** more efficaciously in 58% yield. Acid catalyzed deprotection of **9** to give **oxo-TMPPhos** (**3**) occurred with 72% yield, notably without protonation of the phosphine. Starting from commercially available NH₄H₂PO₂ and phorone, our six-step route to **3** gives a 20% overall yield versus 5% for the four-step synthesis from PhPH₂, and does not require pyrophoric Li or PhPH₂.

We then demonstrated the potential for transformation of the ketone group starting with its reduction which produced **hydroxy-TMPPhos** (**10**, Figure 2b) in 66% yield. Single crystals of compound **10** suitable

a) Synthesis of 2° phosphines



b) Ketone derivatization



c) P derivatization

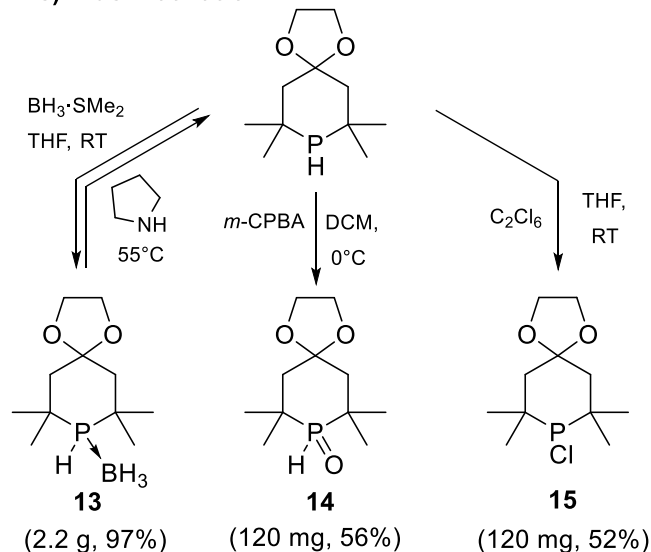


Figure 2. a) Synthesis of 2° phosphines, b) Ketone derivatization, c) P derivatization.

for X-ray diffraction were obtained *via* sublimation and a representation of its molecular structure is shown in the SI (Figure S126). The condensation of **3** with aniline gave imine **11** (65% yield) while the Wittig reaction of **3** with methyltriphenylphosphonium bromide converted the ketone to a methylene group, giving compound **12** in low yield (27%). Next, we explored derivatization of the phosphorus starting with BH_3 protection of **9** to form borane adduct **13** in near quantitative yield (97%), offering a convenient storage form for the 2° phosphine, as it prevents oxidation or quaternization of phosphorus and can be easily deprotected by treatment with pyrrolidine (Figure 2c). Nevertheless, compound **9** was air-stable in solution for up to four days, a trait we had previously observed for **TMPhos**, **1**, in contrast to tBu_2PH which readily decomposes in air to multiple products within a few hours.⁴ However, if the phosphine oxide is desired, it can be obtained cleanly by treatment of **9** with *m*-CPBA, yielding **14** (56%).¹⁹ Dialkylchlorophosphines serve as useful intermediates for the synthesis of *tertiary* phosphines, so we performed the chlorination of **9** with C_2Cl_6 , which afforded compound **15** in 52% yield.²⁰

Electronic Properties

The relative electronic properties of the cyclic phosphinane derivatives were probed using the Huynh Electronic Parameter (HEP), a safer and more accurate alternative to the traditional Tolman Electronic Parameter (Figure 3).²¹⁻²⁵ The HEP uses the ^{13}C NMR signal of the carbene donor (CDCl_3 , referenced to 77.7 ppm) of the $\text{Pr}_2\text{-bimy}$ reporter probe in *trans*- $[\text{PdBr}_2(\text{Pr}_2\text{-bimy})\text{L}]$ ($\text{Pr}_2\text{-bimy}$ = 1,3-diisopropylbenzimidazolin-2-ylidene) complexes. A stronger donor leads to a downfield shift of the $\text{Pr}_2\text{-bimy}$ ^{13}C carbene NMR signal (HEP value), while a weaker donor gives a more upfield shift. In contrast the traditional Tolman Electronic Parameter (TEP) requires the use of toxic $[\text{Ni}(\text{CO})_4]$ and relies on less accurate IR measurements, which may be insufficiently precise in situations where the electronic differences are more subtle, such as here.

To determine the HEP of the 2° phosphinanes we synthesized a series of *trans*- $[\text{PdBr}_2(\text{Pr}_2\text{-bimy})\text{L}]$ complexes (**16** to **21**). They were successfully isolated in the desired *trans* configuration required for HEP

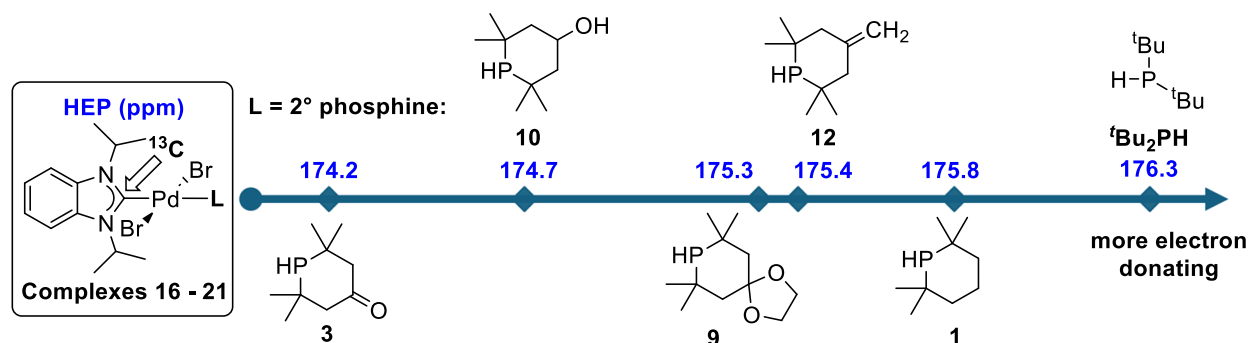


Figure 3. Electronic properties of 2° phosphines represented using the Huynh Electronic Parameter (HEP) in CDCl_3 and referenced to the solvent signal at 77.7 ppm.²²

analysis, despite the known tendency of mixed NHC/phosphine palladium complexes to isomerize to the *cis* form.²⁶⁻²⁷ Single crystal X-ray diffraction (SC-XRD) of complexes **16** and **20** confirmed the expected square planar geometry and a *trans* coordination of the phosphines (see SI Figures S127 – S129).

The measured HEP values of the phosphinanes determined from complexes **16** to **21** ranged from 174.2 to 176.3 ppm. Notably, complex **16** supports that phosphorinone **3** (HEP = 174.2 ppm) is a significantly weaker donor than the non-functionalized **TMPhos**, **1** (HEP = 175.8 ppm), which itself is less donating than acyclic *t*Bu₂PH (HEP = 176.3 ppm). The electron withdrawing effect of the C=O group in **3** is evident when comparing its HEP with its methylene analogue (HEP = 174.2 vs 175.4 ppm), indicating **12** is a stronger donor. The influence of the C=O dipole is also seen when comparing **oxo-TMPhos** (**3**) with the **hydroxy-TMPhos** (**10**) (HEP = 174.7 ppm). Additionally, differences in the hybridization of the γ -carbon in ligands **3** and **12** (sp² vs. sp³) may subtly influence phosphorus donor strength through differences in the ring geometry.²⁸ This can also be seen when comparing the HEP of **TMPhos** with the methylene analogue **12** (Δ = 0.4 ppm) which the latter is a slightly weaker donor. The ²J_{CP} coupling constants across complexes **16** – **21** follow a decreasing trend from 194.2 to 188.2 Hz, consistent with increasing phosphorus donor strength. This is also indicative of the reduced s-character of the P–Pd bond as the electron-donating ability of the phosphorus substituents increases.²⁴

Synthesis of Mono and Bis(phosphine) Ligands

To explore the utility of phosphorinone derivatives, we synthesized the biphenyl phosphine **22** via a Pd-catalyzed coupling of compound **9** with biphenyl triflate (Figure 4, 49%). Deprotection of **22** by heating in an AcOH/H₂O mixture, followed by recrystallization from MeOH, afforded compound **23** (82%). Both **22** and **23** are structurally related to the classical Buchwald ligand JohnPhos, as well as to a series of biphenyl phosphorinanes developed by AbbVie for cross-coupling applications.^{10, 29-30} In AbbVie's approach, the phosphorus heterocycle is introduced at the final step, requiring syntheses of individual biaryl primary phosphines. In contrast, our strategy begins with compound **9**, enabling greater flexibility in modifying the biphenyl ligand backbone without the need to synthesize multiple primary phosphines. The electronic properties of Buchwald-type phosphines have recently been systematically evaluated using the HEP, providing a quantitative basis for comparing donor strengths within this ligand class.³¹

We also synthesized 1,3-bis(tetramethylphosphorinone)propane (**BPP**, **25**), a ligand developed by BASF for the methoxycarbonylation of 3-pentenitrile to produce Nylon monomers.³² Nucleophilic substitution of the *in situ* generated Li salt of **9** with dibromopropane gave the protected bis(phosphine) **24** in 44% yield (Figure 4). Deprotection with aqueous HCl efficiently generated the phosphonium species, avoiding unwanted air oxidation. After neutralization with a mild base, we obtained **BPP** (**25**) in 70% yield. Compared to BASF's original method, this route avoids the need for the highly pyrophoric and volatile 1,3-bis(phosphino)propane, significantly reducing associated hazards. Coordination of **25** with palladium(II) trifluoroacetate gave complex **26** [(**BPP**)Pd(O₂CCF₃)₂]. SC-XRD revealed a square

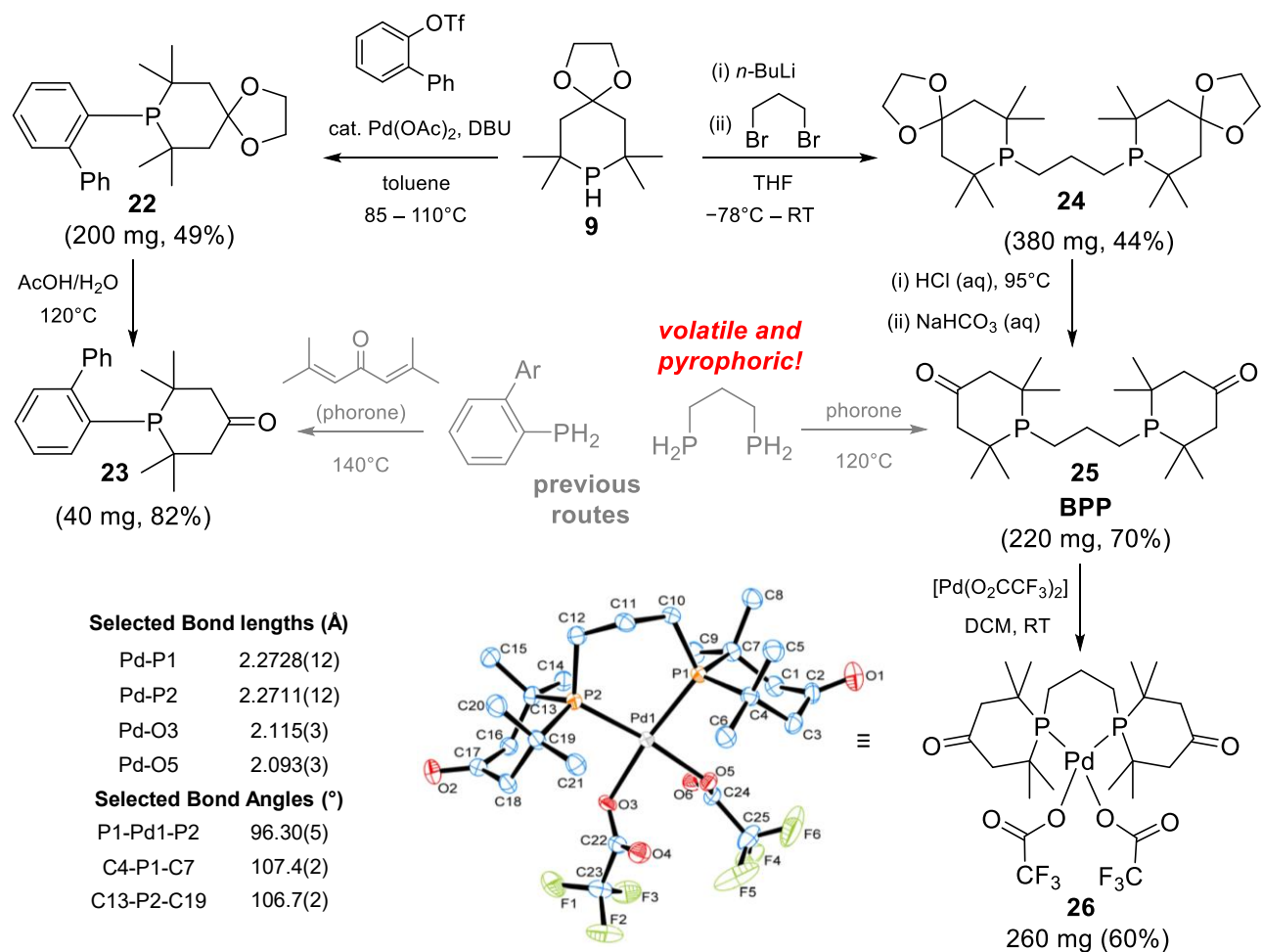


Figure 4. Synthesis of mono- and (bis)phosphorinone ligands.

