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Phosphacycloalkyldiones: Synthesis and coordinative behaviour of 6- and 7-member cyclic diketophosphanyls†

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Glutaryl and adipoyl chlorides undergo facile condensation with the bis(silyl)phosphanes $RP(SiMe_3)_2$ (R = Me, ^{n}Bu, ^{t}Bu, Ph, Mes) to afford exclusively the phosphacycloalkyldiones $(CH_2)_n(C{=}O)_2PR$ (n = 3, 4). Characterised spectroscopically and, for R = Ph, Mes (n = 3) crystallographically, the macrocycles are conformationally fluxional in solution and appreciably moisture sensitive. Though seemingly resistant to chemical oxidation at phosphorus, coordination is readily achieved, as illustrated by isolation of *trans*-$\{Pt(PEt_3)\{P(Ph)(CO)_2(CH_2)_3\}Cl_2]$ and a series of tungsten pentacarboyl complexes, which are characterised crystallographically and by infrared and NMR spectroscopy. Together, these data suggest the macrocycles to be relatively weak σ-donors with no appreciable π-acceptor character.

Introduction

Tertiary phosphanes are ubiquitous to modern organometallic and coordination chemistry. The diversity of electronic and steric profiles achievable through substituent modification renders them valuable tools with which to control and moderate the reactivity of molecular species and/or direct reaction outcomes. As such, the continuing drive toward enhancing catalytic processes provides an enduring impetus for the synthesis and study of phosphanes featuring alkyl, aryl, alkenyl, alkynyl and alkoxy moieties[1] within both symmetric and asymmetric scaffolds.

Somewhat less studied are the acylphosphanes (*viz.* 'phosphomides'[2]). Though a number of such compounds have been described, an apparently intrinsic hydrolytic sensitivity of the phosphomide linkage[3] has typically limited their use. Nonetheless, a small number have been investigated as ligands for rhodium-catalysed hydroformylation[4] and ruthenium-catalysed hydrogenation,[5] while the coordination chemistry of several others has also been described,[4a,5-8] including the bis(phosphomide)s $C_6H_4\{C(O)PPh_2\}_2$-1,3 and $NC_5H_3\{C(O)PPh_2\}_2$-2,6.[4a,7a] Moreover, bis(acyl)phosphanes (Figure 1) are the subject of resurgent interest, driven largely by the electronic features of the {-C(O)}PR{C(O)-} ('diketophosphanyl') moiety.[9] This unit imparts stability to the LUMO of heavily conjugated systems, and thus low HOMO-LUMO separations, affording favourable opto-electronic behaviour. Consequently, a significant range of derivatives based on aromatic backbones has been investigated,[10] primarily in the context of developing discrete components for organic optoelectronic devices (e.g. OLEDs, OPVs). Acyclic derivatives are also prevalent, with aromatic bis(acyl)phosphane oxides (BAPOs) finding particular utility, by virtue of a wavelength-specific photochemistry that leads to cleavage of a phosphomide linkage.[11] The resulting phosphanyl/benzoyl radical pair serves as an effective initiator for radical polymerization, lending a strong impetus for current study of such molecules.

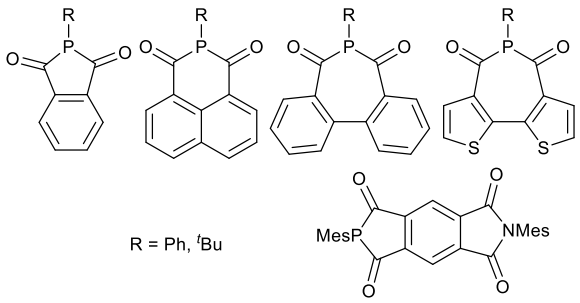

Fig. 1 Representative diketophosphanyl compounds.[9,10]