planar geometry and a relatively large P-Pd-P bite angle of 96.3° (Figure 4), a feature that has been associated with enhanced reactivity in alkene methoxycarbonylation.³³

It was straightforward to synthesize a series of bis(phosphines) (**27** – **33**, Figure 5), showcasing the broad potential of the **oxo-TMPhos** ligands scaffold. Using the BH_3 -protected intermediate **13** significantly improved the efficiency of the nucleophilic substitution steps, affording yields of 84 – 93%. Acid catalyzed deprotection was readily achieved with either aqueous HCl or an AcOH/H₂O (9:1) mixture. In the case of 1,4-bis(2,2,6,6-tetramethylphosphinan-4-one)butane (**BPB**, **28**), treatment with strong acid led to protonation at phosphorus; subsequent neutralization with NaHCO₃ released the free bis(phosphorinone). We also sought an improved route to **BPX** (**5**) which was obtained in respectable yield (58%) *via* the deprotection of **29**. In contrast, our previous synthesis of **BPX** (**5**), based on the condensation of 1,2-bis(phosphinomethyl)benzene with phorone, was low yielding, difficult to scale due to the pyrophoric nature of the primary phosphine, and further complicated by competing side reactions.⁷ Finally, we extended the methodology to prepare aromatic PCP and PNP pincer ligands (**31** and **33**, respectively), since bulky pincer ligands are widely used in homogeneous catalysts.³⁴⁻³⁵ Incorporation of a rigid heterocycle may provide enhanced thermal stability and slower rates of oxidation, thereby addressing key weaknesses in homogeneous catalysis. However, the presence of a functional handle such

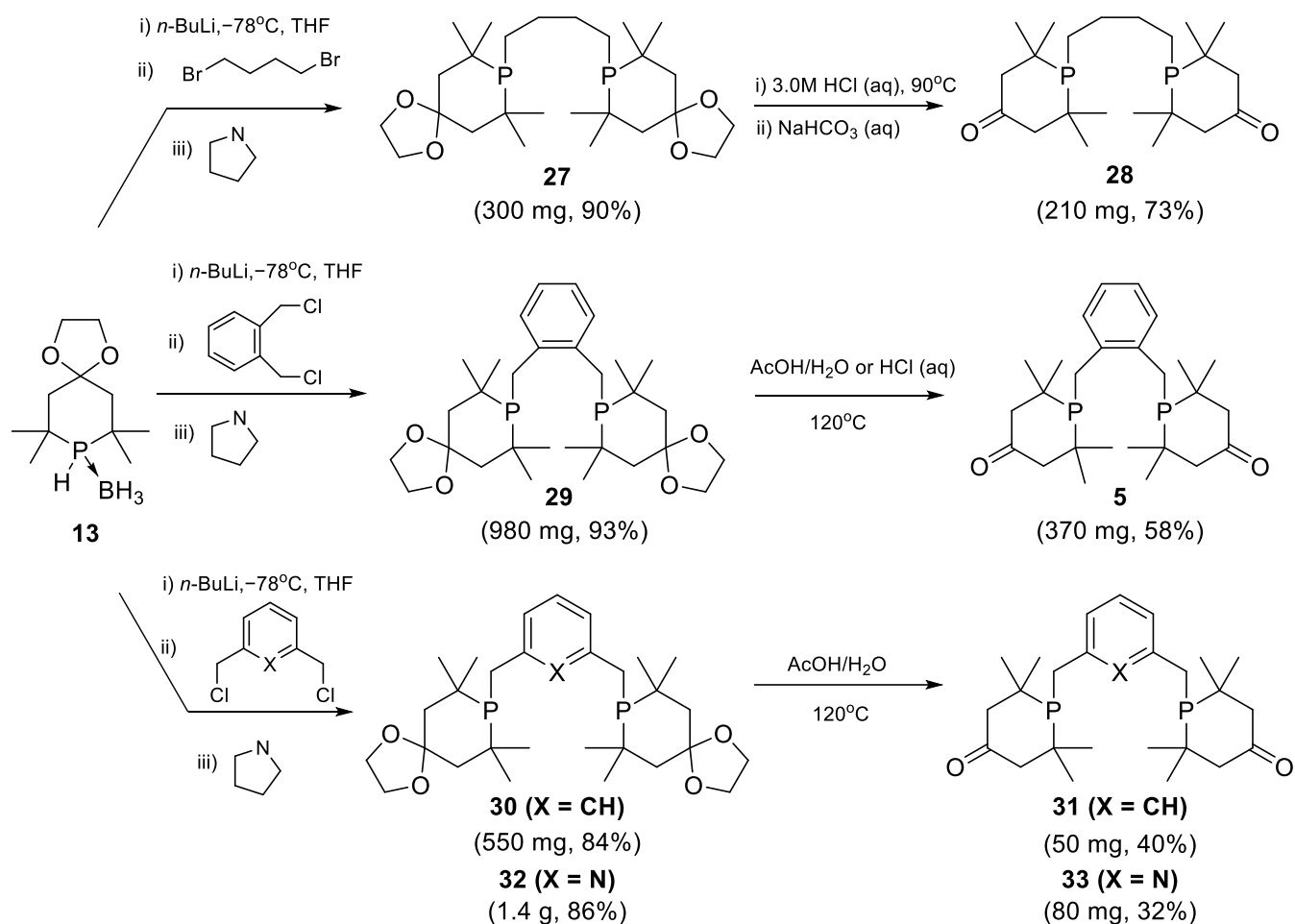


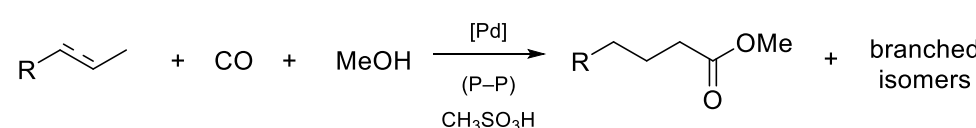
Figure 5. Synthesis of bis(phosphorinone) ligands starting from borane protected 2° phosphine **13**.

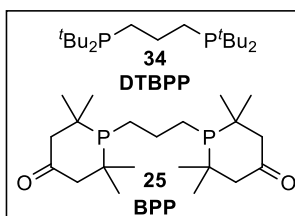
as a ketone may also introduce potential decomposition pathways under harsh conditions (high temperature, acidic, or basic media), including reverse-Michael addition,³⁶ or enolization.³⁷

Methoxycarbonylation of Alkenes

The Pd-catalyzed isomerizing methoxycarbonylation of alkenes is an atom economical method of producing esters, with the methoxycarbonylation of ethene established as a commercial process.³⁸ In this process, the bulky bidentate phosphine 1,2-bis(di-*tert*-butylphosphino)-*o*-xylene (**DTBPX**) serves as the ligand.³⁹ Considerable research effort has since been directed towards the isomerizing methoxycarbonylation of longer-chain alkenes using Pd-**DTBPX** and related catalysts, particularly utilizing bio-based alkenes as alternative feedstocks for the sustainable production of monomers, fragrances, lubricants, and other valuable esters.⁴⁰⁻⁴⁵ Diphosphines bearing bulky *tertiary* alkyl substituents such as *tert*-butyl³⁹ or adamantyl⁴⁶ help produce high linear ester selectivity by disfavoring pathways to branched esters. We have previously shown that the diphosphorinone ligand **BPX (5)**, in combination with Pd, also affords esters in excellent linear selectivity (>95%) while demonstrating

Table 1. Pd-catalyzed methoxycarbonylation of alkenes using **BPP**, **25**.^c





Ligand	Substrate	Major Product	Olefin Conv. (%) ^{b,c}	Yield Ester (%) ^b	TON (ester)	Sel. (l/b) (%)
DTBPP , 34 ^a			5	5	50	87.0
BPP , 25			70	70	670	84.4
BPP , 25			92	92	880	85.4
BPP , 25			51	51	630	88.9
BPP , 25			83	83	1260	89.4
BPP , 25			18	18	80	68.8
BPP , 25			79	76 (+ 3% ether) ^d	770	95.7
BPP , 25			75	75	1110	n.a. ^f
BPP , 25			96	96	1250	90.1

^aDTBPP = 1,3-bis(di-*tert*-butylphosphino)propane, ^bDetermined by GC, ^cTotal olefin conversion to esters and ethers, ^dthe ether, 2-methoxy-2,4,4-trimethylpentane was also obtained in 3% yield, ^eConditions: 50 bar CO pressure, 105°C, 20 μmol of [Pd(OAc)₂], 40 μmol of phosphine ligand, 0.2 mmol of CH₃SO₃H, 3.0 mL of alkene, 6.0 mL of MeOH, time = 4 h, ^fn.a. = not applicable.

significantly higher TONs, up to six times higher than the corresponding Pd-DTBPP analogue when compared under identical conditions.⁷ Diphosphine **25** (BPP) inspired the synthesis of **BPP**. Yet despite previous studies on the related 1,3-bis(di-*tert*-butylphosphino)propane (DTBPP, **34**),^{39, 47-49} **BPP** has remained relatively unexplored since its original disclosure.³² Motivated by this, we explored **BPP** in the Pd-catalyzed isomerizing methoxycarbonylation of a range of alkenes (Table 1).

In a benchmark reaction using *trans*-4-octene, Pd-BPP delivered *more than 13× higher yield and TON* compared to Pd-DTBPP, with only a modest reduction in linear selectivity (84% vs. 87% for methyl nonanoate). The superior activity of **BPP** could be linked to the distinct electronic and structural features of the phosphorinone motif as previously discussed.^{4, 7} It is also possible the carbonyl substituent may participate in key hydrogen-bonded transition states, which have been proposed in models of the rate-determining methanolysis-step.^{47, 50} The substrate scope of Pd-**25** was broad. Functionalized internal olefins such as alkenoic esters (e.g. methyl pent-2-enoate), pent-2-enenitrile and methyl oleate,⁴⁰ all underwent efficient conversion to their corresponding linear esters

as the major products. It should be noted that while activities for Pd-**BPP** are impressive, generally **DTBPX** and **BPX** ligands afford the highest linear selectivity (>95%).⁷ Beyond linear substrates, Pd-**BPP** also mediated selective conversion of branched alkenes (e.g. 2,4,4-trimethylpent-2-ene)⁵¹ and cyclic alkenes (cyclohexene), giving >95% selectivity and >75% yield of the corresponding esters. Moreover, styrene was converted in near-quantitative yield (96%) to methyl 3-phenylpropanoate, with linear regioselectivity of 90%, consistent with other bidentate phosphines.⁵²

CONCLUSION

In summary, we have established a practical and scalable route to **oxo-TMPhos (3)**. The γ -ketone functionality provides a convenient handle for derivatization, while systematic donor strength evaluation of these derivatives revealed the scope for electronic tunability. These building blocks enable access to a diverse range of ligands including bis(phosphines), biphenyl derivatives, and PCP/PNP pincer frameworks, circumventing the use of pyrophoric primary phosphines. Catalytic studies in Pd-catalyzed isomerizing methoxycarbonylation showed that Pd-**BPP** delivered TONs more than an order of magnitude higher than the **DTBPX** analogue, while maintaining a relatively high regioselectivity across a broad substrate scope. Looking ahead, the phosphorinone scaffold offers multiple options for ligand diversification. These could include variation of the ring size to tune the steric environment and donor properties, while the γ -ketone group opens opportunities to adjust electronics, solubility or even to serve as a potential anchor point to immobilise the ligands.