Amidst this varied body of work, notably absent are cyclic bis(acyl)phosphanes based upon fully saturated backbones. Indeed, saturated phosphacycles more generally are somewhat underexplored, with merely a handful of core scaffolds known (Figure 2) albeit with appreciable variation of the pendant phosphorus substituent and some inclusion of functionality on the cyclic skeleton.[12,13] Few among these feature an acyl functionality, the sole examples being the small range of phosphorinanones (**I**)[14] in which the phosphorus and acyl moieties are located distally. Though predominantly investigated for their conformational stability,[14a,b,15] the coordination chemistry of these systems was briefly explored,[16] with a focus on catalytic applications.[17]

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†Electronic Supplementary Information (ESI) available: Characterizing data (NMR, MS) for all compounds; selected ellipsoid plots, X-ray data (CCDC 1988260-1988266). See DOI: 10.1039/x0xx00000x

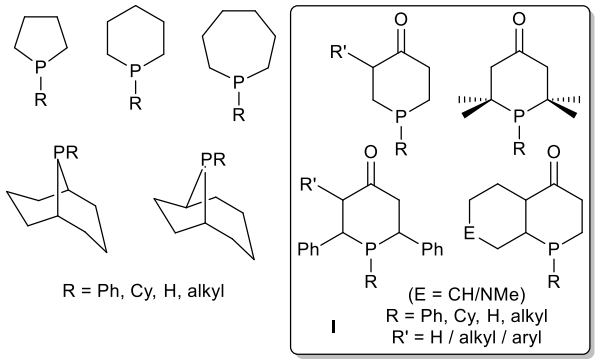


Fig. 2 Representative saturated phosphacycle motifs.[12-15]

Following our recent report of facile access to the unprecedented diphosphametacyclophane (**1**, Scheme 1),[18] and subsequent work by Balakrishna and co-workers on tri- and tetrameric analogues[19] we envisioned using similar methodologies to access a range of cyclic bis(acyl)phosphanes. In particular, we sought to access the first such materials based upon a saturated cyclic motif. We thus report herein the synthesis of the phosphanes $RP\{C(O)\}_2C_nH_{2n}$ (n = 3, 4; R = Aryl, alkyl) and initial investigations of their coordinative behaviour, including synthesis of a series of tungsten complexes, allowing preliminary comment on their donor behaviour.

Results and Discussion

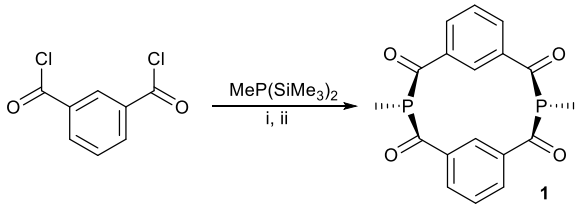
Phosphinanes **2** and phosphepanes **3** were obtained by condensation of the respective $RP(SiMe_3)_2$ (R = Me, ^{n}Bu, ^{t}Bu, Ph, Mes) and acid chlorides $\{C(O)Cl\}_2\{(CH_2)_n\}$ (n = 3, 4; Scheme 2), their identities following from spectroscopic data (Table 1), the observation of consistent molecular ions in the mass spectra, and, in the case of **2d** and **2e**, X-ray structural data (*vide infra*).

In each case the $^{31}P\{^1H\}$ NMR spectra exhibit a single resonance in the region 68 – 31 ppm, in line with precedent diketophosphanyl derivatives,[10,18] while a single acyl carbon environment is apparent from the $^{13}C\{^1H\}$ NMR spectra; the latter also demonstrate the symmetry of the cyclic backbones and retention of the P-alkyl / aryl substituents. These are also reflected in the ^1H NMR spectra, the associated resonances integrating with broad internal consistency. In respect of the cyclic skeleton, the ^1H NMR spectra for **2a-e** broadly reflect the magnetic inequivalences associated with the expected chair-like conformation, though are beset by poor resolution suggestive of conformational non-rigidity in solution. This is most pronounced in the case of **2a** (Figure 3 and ESI) for which only the *endo* and *exo* protons of the distal CH_2 unit can be (barely) distinguished at ambient temperature. The four unique environments become well resolved only at –40 °C, the resonances appearing consistent with the 'strong coupling' regime. Notwithstanding, the slow-exchange limit could not be reached, lower temperatures leading to loss of resolution due to slow-tumbling. Similar dynamic exchange is apparent for **3a-d**, such that only two unique environments are apparent in the ambient temperature spectra.[20]