EXPERIMENTAL SECTION

General Procedures

Reactions were conducted under purified nitrogen or argon using standard Schlenk techniques,⁵³ unless noted otherwise, with compounds stored in an argon-filled glovebox. Solvents were dried using an MBraun solvent purification system where the solvents were passed through oxy- and moisture traps under an atmosphere of purified argon. CO gas was purified by passing through oxy- and moisture traps. NMR spectra were recorded on a Bruker AV Neo 400 MHz spectrometer equipped with an RT BBFO probe at a temperature of 298.0 K. ¹H Chemical shifts were referenced to the residual protonated isomer in the NMR solvent used; ¹³C chemical shifts were referenced to the ¹³C chemical shift of the NMR solvent used (note: according to convention HEP complexes **16** – **21** were internally referenced to the solvent residual signal at 77.7 ppm relative to TMS, with the second decimal place presented in subscript format);^{23, 27} ¹⁹F and ³¹P chemical shifts were unreferenced. Mass spectra were recorded on an Agilent G1969A/6210 TOF-MS. Elemental analyses were determined using an Organic Elemental Analysis Flash 2000 CHNS/O Elemental Analyzer. In several cases the experimental elemental analysis values obtained were outside the 0.4% tolerance or could not be obtained. Therefore, NMR spectra of all new compounds have been included in the SI

(Section 2) to demonstrate the absence of detectable contaminants. **TMPhos (1)** and 2,2,6,6-Tetramethylphosphoric acid (**2**) were prepared as described previously.⁴

2,2,6,6-Tetramethylphosphoric acid, 2. Compound **2** was prepared according to previously reported procedures.⁴ The characterization data matched those reported earlier. In addition, we obtained an FTIR spectrum of **2**, which was not included in the original report. FTIR (KBr, cm^{-1}): $\tilde{\nu}$ 3404, 2988, 2977, 2966, 2935, 2873, 1708 (C=O), 1620, 1476, 1464, 1451, 1384, 1294, 1186, 1161, 984, 965, 899, 879, 815, 684 and 580.

2,2,6,6-Tetramethylphosphinan-4-one, 3. 7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **9**, (2.6 g, 12.0 mmol) was dissolved in THF (8 mL) and degassed 3.0 M HCl (aq) (8 mL) was added. The mixture was stirred for 16 h. After this time degassed, deionized (DI) H₂O (40 mL) was added. The product was then extracted with Et₂O (3 $\times$ 30 mL), dried over MgSO₄, and evaporated to give a colorless oil. Yield = 1.5 g (72%). ¹H NMR (400 MHz, CDCl₃): δ 3.19 (1H, d, ¹J_{PH} = 198.1 Hz, PH), 2.49 (2H, d, ²J_{HH} = 12.1 Hz, CH₂), 2.37 (2H, dd, ²J_{HH} = 12.3 Hz, ²J_{HP} = 3.6 Hz, CH₂), 1.22 (6H, d, ³J_{HP} = 14.0 Hz, CH₃) and 1.16 ppm (6H, dd, ³J_{HP} = 15.0 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 211.6 (s, C=O), 57.6 (d, ²J_{CP} = 6.3 Hz, CH₂), 33.6 (d, ¹J_{CP} = 12.4 Hz, C(CH₃)₂), 32.1 (d, ²J_{CP} = 12.9 Hz, CH₃) and 27.5 ppm (d, ²J_{CP} = 24.3 Hz, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ -11.9 ppm (d, ¹J_{HP} = 198.8 Hz, PH). HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 173.1095; found 173.1096.

4,4-(Ethylenedioxy)-2,2,6,6-tetramethylphosphaninic acid, 7. 2,2,6,6-Tetramethylphosphoric acid, **2**, (4.7 g, 23.0 mmol) and ethylene glycol (12.8 mL) were dissolved in toluene (120 mL) and a catalytic amount of *p*-toluene sulfonic acid (438 mg, 2.3 mmol) was added. The mixture was then heated to reflux temperature using a Dean & Stark apparatus to remove H₂O. After 16 h, the mixture was cooled, then washed with DI H₂O (2 $\times$ 80 mL) and brine (50 mL), dried over MgSO₄ and evaporated to yield a white solid. Yield = 5.1 g (89 %). ¹H NMR (400 MHz, CDCl₃): δ 9.76 (1H, br. s, OH), 3.91 (4H, s, OCH₂), 1.86 (4H, d, ³J_{HP} = 15.3 Hz, CH₂) and 1.28 ppm (12H, d, ³J_{HP} = 13.8 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 108.4 (d, ³J_{CP} = 7.9 Hz, C_q), 64.0 (s, CH₂O), 46.4 (s, CH₂), 33.2 (d, ¹J_{CP} = 84.7 Hz, C_q) and 24.4 ppm (d, ²J_{CP} = 1.1 Hz, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 61.5 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 249.1256; found 249.1251. FTIR (KBr, cm^{-1}): $\tilde{\nu}$ 2964, 2919, 1714, 1473, 1456, 1294, 1217, 1126 and 1038. Elem. Anal. Calcd for C₁₁H₂₁O₄P: C, 53.22; H, 8.53. Found: C, 53.29; H, 8.39.

8-Chloro-7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane 8-oxide, 8. 4,4-(Ethylenedioxy)-2,2,6,6-tetramethylphosphaninic acid, **7**, (5.1 g, 20.4 mmol) was dissolved in CH₂Cl₂ (100 mL), then lutidine (5.5 g, 5.6 mL, 51.2 mmol) and DMF (0.15 g, 0.16 mL, 2.0 mmol) were added. The mixture was cooled to 0 °C, whereupon oxayl chloride (6.5 g, 4.4 mL, 51.2 mmol) was added. A gas evolved, and the solution changed color from yellow to orange. After 96 h, the volatiles were evaporated under reduced pressure. The crude material was extracted with ether (3 $\times$ 40 mL), filtered to remove insoluble impurities, and the solvent was evaporated to yield an off-white solid. Yield = 5.4 g (*quantitative*). ¹H NMR (400 MHz, CDCl₃): δ 3.99 (2H, app. t, J = 5.9 Hz, OCH₂), 3.89 (2H, app. t, J = 5.9 Hz, OCH₂), 2.02 (2H, dd, ²J_{HH} = 14.1 Hz, ³J_{HP} = 10.8 Hz, CCH₂), 1.89 (2H, dd, ³J_{HP} = 27.1 Hz, ²J_{HH} = 14.3 Hz, CCH₂), 1.52 (6H, d, ³J_{PH} = 15.7 Hz, CH₃) and 1.38 ppm (6H, d, ³J_{PH} = 16.5 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 107.5 (d, ³J_{CP} = 7.5 Hz, O₂C_q), 64.8 (s, OCH₂), 63.8 (s, OCH₂), 46.4 (d, ²J_{CP} = 1.2 Hz, CCH₂), 39.1 (d, ¹J_{CP} = 62.2 Hz, C(CH₃)₂), 26.7 (d, ²J_{CP} = 3.4 Hz, CH₃) and 24.1 ppm (s, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 85.9 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 267.0917; found 267.0906.

7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, 9. Method A: 8-Chloro-7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane 8-oxide, **8**, (5.4 g, 20.3 mmol) in Et₂O (20 mL) was added dropwise over 15 mins to a suspension of LiAlH₄ (1.5 g, 40.5 mmol) in Et₂O (200 mL) cooled to 0 °C. The mixture was allowed to warm to RT and stirred for 16 h. It was then cooled to 0 °C and quenched slowly with NaOH (aq, 20%, 4.0 mL), followed by degassed DI H₂O (2.0 mL). The mixture was warmed to RT, dried over MgSO₄, filtered, and the volatiles were evaporated under reduced pressure to give a white solid. Yield = 2.6 g (58%). ¹H NMR (400 MHz, CDCl₃): δ 3.98

(2H, app. t, $J = 6.4$ Hz, OCH_2), 3.87 (2H, app. t, $J = 6.4$ Hz, OCH_2), 2.68 (1H, d of sept, $^1J_{\text{HP}} = 199.1$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, PH), 1.85 (2H, dd, $^1J_{\text{HH}} = 13.6$ Hz, $^3J_{\text{HP}} = 4.4$ Hz, CH), 1.49 (2H, d, $^1J_{\text{HH}} = 13.6$ Hz, CH), 1.26 (6H, dd, $^3J_{\text{HP}} = 14.4$ Hz, $^4J_{\text{HP}} = 1.8$ Hz, CH_3) and 1.09 ppm (6H, d, $^3J_{\text{HP}} = 14.1$ Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 111.1 (s, O_2C_q), 65.1 (s, CH_2O), 63.1 (s, CH_2O), 49.4 (d, $^2J_{\text{CP}} = 6.5$ Hz, CH_2), 33.1 (d, $^2J_{\text{CP}} = 13.0$ Hz, CH_3), 29.5 (d, $^1J_{\text{CP}} = 10.1$ Hz, $\text{C}(\text{CH}_3)_2$) and 27.0 ppm (d, $^2J_{\text{CP}} = 25.3$ Hz, $\text{C}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ -16.3 ppm. ^{31}P NMR (162 MHz, CDCl_3): δ -16.3 ppm (d, $^1J_{\text{HP}} = 198.8$ Hz, PH). HR-MS (+ve ESI): m/z (calc.) $[\text{M}+\text{H}]^+$ 217.1357; found 217.1348. FTIR (KBr, cm^{-1}): $\tilde{\nu}$ 2925, 2262 (P-H), 1472, 1449, 1298, 1211, 1186, 1093, 1028, 1015, 967, 947, 882, 834, 786, 724, 629 and 532. **Method B:** 7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane borane complex, **13** (60 mg, 0.26 mmol) and pyrrolidine (3 mL, 48.7 mmol) were heated at 55 °C for 16 h. After this time, the volatiles were removed *in vacuo* to give a colorless solid. The crude material was taken up in CHCl_3 and passed through a small plug of neutral alumina (~2 cm). Evaporation of the solvent yielded a solid. Yield = 40 mg (71%). The characterization was consistent with that obtained using Method A.

2,2,6,6-Tetramethylphosphinan-4-ol, 10. 2,2,6,6-Tetramethylphosphinan-4-one, **3**, (600 mg, 3.48 mmol) was dissolved in THF (5 mL) and added to a suspension of LiAlH_4 (260 mg, 6.97 mmol) cooled to 0 °C. The mixture was allowed to warm to RT and stirred for 16 h. After this, the reaction was cooled to 0 °C and quenched slowly with degassed $\text{DI H}_2\text{O}$ (1.0 mL). The mixture was dried over MgSO_4 , filtered, and the solvent was evaporated under reduced pressure to give the crude product. The crude material was sublimed under vacuum (50 °C, 0.1 mbar) to give a white crystalline solid. Yield = 400 mg (66%). ^1H NMR (400 MHz, d_6 -DMSO): δ 4.49 (1H, d, $^3J_{\text{HH}} = 4.7$ Hz, OH), 3.66 (1H, tdt, $^3J_{\text{HH}} = 11.6$, $^3J_{\text{HH}} = 4.8$ Hz, $^3J_{\text{HH}} = 3.4$ Hz, CHOH), 2.53 (1H, $^1J_{\text{HP}} = 196.9$ Hz, PH), 1.91 – 1.85 (2H, m, CH_2), 1.13 – 1.10 (2H, m, CH_2), 1.10 (6H, dd, $^3J_{\text{HP}} = 15.3$ Hz and $^4J_{\text{HH}} = 1.6$ Hz, CH_3) and 1.04 ppm (6H, d, $^3J_{\text{HP}} = 14.0$ Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, d_6 -DMSO): δ 64.10 (s, CHOH), 52.3 (d, $^2J_{\text{CP}} = 6.4$ Hz, CH_2), 32.2 (d, $^2J_{\text{CP}} = 13.3$ Hz, CH_3), 29.4 (d, $^1J_{\text{CP}} = 10.2$ Hz, C_q) and 27.0 ppm (d, $^2J_{\text{CP}} = 25.7$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, d_6 -DMSO): δ -14.4 ppm. ^{31}P NMR (162 MHz, d_6 -DMSO): δ -14.4 ppm (d, $^1J_{\text{HP}} = 196.8$ Hz, PH). HR-MS (+ve ESI): m/z (calc.) $[\text{M}+\text{H}]^+$ 175.1252; found 175.1241. FTIR (KBr, cm^{-1}): $\tilde{\nu}$ 2952, 2913, 2858, 2836, 2272, 2259 (P-H), 1631, 1467, 1452, 1380, 1363, 1345, 1275, 1224, 1175, 1156, 1101, 1039, 1024, 968, 902, 878, 852, 782, 629 and 620. Elem. Anal. Calcd for $\text{C}_9\text{H}_{19}\text{OP}$: C, 62.05; H, 10.99. Found: C, 62.00; H, 10.83. Single crystals of compound **10** suitable for X-ray diffraction were obtained from the sublimation of the crude material.