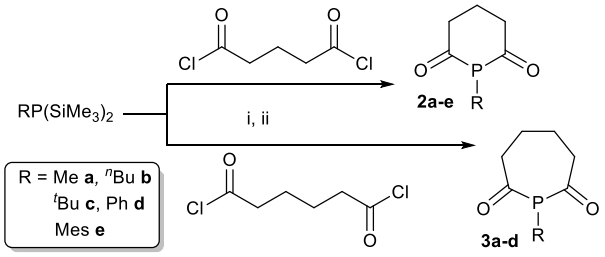
Table 1 Selected Spectroscopic data for **2** and **3**.

	δ_P[a]	δ_C ($^1J_{CP}$[b])	ν_{CO}[c] / cm^{-1}
2a	36.9	220.5 (42)[d]	1739 (w), 1668 (s)
2b	47.7	219.6 (43)[a]	1768 (w), 1660 (s)
2c	68.2	218.8 (48)[a]	1736 (w), 1655 (s)
2d	49.2	218.5 (44)[e]	1737 (w), 1667 (s)
2e	31.3	217.0 (41)[a]	1738 (w), 1659 (s)
3a	39.7	217.7 (48)[a]	1659 (s)[f]
3b	48.9	218.5 (48)[a]	1736 (w), 1657 (s)
3c	60.9	221.5 (50)[d]	1736 (m), 1652 (s)
3d	49.0	218.1 (47)[d]	1735 (w), 1665 (s)

[a]as C_6D_6 solution. [b]in Hz. [c]as THF solution. [d]as $CDCl_3$ solution. [e]as CD_2Cl_2 solution. [f]symmetric mode not observed.



Scheme 1. Synthesis of phosphametacyclophanes. *Reagents and Conditions:* i) Et_2O, –78 °C; ii) –78 °C → r.t., 12 h.



Scheme 2. Synthesis of phosphacycloalkyldiones **2** and **3**. *Reagents and Conditions:* i) Et_2O, –78 °C, 30 min; ii) –78 °C → r.t., 16 h.

The solid-state structural data for **2d** and **2e** (Fig. 4 and 5, Table 2) confirm the chair-like conformation of the phosphacyclic core, with the respective arenes (Ph, Mes) aligning essentially orthogonal to the plane of the heterocycle (∠ 74 ° **2d**, 87 ° **2e**). Though no direct comparators for these

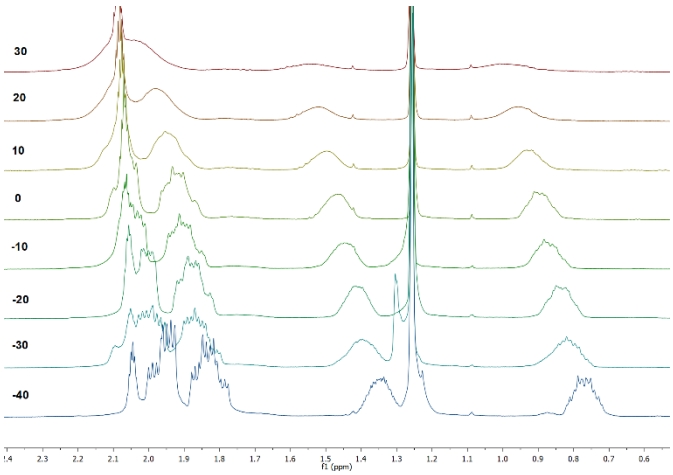


Fig. 3 Variable temperature ^1H NMR (C_7D_8) for **2a** for the alkyl region in the range 30 °C to –40 °C. Full spectrum plot is presented in the ESI (Fig. S8).