2,2,6,6-Tetramethyl-N-phenylphosphinan-4-imine, 11. 2,2,6,6-Tetramethylphosphinan-4-one, **3**, (600 mg, 3.48 mmol) was added to THF (6.0 mL) containing 3 Å mol. sieves (1 g, activated by heating to 200 °C under vacuum for 3 h). Aniline (320 mg, 0.32 mL, 3.48 mmol) and *p*-toluenesulfonic acid (66 mg, 0.35 mmol) were added, and the mixture was heated to 60 °C for 16 h. The reaction was monitored by ^{31}P NMR spectroscopy, which indicated approximately 80% conversion. Heating was continued for another 72 h, after which time the desired compound was isolated by fractional distillation. A colorless liquid was distilled off under high vacuum (0.1 mbar) at 150 °C. Yield = 620 mg (65%). ^1H NMR (400 MHz, CDCl_3): 7.27 (2H, td, $^3J_{\text{HH}} = 8.3$ Hz, $^3J_{\text{HH}} = 7.4$ Hz, ArH), 7.03 (1H, tt, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, ArH), 6.68 (2H, td, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, ArH), 3.08 (1H, dt, $^1J_{\text{HP}} = 198.2$ Hz, $^4J_{\text{HH}} = \text{PH}$), 2.66 – 2.57 (2H, m, CH_2), 2.46 (1H, d, $^2J_{\text{HH}} = 12.6$ Hz, CH_2), 1.95 (1H, d, $^2J_{\text{HH}} = 13.0$ Hz, CH_2), 1.29 (3H, dd, $^3J_{\text{HP}} = 15.0$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, CH_3), 1.23 (3H, d, $^3J_{\text{HP}} = 14.1$ Hz, CH_3), 1.05 (3H, d, $^3J_{\text{HP}} = 13.9$ Hz, CH_3) and 1.01 ppm (3H, d, $^3J_{\text{HP}} = 20.4$ Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 172.5 (s, $\text{C}=\text{N}$), 150.7 (s, ArC_q), 128.9 (s, ArCH), 123.1 (s, ArCH), 119.7 (s, ArCH), 55.5 (d, $^2J_{\text{CP}} = 6.5$ Hz, CH_2), 46.6 (d, $^2J_{\text{CP}} = 6.5$ Hz, CH_2), 32.2 (d, $^1J_{\text{CP}} = 4.8$ Hz, $\text{C}(\text{CH}_3)_2$), 32.1 (d, $^1J_{\text{CP}} = 4.2$ Hz, $\text{C}(\text{CH}_3)_2$), 32.0 (d, $^2J_{\text{CP}} = 13.3$ Hz, CH_3), 31.7 (d, $^2J_{\text{CP}} = 13.3$ Hz, CH_3), 27.7 (d, $^2J_{\text{CP}} = 24.7$ Hz, CH_3) and 26.8 ppm (d, $^2J_{\text{CP}} = 24.0$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ -8.7 ppm. ^{31}P NMR (162 MHz, CDCl_3): δ -8.7 ppm (d, $^1J_{\text{HP}} = 198.8$ Hz, PH). HR-MS (+ve ESI): m/z (calc.) $[\text{M}+\text{H}]^+$ 248.1568; found 248.1560.

2,2,6,6-Tetramethyl-4-methylenephosphinane, 12. Potassium tert-butoxide (200 mg, 1.7 mmol) was added to methyltriphenylphosphonium bromide (600 mg, 1.7 mmol) suspended in Et_2O (20 mL) at RT. The mixture was stirred for 20 mins, producing a bright yellow suspension. The solution was cooled to 0 °C, and 2,2,6,6-

tetramethylphosphinan-4-one, **3**, (100 mg, 0.7 mmol) in Et₂O (5.0 mL) was added dropwise. Upon complete addition, the solution's color changed from bright yellow to white. The reaction was stirred for 15 h at RT. The solvent was first removed through atmospheric distillation, followed by vacuum distillation (50 °C, 0.1 mbar) to obtain the crude product. Yield = 32 mg (27%). ¹H NMR (400 MHz, CDCl₃): δ 4.79 (1H, s, C=CH₂), 2.86 (1H, d of sept, ¹J_{HP} = 198.7 Hz, ⁴J_{HH} = 1.6 Hz, PH), 2.24 (2H, dd, ²J_{HH} = 12.8 Hz, ³J_{HP} = 4.3 Hz, CH₂), 2.06 (2H, d, ²J_{HH} = 12.8 Hz, CH₂), 1.10 (6H, d, ³J_{HP} = 14.1 Hz CH₃) and 1.08 (6H, dd, ³J_{HP} = 15.2 Hz, ⁴J_{HP} = 1.5 Hz CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 145.6 (s, C=CH₂), 112.6 (s, C=CH₂), 52.4 (d, ²J_{CP} = 6.6 Hz, PCCH₂), 31.8 (d, ²J_{CP} = 12.3 Hz, PC(CH₃)₂), 30.1 (d, ¹J_{CP} = 9.8 Hz, PC(CH₃)₂) and 25.7 ppm (d, ²J_{CP} = 23.3 Hz, PC(CH₃)₂). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -9.4 ppm. ³¹P NMR (162 MHz, CDCl₃): δ -9.4 ppm (d, ¹J_{HP} = 198.8 Hz, PH). HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 171.1298; found 171.1291. **Note:** The crude material contained volatile impurities (benzene, Et₂O and *t*-BuOH) that were challenging to remove completely due to the volatile nature of compound **12**, as confirmed by NMR spectroscopy (See SI, Figures S23 and S24).

7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane borane complex, 13. 7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **9**, (2.1 g, 9.9 mmol) was dissolved in THF (10 mL) and BH₃·SMe₂ (2.0 M in THF, 5.2 mL, 10.4 mmol) was added. The reaction was stirred for 16 h at RT. The solvent was evaporated under reduced pressure to give a white solid, which was washed with pentane (2 × 10 mL) and dried *in vacuo*. Yield = 2.2 g (97%). ¹H NMR (400 MHz, CDCl₃): δ 4.03 (1H, d of q, ¹J_{HP} = 346.7 Hz, ³J_{HH} = 6.3 Hz, PH), 4.03 – 3.85 (4H, m, OCH₂), 1.91 (2H, dd, ³J_{HP} = 17.2 Hz, ²J_{HH} = 14.0 Hz, CH), 1.69 (2H, dd, ²J_{HH} = 13.8 Hz, ³J_{HP} = 2.2 Hz, CH), 1.33 (6H, d, ³J_{HP} = 14.3 Hz, CH₃), 1.23 (6H, d, ³J_{HP} = 15.4 Hz, CH₃) and 0.46 ppm (3H, q, ¹J_{BH} = 99.2 Hz, BH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 108.4 (d, ³J_{CP} = 5.0 Hz, OC_q), 65.3 (s, OCH₂), 63.4 (s, OCH₂), 48.1 (d, ²J_{CP} = 5.2 Hz, CH₂), 30.8 (d, ²J_{CP} = 1.2 Hz, CH₃), 29.0 (d, ¹J_{CP} = 28.9 Hz, C_q) and 22.7 ppm (d, ²J_{CP} = 7.5 Hz, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 31.3 ppm (br. q, ¹J_{PB} = 59.4 Hz). HR-MS (+ve ESI): m/z (calc.) [M+Na]⁺ 253.1505; found 253.1500. FTIR (KBr, cm⁻¹): $\tilde{\nu}$ 2957, 2925, 2852, 2323 (P–H), 1738, 1639, 1468, 1455, 1424, 1396, 1169, 1094, 1026, 978, 947, 925, 803, 677 and 548. Elem. Anal. Calcd for C₁₁H₂₄BO₂P: C, 57.42; H, 10.51. Found: C, 57.19; H, 10.40.

7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane 8-oxide, 14. 7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **9**, (200 mg, 0.92 mmol) was dissolved in CH₂Cl₂ (5 mL) and cooled to 0 °C. *m*-CPBA (70%, aq) (240 mg, 0.97 mmol) in CH₂Cl₂ (3 mL) was added slowly. After 10 mins, the reaction mixture was allowed to warm to RT and stirred for 2 h. The volatiles were removed *in vacuo* to yield a white solid. The crude material was dissolved in CH₂Cl₂ (10 mL) and washed with saturated NaHCO₃ (aq. 2 × 10 mL). The combined aqueous phases were backwashed with CH₂Cl₂ (10 mL), and the combined organic phases were washed with brine (10 mL) and dried over MgSO₄. Filtration and evaporation of the solvent gave a white hygroscopic solid, which was handled under argon to prevent moisture absorption. Yield = 120 mg (56%). ¹H NMR (400 MHz, CDCl₃): δ 6.30 (1H, d, ¹J_{HP} = 432.4 Hz, PH), 3.98 (2H, t, ³J_{HH} = 6.4 Hz, CH₂O), 3.84 (2H, t, ³J_{HH} = 6.6 Hz, CH₂O), 1.89 – 1.71 (4H, m, C_qCH₂), 1.38 (6H, d, ³J_{HP} = 12.4 Hz, CH₃) and 1.27 ppm (6H, d, ³J_{HP} = 15.8 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 107.6 (d, ³J_{CP} = 6.5 Hz, O₂C_q), 65.0 (s, CH₂O), 63.5 (s, CH₂O), 45.7 (d, ²J_{CP} = 2.4 Hz, CH₂), 32.8 (d, ¹J_{CP} = 59.4 Hz, C(CH₃)₂), 28.2 (d, ²J_{CP} = 1.0 Hz, CH₃) and 20.8 ppm (s, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 57.1 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 233.1307; found 233.1299. FTIR (KBr, cm⁻¹): $\tilde{\nu}$ 3010, 2962, 2929, 2910, 2306 (P–H), 1474, 1385, 1369, 1343, 1301, 1216, 1172, 1151, 1093, 1018, 978, 947, 926, 899, 841, 830, 789, 726, 665, 612, and 527. Elem. Anal. Calcd for C₁₁H₂₁O₃P: C, 56.89; H, 9.11. Found: C, 57.52; H, 8.94.

8-chloro-7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, 15. 7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **9**, (200 mg, 0.92 mmol) was dissolved in THF (2 mL). Hexachloroethane (220 mg, 0.92 mmol) in THF (2 mL) was added. The mixture was stirred continuously at RT for 3 weeks. After this time, the volatiles were removed *in vacuo*. Yield = 120 mg (52%). ¹H NMR (400 MHz, CDCl₃): δ 3.98 (2H, dt, ³J_{HH} = 6.5 Hz, J = 0.7 Hz, CH₂O), 3.88 (2H, dt, ³J_{HH} = 6.8 Hz, J = 0.7 Hz, CH₂O), 1.95 (2H, d, ²J_{HH} = 14.2 Hz, CH₂), 1.52 (2H, dd, ²J_{HH} = 14.1 Hz, ³J_{HP} = 6.2 Hz, CH₂), 1.33 (6H, d, ³J_{HP} = 18.5 Hz, CH₃) and 1.20 ppm (6H, d, ³J_{HP} = 12.3 Hz, CH₃). ¹³C{¹H}

NMR (101 MHz, CDCl₃): δ 110.2 (s, O₂C_q), 65.1 (s, CH₂O), 63.1 (s, CH₂O), 40.9 (d, ²J_{CP} = 2.9 Hz, C_qCH₂), 35.1 (d, ¹J_{CP} = 33.4 Hz, C(CH₃)₂), 31.2 (d, ²J_{CP} = 11.6 Hz, CH₃) and 25.4 ppm (d, ²J_{CP} = 34.7 Hz, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 120.6 ppm. FTIR (KBr, cm⁻¹): $\tilde{\nu}$ 2946, 2913, 1637, 1476, 1448, 1383, 1358, 1348, 1300, 1260, 1175, 1091, 1026, 965, 948, 902, 820, 789, 728, 615 and 551. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 251.0968; found 251.0960.

[trans-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(2,2,6,6-tetramethylphosphinan-4-one)palladium(II)], 16.

Di- μ -bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II)²⁷ (66 mg, 0.07 mmol) and 2,2,6,6-tetramethylphosphinan-4-one, **3**, (24 mg, 0.14 mmol) were stirred and heated at 40 °C for 96 h in CH₂Cl₂ (8 mL). The volatiles were evaporated to obtain a yellow powder. Yield = 78 mg (87%). Recrystallization in CH₂Cl₂/hexane afforded yellow crystals suitable for SC-XRD. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (2H, dd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 3.2 Hz, ArH), 7.24 (2H, dd, ³J_{HH} = 6.3 Hz, ⁴J_{HH} = 3.3 Hz, ArH), 5.93 (2H, hept, ³J_{HH} = 7.1 Hz, NCH(CH₃)₂), 4.60 (1H, d, ¹J_{HP} = 345.7 Hz, PH), 3.18 (2H, dd, ²J_{HH} = 13.0 Hz, ³J_{HP} = 7.5 Hz, PCCH₂), 2.35 (2H, app t, ²J_{HH} = 13.0 Hz, PCCH₂), 1.77 (12H, d, ³J_{HH} = 7.2 Hz, NCH(CH₃)₂), 1.71 (6H, d, ³J_{HP} = 17.0 Hz, PC(CH₃)₂) and 1.49 ppm (6H, d, ³J_{HP} = 12.1 Hz, PC(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 209.0 (d, ³J_{CP} = 5.1 Hz, CO), 174.2₀ (d, ²J_{CP} = 194.2 Hz, C-Pd-P), 134.1 (d, ⁴J_{CP} = 6.2 Hz, C_qNC-Pd), 123.2 (s, ArCH), 113.5 (s, ArCH), 55.4 (d, ²J_{CP} = 2.2 Hz, PCCH₂), 54.7 (s, NCH(CH₃)₂), 35.6 (d, ¹J_{CP} = 16.0 Hz, PC), 32.6 (d, ²J_{CP} = 1.8 Hz, PC(CH₃)₂), 30.7 (d, ²J_{CP} = 10.2 Hz, PC(CH₃)₂) and 21.6 ppm (s, NCH(CH₃)₂). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 37.0 ppm (s, PH). ³¹P NMR (162 MHz, CDCl₃): δ 37.0 ppm (d, ¹J_{HP} = 345.4 Hz, PH). HR-MS (+ve ESI): m/z (calc.) [M – Br]⁺ = 559.0705; found 559.0708. FTIR (KBr, cm⁻¹): $\tilde{\nu}$ 2974, 2962, 2933, 2918, 1702 (C=O), 1610, 1477, 1422, 1407, 1373, 1314, 1297, 1174, 1143, 1094, 1023, 967, 878, 849, 836, 745, 686, 626 and 548. Elem. Anal. Calcd for C₂₂H₃₅Br₂N₂OPPd: C, 41.24; H, 5.51; N, 4.37. Found: C, 41.54; H, 5.32; N, 4.37.

[trans-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(2,2,6,6-tetramethylphosphinan-4-ol)palladium(II)], 17.

Di- μ -bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II)²⁷ (66 mg, 0.07 mmol) and 2,2,6,6-tetramethylphosphinan-4-ol, **10**, (24 mg, 0.14 mmol) were stirred at 40 °C for 18 h in degassed CH₂Cl₂ (8 mL). The solvent was evaporated under reduced pressure to obtain a yellow powder. Yield = 82.9 mg (92%). ¹H NMR (400 MHz, CDCl₃): δ 7.57 (2H, dd, ³J_{HH} = 6.2 Hz, ³J_{HH} = 3.2 Hz, ArH), 7.22 (2H, dd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 3.2 Hz, ArH), 5.95 (2H, hept, ³J_{HH} = 7.1 Hz, NCH(CH₃)₂), 4.12 (1H, d, ¹J_{HP} = 339.6 Hz, PH), 4.02 (1H, app t, ³J_{HH} = 11.4 Hz, CHOH), 2.05 (2H, app t, ²J_{HH} = 14.7 Hz, PCCH₂), 1.78 (12H, d, ³J_{HH} = 7.1 Hz, NC(CH₃)₂), 1.58 (6H, d, ³J_{HP} = 13.5 Hz, P(CCH₃)₂), 1.48 (2H, m, PCCH₂) and 1.46 ppm (6H, d, ³J_{HP} = 16.6 Hz, PC(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 174.6₆ (d, ²J_{CP} = 191.8 Hz, C-Pd-P), 134.2 (d, ⁴J_{CP} = 6.1 Hz, C_qNC-Pd), 123.0 (s, ArCH), 113.4 (s, ArCH), 65.8 (d, ³J_{CP} = 3.2 Hz, C-OH), 54.6 (s, NCH(CH₃)₂), 53.0 (d, ²J_{CP} = 6.2 Hz, PCCH₂), 33.9 (d, ¹J_{CP} = 15.9 Hz, PC(CH₃)₂), 32.7 (d, ²J_{CP} = 6.5 Hz, PC(CH₃)₂), 26.8 (d, ²J_{CP} = 7.7 Hz, PC(CH₃)₂), and 21.6 ppm (s, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 31.2 ppm (d, ¹J_{HP} = 339.3 Hz, PH). HR-MS (+ve ESI): m/z (calc) [M – Br]⁺ = 561.0862; found 561.0850. FTIR (KBr, cm⁻¹): $\tilde{\nu}$ 3491, 2978, 2952, 2925, 2344 (P–H), 1603, 1475, 1421, 1403, 1371, 1335, 1313, 1295, 1229, 1173, 1143, 1093, 1043, 968, 903, 859, 836, 806, 756, 748, 686, 636 and 548. Elem. Anal. Calcd for C₂₂H₃₇Br₂N₂OPPd: C, 41.11; H, 5.80; N, 4.36. Found: C, 40.95; H, 5.63; N, 4.34.

[trans-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane)palladium(II)], 18.

Di- μ -bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II)²⁷ (66 mg, 0.07 mmol) and 7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **9**, (30 mg, 0.14 mmol) were stirred at 40 °C for 18 h in THF (8 mL). The solvent was evaporated to obtain yellow powder. Yield = 59.8 mg (62%). ¹H NMR (400 MHz, CDCl₃): δ 7.56 (2H, dd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 3.2 Hz, ArH), 7.21 (2H, dd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 3.2 Hz, ArH), 5.94 (2H, hept, ³J_{HH} = 7.1 Hz, NCH(CH₃)₂), 4.28 (1H, d, ¹J_{HP} = 341.0 Hz, PH), 3.94 (4H, m, OCH₂CH₂O), 2.18 (2H, dd, ²J_{HH} = 14.1 Hz, ³J_{HP} = 10.4 Hz, P(CCH₂)), 1.76 (12H, d, ³J_{HH} = 7.1 Hz, CH₃), 1.67 (6H, d, ³J_{HP} = 16.0 Hz, PC(CH₃)₂), 1.65 (2H, dd, ²J_{HH} = 14.1 Hz, ³J_{HP} = 10.4 Hz, P(CCH₂)), and 1.48 ppm (6H, d, ³J_{HP} = 14.1 Hz, PC(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 175.2₆ (d, ²J_{CP} = 191.6 Hz, C-Pd-P), 134.2 (d, ⁴J_{CP} = 6.1 Hz, CNC-Pd), 122.9 (s, ArCH), 113.4 (s, ArCH), 110.0 (d, ³J_{CP} = 4.3 Hz, OC_q), 64.9 (s, OCH₂), 64.5 (s,

OCH₂), 54.6 (s, NCH(CH₃)₂), 48.4 (d, ²J_{CP} = 3.3 Hz, PCCH₂), 33.0 (d, ²J_{CP} = 1.6 Hz, PCCH₃), 32.9 (d, ¹J_{CP} = 18.2 Hz, PC), 29.4 (d, ²J_{CP} = 9.2 Hz, PCCH₃) and 21.5 ppm (s, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 34.7 ppm (d, ¹J_{HP} = 341.2 Hz, PH). HR-MS (+ve ESI): m/z (calc) [M – Br]⁺ = 603.0967; found 603.0936.

[*trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(2,2,6,6-tetramethyl-4-methylenephosphinane)palladium(II)], 19.

Di-*μ*-bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II)²⁷ (66 mg, 0.07 mmol) and 2,2,6,6-tetramethyl-4-methylenephosphinane, **12**, (24 mg, 0.14 mmol) were stirred at 40 °C for 18 h in CH₂Cl₂ (8 mL). The solvent was evaporated to obtain yellow powder. Yield = 81.9 mg (88%). ¹H NMR (400 MHz, CDCl₃): δ 7.56 (2H, dd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 3.2 Hz, ArH), 7.22 (2H, dd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 3.2 Hz, ArH), 5.95 (2H, hept, ³J_{HH} = 7.1 Hz, NCH(CH₃)₂), 4.87 (2H, s, C=CH₂), 4.35 (1H, d, ¹J_{HP} = 340.1 Hz, PH), 2.59 (2H, dd, ²J_{HH} = 13.1 Hz, ³J_{HP} = 11.2 Hz, PCCH₂), 2.14 (2H, dd, ²J_{HH} = 13.2 Hz, ³J_{HP} = 10.3 Hz, PCCH₂), 1.77 (12H, d, ³J_{HH} = 7.0 Hz, CH₃), 1.56 (6H, d, ³J_{HP} = 15.7 Hz, PC(CH₃)₂), and 1.43 ppm (6H, d, ³J_{HP} = 14.5 Hz, PC(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 175.4₀ (d, ²J_{CP} = 191.2 Hz, C-Pd-P), 134.2 (d, ⁴J_{CP} = 6.1 Hz, C_qNC-Pd), 123.0 (s, ArCH), 115.7 (s, C=CH₂), 115.4 (s, C=CH₂), 113.4 (s, ArCH), 54.6 (s, NCH(CH₃)₂), 51.2 (d, ²J_{CP} = 4.0 Hz, PCCH₂), 34.0 (d, ¹J_{CP} = 16.7 Hz, PC), 32.0 (d, ²J_{CP} = 2.1 Hz, PCCH₃), 28.1 (d, ²J_{CP} = 8.9 Hz, PC(CH₃)₂), and 21.6 ppm (s, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 37.4 ppm (d, ¹J_{HP} = 342.1 Hz, PH). HR-MS (+ve ESI): m/z (calc) [M – Br]⁺ = 557.0913; found 557.0905. FTIR (KBr, cm⁻¹): ν̄ 2978, 2934, 1953, 1910, 1601, 1472, 1417, 1391, 1372, 1311, 1294, 1174, 1141, 1091, 1022, 85, 803, 751 and 548.

[*trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(2,2,6,6-tetramethylphosphinane)palladium(II)], 20.

Di-*μ*-bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II)²⁷ (66 mg, 0.07 mmol) and 2,2,6,6-tetramethylphosphinane, **1**, (22 mg, 0.14 mmol) were stirred at 40 °C for 18 h in CH₂Cl₂ (8 mL). The mixture was further stirred at RT for 72 h. The solvent was evaporated to obtain yellow powder. Yield = 74 mg (85%). Recrystallization in CH₂Cl₂/pentane afforded yellow crystals. ¹H NMR (400 MHz, CDCl₃): δ 7.56 (2H, dd, ³J_{HH} = 6.1 Hz, ⁴J_{HH} = 3.1 Hz, ArH), 7.21 (2H, dd, ³J_{HH} = 6.1 Hz, ⁴J_{HH} = 3.1 Hz, ArH), 5.96 (2H, hept, ³J_{HH} = 7.1 Hz, NCH(CH₃)₂), 4.22 (1H, d, ¹J_{HP} = 339.7 Hz, PH), 1.96 – 1.86 (2H, m, PCCH₂), 1.77 (12H, d, ³J_{HH} = 7.1 Hz, CH₃), 1.70 (2H, m, PCCCH₂), 1.57 (6H, d, ³J_{HP} = 14.9 Hz, PC(CH₃)₂), 1.47 (2H, m, PCCCH₂), 1.41 ppm (6H, d, ³J_{HP} = 15.1 Hz, PCCCH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 175.8₂ (d, ²J_{CP} = 190.0 Hz, C-Pd-P), 134.2 (d, ⁴J_{CP} = 6.2 Hz, CNC-Pd), 122.9 (s, ArCH), 113.4 (s, ArCH), 54.5 (s, NCH(CH₃)₂), 42.9 (d, ²J_{CP} = 4.4 Hz, PCCH₂), 32.6 (d, ¹J_{CP} = 16.4 Hz, PC), 32.5 (d, ²J_{CP} = 2.9 Hz, PCCH₃), 27.8 (d, ²J_{CP} = 8.7 Hz, PCCH₃), 21.6 (s, CH₃) and 20.6 ppm (d, ³J_{CP} = 4.4 Hz, PCCCH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 37.2 ppm (s, PH). ³¹P NMR (162 MHz, CDCl₃): δ 37.2 ppm (d, ¹J_{HP} = 340.2 Hz, PH). HR-MS (+ve ESI): m/z (calc) [M – Br]⁺ = 545.0912; found 545.0912. FTIR (KBr, cm⁻¹): ν̄ 2978, 2932, 2860, 2338 (P–H), 1642, 1607, 1476, 1454, 1434, 1404, 1386, 1371, 1313, 1295, 1231, 1174, 1104, 1093, 1023, 973, 943, 934, 806, 746, 613, 594 and 543. Elem. Anal. Calcd for C₂₂H₃₇Br₂N₂PPd: C, 42.16; H, 5.95; N, 4.47. Found: C, 42.25; H, 5.87; N, 4.37.

[*trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(di-*tert*-butylphosphane)palladium(II)], 21.

Di-*μ*-bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II)²⁷ (66 mg, 0.07 mmol) and di(*t*-butyl)phosphine (20 mg, 0.14 mmol) were stirred at 40 °C for 96 h in CH₂Cl₂ (8 mL). The resulting mixture was filtered to remove the white precipitate, and the filtrate was evaporated to obtain a yellow powder. Yield = 32 mg (37%). ¹H NMR (400 MHz, CDCl₃): 7.56 (2H, dd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 3.2 Hz, ArH), 7.21 (2H, dd, ³J_{HH} = 6.2 Hz, ³J_{HH} = 3.2 Hz, ArH), 5.97 (2H, hept, ³J_{HH} = 7.1 Hz, NCH(CH₃)₂), 4.37 (1H, d, ¹J_{HP} = 343.2 Hz, PH), 1.76 (12H, d, ³J_{HH} = 7.1 Hz, CH₃) and 1.56 ppm (18H, d, ³J_{HP} = 13.9 Hz, PC(CH₃)₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 176.2₈ (d, ²J_{CP} = 188.2 Hz, C-Pd-P), 134.2 (d, ⁴J_{CP} = 5.8 Hz, C_qNC-Pd), 122.9 (s, ArCH), 113.4 (s, ArCH), 54.6 (s, NCH(CH₃)₂), 34.4 (d, ¹J_{CP} = 14.6 Hz, PC_q), 32.1 (d, ²J_{CP} = 3.3 Hz, PC(CH₃)₂) and 21.5 ppm (s, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 55.2 ppm (d, ¹J_{HP} = 343.4 Hz, PH). HR-MS (+ve ESI): m/z (calc) [M – Br]⁺ = 533.0912; found 533.0907. Note: this compound formed both *cis* and *trans* isomers.

8-([1,1'-Biphenyl]-2-yl)-7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, 22. 7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **9**, (340 mg, 1.57 mmol), [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (340 mg, 1.12 mmol), palladium(II) acetate (1.26 mg, 0.006 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (340 mg, 2.24 mmol) were dissolved in toluene (5 mL) and heated to 85 °C for 16 h. The reaction progress was monitored by ³¹P NMR spectroscopy, which indicated approximately 60% conversion to the desired product. Additional palladium(II) acetate was added (1.26 mg, 0.006 mmol) and the mixture heated at 110 °C for a further 16 h. After this time, the clear dark orange solution was diluted with toluene (3 mL) and washed with DI H₂O (3 × 5 mL). The organic phase was separated, dried over MgSO₄, filtered, and evaporated to dryness under reduced pressure. The crude material was triturated with MeOH (3 mL) to yield a pale brown precipitate. Yield = 200 mg (49%) ¹H NMR (400 MHz, CDCl₃): δ 7.77 (1H, d, ³J_{HP} = 7.6 Hz, ArH), 7.39 – 7.20 (8H, m, ArH), 4.03 – 3.90 (4H, m, CH₂O), 2.08 (2H, dd, ²J_{HH} = 14.3 Hz, ³J_{HP} = 2.3 Hz, CH), 1.65 (2H, dd, ²J_{HH} = 14.4 Hz, ³J_{HP} = 5.6 Hz, CH), 1.25 (6H, d, ³J_{HP} = 19.3 Hz, CH₃) and 0.84 ppm (6H, d, ³J_{HP} = 10.1 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 151.9 (d, ²J_{CP} = 34.2 Hz, ArC_qPh), 143.8 (d, ³J_{CP} = 8.0 Hz, ArC_qP), 135.6 (d, ¹J_{CP} = 31.2 Hz, ArC_q), 134.1 (d, ³J_{CP} = 4.0 Hz, ArCH), 131.0 (d, ²J_{CP} = 6.2 Hz, ArC), 130.8 (d, ³J_{CP} = 4.4 Hz, ArCH), 128.6 (d, ⁴J_{CP} = 1.5 Hz, ArCH), 127.4 (s, ArCH), 126.6 (d, ⁴J_{CP} = 1.8 Hz, ArCH), 111.2 (s, O₂C_q), 64.9 (s, CH₂O), 63.3 (s, CH₂O), 44.5 (d, ²J_{CP} = 2.2 Hz, C_qCH₂), 32.0 (d, ²J_{CP} = 36.3 Hz, CH₃), 31.5 (d, ¹J_{CP} = 19.6 Hz, C(CH₃)₂) and 31.2 ppm (d, ²J_{CP} = 7.3 Hz, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -8.5 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 369.1983; found 369.1974. FTIR (KBr, cm⁻¹): ν̃ 3078, 3058, 3046, 2960, 2889, 2857, 1965, 1584, 1493, 1462, 1444, 1381, 1354, 1311, 1291, 1262, 1205, 1172, 1129, 1086, 1013, 961, 942, 890, 827, 751, 702, 622, 555 and 532. Elem. Anal. Calcd for C₂₃H₂₉O₂P: C, 74.98; H, 7.93. Found: C, 73.26; H, 7.66.

1-([1,1'-Biphenyl]-2-yl)-2,2,6,6-tetramethylphosphinan-4-one, 23. 8-([1,1'-Biphenyl]-2-yl)-7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **22**, (50 mg, 0.15 mmol) was dissolved in glacial acetic acid (2.0 mL) and heated to 120 °C for 16 h. After this time the volatiles were removed *in vacuo* to give a white solid. Yield = 40 mg (82%). ¹H NMR (400 MHz, CDCl₃): δ 7.82 (1H, d, ³J_{HH} = 7.4 Hz, ArH), 7.43 – 7.22 (6H, m, ArH), 7.22 – 7.09 (2H, m, ArH), 2.86 (2H, dd, ²J_{HH} = 12.9 Hz, ³J_{HP} = 3.4 Hz, CH₂), 2.21 (2H, dd, ²J_{HH} = 13.1 Hz, ³J_{HP} = 4.9 Hz, CH₂), 1.09 (6H, d, ³J_{HP} = 18.6 Hz, CH₃) and 0.88 ppm (6H, ³J_{HP} = 10.0 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 212.0 (s, C=O), 152.3 (d, ²J_{CP} = 34.8 Hz, ArC_qPh), 143.3 (d, ³J_{CP} = 8.0 Hz, ArC_q), 134.5 (d, ¹J_{CP} = 30.3 Hz, ArC_q), 133.5 (d, ³J_{CP} = 4.0 Hz, ArCH), 131.3 (d, ⁴J_{CP} = 6.0 Hz, ArCH), 130.8 (d, ⁴J_{CP} = 4.4 Hz, ArCH), 129.2 (s, ArCH), 127.5 (s, ArCH), 127.0 (s, ArCH), 126.8 (s, ArCH), 53.5 (s, CH₂), 35.9 (d, ¹J_{CP} = 21.8 Hz, C(CH₃)₂), 32.0 (d, ²J_{CP} = 34.6 Hz, CH₃) and 30.0 ppm (d, ²J_{CP} = 7.6 Hz, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -3.5 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 325.1721; found 325.1715.

1,3-Bis(7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)propane, 24. *n*-BuLi (2.0M in hexanes, 2.3 mL, 4.62 mmol) was added dropwise to a solution of 7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decane, **9** (1.0 g, 4.62 mmol) in THF (15 mL) at -78 °C. The solution turned instantly yellow. The mixture was allowed to warm to RT, where it became milky white in appearance. After stirring for 1 h, the solution was cooled to -78 °C, and 1,3-dibromopropane (0.37 g, 1.85 mmol) in THF (5.0 mL) was added dropwise. The solution was then warmed to RT, forming a clear yellow solution. After 16 h, the volatiles were removed *in vacuo*. MeOH (8.0 mL) was added to dissolve the residue, and the solution was placed at -20 °C for 16 h. The resulting solid was filtered and dried *in vacuo*. Yield = 380 mg (44%). ¹H NMR (400 MHz, CDCl₃): δ 3.91 (8H, s, OCH₂), 1.77 – 1.67 (2H, m, -CH₂-), 1.63 (8H, d, ³J_{HP} = 8.1 Hz, CH₂), 1.53 – 1.48 (4H, m, CH₂), 1.20 (12H, d, ³J_{HP} = 16.8 Hz, CH₃) and 1.12 ppm (12H, d, ³J_{HP} = 7.7 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 110.4 (s, O₂C_q), 64.1 (s, OCH₂), 63.9 (s, OCH₂), 45.9 (s, CH₂C_q), 31.6 (d, ²J_{CP} = 26.3 Hz, CH₃), 30.4 (d, ¹J_{CP} = 15.0 Hz, C(CH₃)₂), 29.0 (t, ²J_{CP} = 24.0 Hz, CH₂CH₂CH₂), 27.6 (s, CH₃) and 22.3 ppm (dd, ¹J_{CP} = 22.0 Hz, ³J_{CP} = 12.8 Hz, PCH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 4.0 ppm. FTIR (KBr, cm⁻¹): ν̃ 3436, 2952, 2938, 2918, 2893, 1637, 1472, 1450, 1389, 1367, 1341, 1297, 1133, 1091, 1028, 1012, 960, 946, 898, 841, 826, 786, 720, 711, 667, 619 and 598.

1,3-Bis(2,2,6,6-tetramethylphosphinan-4-one)propane (BPP), 25. Method A: 1,3-Bis(7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)propane, **24** (380 mg, 0.80 mmol) was dissolved in THF (3 mL) and 3M HCl

(aq, 5 mL) was added. The mixture was heated at 90 °C for 72 h. After this time, CH₂Cl₂ (15 mL) was added, and the solution was washed with 1M NaHCO₃ (aq, 25 mL). The organic layer was separated, dried (MgSO₄), and the volatiles removed *in vacuo* to give the crude material, which was recrystallized from MeOH. Yield = 220 mg (70%). ¹H NMR (400 MHz, CDCl₃): δ 2.41 – 2.35 (8H, m, CH₂), 1.90 – 1.78 (2H, m, CH₂), 1.71 – 1.67 (4H, m, CH₂), 1.20 (12H, d, ³J_{PH} = 16.2 Hz, CH₃) and 1.13 ppm (12H, d, ³J_{PH} = 8.0 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 210.7 (C=O), 53.9 (CH₂CO), 34.7 (d, ¹J_{CP} = 17.5 Hz, C_q), 31.2 (d, ²J_{CP} = 25.7 Hz, CH₃), 28.6 (t, ²J_{CP} = 9.3 Hz, -CH₂-), 27.4 (d, ²J_{CP} = 4.8 Hz, CH₃) and 22.8 ppm (dd, ¹J_{CP} = 22.7 Hz and ³J_{CP} = 13.4 Hz, PCH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 6.4 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 385.2425; found 385.2432. FTIR (KBr, cm⁻¹): ν̃ 2922, 1702 (C=O), 1639, 1467, 1385, 1369, 1295, 1230, 1204, 871, 823 and 620. Elem. Anal. Calcd for C₂₁H₃₈O₂P₂: C, 65.60; H, 9.96 Found: C, 65.50; H, 9.85. **Method B:** 1,3-Bis(phosphino)propane (3.6 g, 18.5wt%, 6.2 mmol) and phorone (1.8 g, 13.0 mmol) were heated at 120 °C for 36 h. The resulting sticky solid was triturated with pentane (10 mL) and dried *in vacuo* to furnish a white solid. Yield = 0.94 g (40%). The characterization was consistent with that obtained using Method A.

1,3-Bis(phosphino)propane. CAUTION: 1,3-Bis(phosphino)propane is **extremely pyrophoric, volatile, and malodorous!** It must be handled under an **inert gas atmosphere** using proper Schlenk line techniques.⁵³ In our work, we synthesized and handled this compound in solution and used the solution to prepare compound **25** via **Method B**. If compound **25** is required, we recommend using **Method A** which avoids the use of the pyrophoric intermediate **1,3-bis(phosphino)propane**. **Tetrabutyl propane-1,3-diylbis(phosphonate):** 1,3-Dibromopropane (9.9 g, 5.0 mL, 49.2 mmol) and tri(*n*-butyl)phosphite (49.3 g, 53.0 mL, 197.0 mmol) were heated at 120 °C for 16 h. The volatiles were distilled off leaving behind a colourless liquid. Yield = 16.7 g (80 %). ¹H NMR (400 MHz, CDCl₃): δ 4.06 – 3.94 (8H, m, -CH₂O-), 1.94 – 1.78 (6H, m, -P(CH₂)₃P-), 1.66 – 1.59 (8H, m, OCH₂CH₂), 1.43 – 1.33 (8H, m, CH₂) and 0.92 ppm (12H, t, ³J_{HH} = 7.4 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 65.5 (t, ²J_{CP} = 3.3 Hz, OCH₂), 32.7 (t, ³J_{CP} = 3.3 Hz, OCH₂CH₂), 26.3 (dd, ¹J_{CP} = 141.7 Hz, ³J_{CP} = 15.3 Hz, CH₂P), 18.9 (s, OCH₂CH₂CH₂), 16.5 (t, ²J_{CP} = 4.3 Hz, PCH₂CH₂CH₂P) and 13.8 ppm (s, CH₃). δ ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 30.7 ppm. HR-MS (+ve ESI): 429.2539 [M+H]⁺ *calc.* 429.2529. FTIR (neat, cm⁻¹): ν̃ 3530, 3477, 2960, 2936, 2875, 1651, 1465, 1408, 1355, 1242, 1150, 1119, 1068, 1026, 979, 900, 834, 799, 735, 699 and 555. 1,3-Bis(phosphino)propane: Chlorotrimethylsilane (5.1 g, 5.9 mL, 46.7 mmol) was added dropwise to a suspension of LiAlH₄ (2.0 M in THF, 23.3 mL, 46.6 mmol) in THF (150 mL) at -78 °C. After complete addition, the reaction was warmed to RT and stirred for 1 h. The mixture was re-cooled to -78 °C and tetrabutyl propane-1,3-diylbis(phosphonate) (5.0 g, 11.7 mmol) in THF was added dropwise. **CAUTION:** Even at -78 °C a vigorous reaction ensued. The mixture was then allowed to warm to RT and stirred under argon for 16 h. The reaction was then cooled in an ice bath and quenched by dropwise addition of NaOH (20% aq, 2.5 mL). Additional THF (100 mL) was added to ensure efficient stirring. The mixture was filtered, dried over MgSO₄, and then filtered again. The majority of the THF was distilled off under argon leaving behind the product 1,3-bis(phosphino)propane, THF and *n*-butanol (see Figure S75). Yield = 3.6 g (18.5 wt% by ¹H NMR corresponding to 52% overall yield). ¹H NMR (400 MHz, CDCl₃): δ 2.7 (4H, dt, ¹J_{HP} = 194.8 Hz and ³J_{HH} = 7.4 Hz, PH₂), 1.78 – 1.67 (2H, m, -CH₂-) and 1.59 – 1.33 ppm (4H, m, PCH₂) ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -138.6 ppm.

[(BPP)Pd(O₂CCF₃)₂], 26. BPP (0.24 g, 0.61 mmol) and [Pd(O₂CCF₃)₂] (0.20 g, 0.61 mmol) were stirred together in CH₂Cl₂ (20 mL) for 4 h. The mixture was passed through a glass filter producing an orange filtrate. The reaction volume was reduced to 5 mL and then pentane (15 mL) was added to induce precipitation. The tan colored solid was filtered off and dried. Crystals suitable for single crystal X-ray diffraction were obtained from the slow evaporation of a saturated solution of the complex in chloroform. Yield: 0.26 g (60%). ¹H NMR (400 MHz, CDCl₃): δ 3.41 (4H, dd, ²J_{HH} = 12.9 Hz, ³J_{HP} = 3.1 Hz, PCH₂), 2.18 (4H, dd, ³J_{HP} = 25.4 Hz, ²J_{HH} = 12.9 Hz), 2.18 (2H, m, CH₂CH₂CH₂), 1.88 (12H, d, ³J_{HP} = 19.0 Hz, CH₃), 1.86 – 1.75 (4H, m, CH₂P) and 1.28 ppm (12H, ³J_{HP} = 10.8 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 206.6 (t, ³J_{CP} = 3.3 Hz, C=O), 162.9 (q, ²J_{CF} = 37.7 Hz, CO₂), 115.8 (q, ¹J_{CF} = 285.5 Hz, CF₃), 53.6 (s, CH₂CO), 40.1 – 39.7 (m, C_q(CH₃)₂), 32.5 (app. t, ²J_{CP} = 3.5 Hz, CH₃), 27.9 (s, CH₃), 20.4 (s, CH₂CH₂CH₂) and 18.4 ppm (dd, ¹J_{CP} = 16.8 Hz, ³J_{CP} = 13.7 Hz, PCH₂). ¹⁹F{¹H} (376 MHz, CDCl₃): δ -75.3 ppm (CF₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 35.4 ppm. FTIR (KBr, cm⁻¹): ν̃ 3445, 2961, 2925, 2852, 1703 (C=O),

1468, 1425, 1404, 1303, 1193, 1135, 1021, 981, 873, 790, 726, 704 and 520. Elem. Anal. Calcd for C₂₅H₃₈F₆O₆P₂Pd: C, 41.88; H, 5.34. Found: C, 41.00; H, 5.03.

1,4-Bis(7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)butane, 27. *n*-BuLi (2.0M in cyclohexane, 0.84 mL, 1.67 mmol) was added dropwise to a solution of 7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)butane, **9** (0.35 g, 1.52 mmol) in THF (5 mL) at -78 °C. The mixture was warmed to RT and stirred for 1 h. It was then cooled to -78 °C and 1,4-dibromobutane (0.15 g, 0.68 mmol) in THF (5 mL) was added. The mixture was warmed to RT and stirred for 16 h. The volatiles were then removed *in vacuo* and pyrrolidine (5 mL) was added and the mixture was heated at 55°C for a further 16 h. After this time the volatiles were removed *in vacuo* and the mixture was recrystallized from MeOH (5 mL) and dried *in vacuo* to give a white solid. Yield = 300 g (90%). ¹H NMR (400 MHz, CDCl₃): δ 3.91 (8H, s, OCH₂), 1.66 – 1.54 (12H, m, CH₂), 1.43 – 1.32 (4H, m, CH₂P), 1.20 (12H, d, ³J_{HP} = 16.6 Hz, CH₃) and 1.11 ppm (12H, d, ³J_{HP} = 7.6 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 110.5 (s, O₂C_q), 64.1 (s, CH₂O), 63.9 (s, CH₂O), 45.8 (s, CH₂C_q), 31.5 (d, ²J_{CP} = 26.9 Hz, CH₃) 31.4 (t, ²J_{CP} = 17.8 Hz, CH₂CH₂), 30.4 (d, ¹J_{CP} = 14.5 Hz, C_q(CH₃)₂), 27.6 (s, CH₃) and 20.0 ppm (d, ¹J_{CP} = CH₂P, 21.8 Hz.). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 5.1 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 487.3101; found 487.3081. FTIR (KBr, cm⁻¹): ν̃ 3439, 3012, 2974, 2925, 2868, 1632, 1474, 1457, 1450, 1419, 1389, 1367, 1342, 1317, 1297, 1186, 1152, 1093, 1027, 1013, 963, 949, 901, 841, 827, 787, 731, 717, 643, 620 and 528. Elem. Anal. Calcd for C₂₆H₄₈O₄P₂: C, 64.18; H, 9.94. Found: C, 63.55; H, 9.57.

1,4-Bis(2,2,6,6-tetramethylphosphinan-4-one)butane (BPB), 28. Compound **28** was prepared according to the procedure used for compound **25** (Method A) using 1,4-bis(7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)butane (350 mg, 0.72 mmol). Yield = 0.21 g (73%). ¹H NMR (400 MHz, CDCl₃): δ 2.37 (8H, ³J_{HP} = 7.3 Hz, CH₂C_q), 1.76 – 1.68 (4H, m, CH₂) 1.57 – 1.53 (4H, m, CH₂), 1.20 (12H, d, ³J_{HP} = 16.1 Hz, CH₃) and 1.12 ppm (12H, ³J_{HP} = 7.9 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 210.8 (s, C=O), 54.0 (d, ²J_{CP} = 1.8 Hz, CH₂C_q), 34.7 (d, ¹J_{CP} = 17.4 Hz, C_q(CH₃)₂), 31.2 (d, ²J_{CP} = 25.8 Hz, CH₃), 31.2 (dd, ²J_{CP} = 23.6 Hz, ³J_{CP} = 12.4 Hz, CH₂CH₂), 27.3 (d, ²J_{CP} = 4.7 Hz, CH₃) and 20.8 ppm (d, ¹J_{CP} = 22.5 Hz, CH₂P). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 7.7 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 399.2576; found 399.2560. FTIR (KBr, cm⁻¹): ν̃ 3443, 3001, 2973, 2943, 2929, 2862, 1700 (C=O), 1456, 1438, 1423, 1367, 1298, 1288, 1262, 1239. 1179, 1149, 1093, 1074, 1017, 873, 822, 805, 722, 701, 613 and 559. Elem. Anal. Calcd for C₂₂H₄₀O₂P: C, 66.31; H, 10.12. Found: C, 64.06; H, 9.56.

1,2-Bis((7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)methyl)benzene, 29. Prepared according to the procedure used for compound **27** using *n*-BuLi (2.0M in hexanes, 2.5 mL, 5.0 mmol), 7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)butane borane complex (1.0 g, 4.35 mmol) and α,α-dichloro-*o*-xylene (0.35 g, 1.98 mmol). Yield = 0.98 g (93%). ¹H NMR (400 MHz, CDCl₃): δ 7.49 – 7.40 (2H, m, ArH), 7.10 – 7.03 (2H, m, ArH), 3.99 – 3.84 (8H, m, CH₂O), 3.10 (4H, s, CH₂P), 1.74 – 1.65 (8H, m, CH₂), 1.27 (12H, d, ³J_{HP} = 5.3 Hz, CH₃) and 1.21 ppm (12H, d, ³J_{HP} = 17.4 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 137.9 (dd, ²J_{CP} = 8.0 Hz, ³J_{CP} = 3.0 Hz, ArC_q), 131.1 (d, ³J_{CP} = 11.4 Hz, ArC), 125.7 (d, ⁴J_{CP} = 1.6 Hz, ArC), 110.0 (s, O₂C_q), 64.5 (s, CH₂O), 63.6 (s, CH₂O), 47.6 (d, ²J_{CP} = 6.9 Hz, CH₂), 32.3 (d, ²J_{CP} = 25.7 Hz, CH₃), 31.2 (d, ²J_{CP} = 17.4 Hz, CH₃), 25.8 (s, C_q) and 25.6 ppm (dd, ¹J_{CP} = 26.3 Hz, ⁴J_{CP} = 7.3 Hz, PCH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 5.90 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 585.3581; found 585.3580. FTIR (KBr, cm⁻¹): ν̃ 3436, 3007, 2948, 2923, 2897, 2857, 1597, 1471, 1415, 1382, 1365, 1355, 1345, 1300, 1263, 1211, 1183, 1156, 1079, 1027, 1010, 965, 899, 843, 827, 803, 790, 768, 766, 756, 727, 622, 596, 555 and 527.

1,2-Bis(2,2,6,6-tetramethylphosphinan-4-one)xylene (BPX), 5. Method A: Prepared according to the procedure used for compound **25** (Method A) using 1,2-bis((7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)methyl)benzene (0.1 g, 0.212 mmol) and degassed 3.0 M HCl (3.0 mL) at 95°C for 20 h. White solid. Yield = 36 mg (38%). **Method B:** Compound **29** (0.77 g, 1.44 mmol) was dissolved in AcOH/H₂O (9:1, 15 mL) and heated at 120 °C for 2 h after which time it was evaporated to dryness and recrystallized from MeOH to give a white solid. Yield = 370 mg (58%). The characterization was consistent with our earlier report.⁷

1,3-Bis((7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)methyl)benzene, 30. Compound **30** was prepared using the same procedure as compound **27** using 7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl borane complex (0.70 g, 3.10 mmol), *n*-BuLi (2.0M in hexanes, 1.67 mL, 3.35 mmol) and 1,3-dibromomethylbenzene (360 mg, 1.4 mmol). Yield = 550 mg (84%). ¹H NMR (400 MHz, CDCl₃): δ 7.30 (1H, br. s, ArH), 7.15 (3H, br. s, ArH), 3.97 – 3.87 (8H, m, CH₂O), 2.82 (4H, d, ²J_{HP} = 2.6 Hz, CH₂P), 1.70 – 1.67 (8H, m, CH₂C_q), 1.21 (12H, d, ³J_{HP} = 6.1 Hz, CH₃) and 1.04 ppm (12H, d, ³J_{HP} = 17.3 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 140.4 (d, ²J_{CP} = 10.5 Hz, ArC_q), 130.8 (t, ³J_{CP} = 7.5 Hz, ArC), 128.4 (s, ArC), 127.0 (dd, ³J_{CP} = 8.4 Hz, ⁵J_{CP} = 2.2 Hz, ArC), 110.1 (d, ³J_{CP} = 0.8 Hz, O₂C_q), 64.3 (s, CH₂O), 63.8 (s, CH₂O), 46.8 (d, ²J_{CP} = 5.1 Hz, CH₂C_q), 31.8 (d, ²J_{CP} = 25.8 Hz, CH₃), 31.0 (d, ¹J_{CP} = 16.7 Hz, C_q(CH₃)₂), 27.4 (d, ¹J_{CP} = 24.7 Hz, CH₂P) and 26.7 ppm (s, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 12.6 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 535.3101; found 535.3079. FTIR (KBr, cm⁻¹): ν̃ 3439, 3010, 2957, 2919, 2894, 1597, 1470, 1446, 1389, 1413, 1366, 1343, 1187, 1155, 1094, 1029, 1010, 962, 905, 841, 828, 802, 787, 748, 722, 686, 622 and 593. Elem. Anal. Calcd for C₃₀H₄₈O₄P₂: C, 67.39; H, 9.05. Found: C, 65.03; H, 8.87.

1,3-Bis(2,2,6,6-tetramethylphosphinan-4-one)xylene, 31. Compound **31** was prepared using the same procedure used for compound **5** (Method B), using 1,3-bis((7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)methyl)benzene (150 mg, 0.28 mmol) and AcOH/H₂O (9:1, 4.0 mL). Yield = 50 mg (40%). ¹H NMR (400 MHz, CDCl₃): δ 7.37 (1H, br. s, ArH), 7.22 – 7.18 (3H, m, ArH), 2.97 (4H, d, ²J_{HP} = 2.9 Hz, CH₂P), 2.54 (4H, dd, ²J_{HH} = 12.6 Hz, ³J_{HP} = 4.4 Hz, CH₂C_q), 2.36 (4H, dd, ³J_{HP} = 14.7 Hz, ²J_{HH} = 12.6 Hz, CH₂C_q), 1.18 (12H, d, ³J_{HP} = 6.5 Hz, CH₃) and 1.09 ppm (12H, d, ³J_{HP} = 16.6 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 209.9 (s, C=O), 139.3 (d, ²J_{CP} = 9.8 Hz, ArC_q), 130.7 (t, ³J_{CP} = 7.8 Hz, ArC), 129.0 (s, ArC), 127.4 (dd, ³J_{CP} = 8.4 Hz, ⁵J_{CP} = 2.2 Hz, ArC), 54.8 (d, ²J_{CP} = 4.7 Hz, CH₂C_q), 35.1 (d, ¹J_{CP} = 17.1 Hz, C_q(CH₃)₂), 31.2 (d, ²J_{CP} = 24.3 Hz, CH₃), 27.7 (d, ¹J_{CP} = 22.9 Hz, CH₂P) and 26.4 ppm (s, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 14.4 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 447.2576; found 447.2566. FTIR (KBr, cm⁻¹): ν̃ 3439, 2999, 2957, 2923, 2865, 1703 (C=O), 1596, 1582, 1479, 1457, 1434, 1383, 1370, 1292, 1246, 1210, 1186, 1148, 1076, 1020, 934, 889, 816, 790, 715, 694, 617 and 563. Elem. Anal. Calcd for C₂₆H₄₀O₂P₂: C, 69.93; H, 9.03. Found: C, 67.96; H, 8.68.

2,6-Bis((7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)methyl)pyridine, 32. Compound **32** was prepared according to the procedure used for compound **27** using 7,7,9,9-Tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl borane complex, **15** (1.52 g, 6.60 mmol), *n*-BuLi (2.0M in cyclohexane, 3.65 mL, 7.26 mmol) and 2,6-bis(chloromethyl)pyridine (0.52 g, 2.97 mmol). Yield = 1.37 g (86%). ¹H NMR (400 MHz, CDCl₃): δ 7.47 (1H, t, ³J_{HH} = 7.7 Hz, ArH), 7.20 (2H, ³J_{HH} = 7.6 Hz, ArH), 3.95 – 3.88 (8H, m, CH₂O), 3.00 (4H, d, ²J_{HP} = 2.9 Hz, CH₂P), 1.75 – 1.64 (8H, m, CH₂C_q), 1.21 (12H, d, ³J_{HP} = 7.1 Hz, CH₃) and 1.08 ppm (12H, d, ³J_{HP} = 17.3 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 160.3 (d, ²J_{CP} = 12.0 Hz, ArC_q), 136.3 (s, ArC), 120.9 (d, ³J_{CP} = 9.9 Hz, ArC), 110.3 (s, C_qO₂), 64.1 (s, CH₂O), 64.0 (s, CH₂O), 46.2 (d, ²J_{CP} = 4.2 Hz, CH₂C_q), 31.4 (d, ²J_{CP} = 26.8 Hz, CH₃), 31.1 (d, ¹J_{CP} = 17.0 Hz, C_q(CH₃)₂) and 30.7 (d, ¹J_{CP} = 25.4 Hz, CH₂P) and 27.4 ppm (s, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 13.0 ppm. HR-MS (+ve ESI): m/z (calc.) [M+H]⁺ 536.3053; found 536.3056. FTIR (KBr, cm⁻¹): ν̃ 3439, 2957, 2897, 1586, 1568, 1454, 1366, 1352, 1343, 1298, 1265, 1216, 1188, 1155, 1092, 1078, 1029, 1011, 962, 898, 829, 804, 789, 755, 725, 693, 626 and 593. Elem. Anal. Calcd for C₂₉H₄₇NO₄P₂: C, 65.03; H, 8.84; N, 2.61. Found: C, 64.85; H, 8.52; N, 2.91.

2,6-Bis(2,2,6,6-tetramethylphosphinan-4-one)methyl)pyridine, 33. Compound **33** was prepared using the same procedure used for compound **5** (Method B) using 2,6-bis((7,7,9,9-tetramethyl-1,4-dioxo-8-phosphaspiro[4.5]decan-8-yl)methyl)pyridine and AcOH/H₂O (9:1, 4.0 mL). Yield = 80 mg (32%). ¹H NMR (400 MHz, CDCl₃): δ 7.55 (1H, t, ³J_{HH} = 7.8 Hz, ArH), 7.25 (2H, d, ³J_{HH} = 7.5 Hz, ArH), 3.14 (4H, d, ²J_{HP} = 2.9 Hz, CH₂P), 2.48 – 2.40 (8H, m, CH₂C_q), 1.19 (12H, d, ³J_{HP} = 7.5 Hz, CH₃) and 1.12 ppm (12H, d, ³J_{HP} = 16.6 Hz, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 210.4 (s, C=O), 159.7 (d, ²J_{CP} = 12.7 Hz, ArC_q), 136.8 (s, ArC), 121.2 (dd, ³J_{CP} = 9.1 Hz, ⁵J_{CP} = 2.2 Hz, ArC), 54.2 (d, ²J_{CP} = 3.3 Hz, CH₂C_q), 35.3 (d, ¹J_{CP} = 18.9 Hz, C_q(CH₃)₂), 31.4 (d, ¹J_{CP} = 25.8 Hz, CH₂P), 31.0 (d, ²J_{CP} = 26.2 Hz, CH₃) and 27.4 ppm (d, ²J_{CP} = 3.6 Hz, CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 14.6 ppm. HR-MS (+ve

ESI): m/z (calc.) $[M+H]^+$ 448.2529; found 448.2518. FTIR (KBr, cm^{-1}): $\tilde{\nu}$. 3439, 3049, 2961, 2934, 2868, 1704 (C=O), 1585, 1577, 1461, 1422, 1390, 1384, 1369, 1292, 1245, 1208, 1172, 1148, 1078, 1020, 992, 933, 893, 878, 834, 807, 759, 698, 618 and 518. Elem. Anal. Calcd for $\text{C}_{25}\text{H}_{39}\text{NO}_2\text{P}_2$: C, 67.09; H, 8.78; N, 3.13. Found: C, 66.06; H, 8.54; N, 3.39.

General Methoxycarbonylation Procedure. Following our earlier procedure for the methoxycarbonylation of olefins:⁷ parallel stainless steel reactors (12 mL) were pressurized with argon (60 bar) and then depressurized (to 2 bar) three times to remove air. Catalyst solution (20 μmol of $\text{Pd}(\text{OAc})_2$, 40 μmol of ligand, and 0.2 mmol of $\text{CH}_3\text{SO}_3\text{H}$) in methanol (6 mL) and substrate (3.0 mL) were injected into each autoclave under a stream of argon gas. The autoclaves were then pressurized with CO (20 bar), and magnetic stirring was initiated at 1000 rpm. After the reaction temperature of 105 °C was reached, the CO pressure was increased to 50 bar and the stirring rate increased to 2000 rpm. The CO pressure was maintained at 50 bar. The reaction start point was marked here. After 4 h the stirring was stopped and the reactors were cooled to room temperature. An accurate amount of anisole (~0.5 g, GC internal standard) was placed in each vessel, and a sample was analyzed by GC using an Agilent 6890N GC instrument equipped with a DB5 column.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details and characterization data for new compounds, ^1H , ^{13}C and ^{31}P NMR spectra for all compounds, IR spectra, and SC-XRD data for compounds **10**, **16**, **20** and **26** (CCDC 2464763 – 2464765 and 1454965), (PDF).

AUTHOR INFORMATION

Corresponding Author

*james_nobbs@a-star.edu.sg, chmhhv@nus.edu.sg

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare the following competing interest: some of the authors are inventors on a patent application that has recently been published.⁵⁴ All other authors declare no competing interests.

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