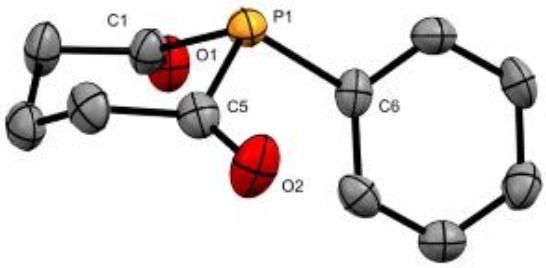


Fig. 4 Molecular structure of **2d** with hydrogen atoms omitted for clarity; displacement ellipsoids at 50 %.

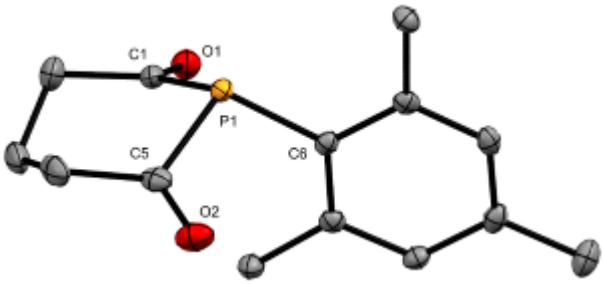


Fig. 5 Molecular structure of **2e** with hydrogen atoms omitted for clarity; displacement ellipsoids at 50 %.

Table 2 Selected bond distances (Å) and angles (°) for compounds **2d** and **2e**, with estimated standard uncertainties in parentheses.[a]

	2d	2e
P1–C1	1.864(6)	1.853(2)
P1–C5	1.888(6)	1.857(2)
P1–C6	1.825(5)	1.816(2)
C1–O1	1.202(7)	1.208(2)
C5–O2	1.192(8)	1.214(2)
C1–P1–C5	97.0(3)	100.11(7)
C1–P1–C6	102.8(2)	107.89(7)
C5–P1–C6	103.6(3)	105.41(7)
P1–C1–O1	121.2(5)	121.80(12)
P1–C5–O2	119.9(5)	120.62(13)

[a]crystals from benzene solution

heterocycles exist, the internal parameters of the diketophosphanyl moiety are consistent with the small number of precedents for this unit recorded in the CCDC,[21] and indeed the wider range of acylphosphanes. It is, however, notable that the P–C_{CO} distances within **2e** are somewhat shorter than those of **2d**, the average for acylphosphanes in the CCDC (by ca 0.02 Å) and indeed our previously reported cyclophane **1** (1.886(3) – 1.894(3) Å).[18] In contrast, the CO distances are in line with these comparators and among the shorter examples recorded for acyl functions more generally, thus offering little evidence for any significantly enhanced phosphomide character within the diketophosphanyl moiety. It is also noted that while the P–Aryl distances appear largely typical of both phosphomides and arylphosphanes more generally, they are somewhat shortened relative to that of $MesP(SiMe_3)_2$ (1.851(2) Å; ESI, Figure S1) and indeed the small range of precedent $ArP(SiR_3)_2$ (Ar = $C_6H_3{}^iPr_2$-2,6,[22] Mes*,[23] $C_6H_2{}^iPr_2$-2,4,6,[24] Ph[25]) and their complexes[26] (1.829 – 1.884 Å).

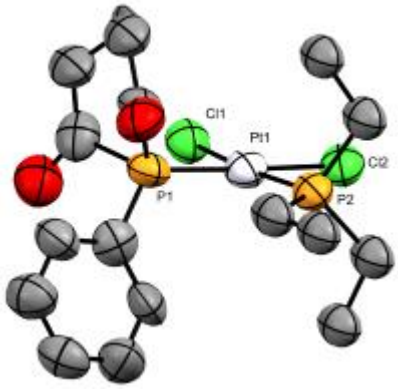
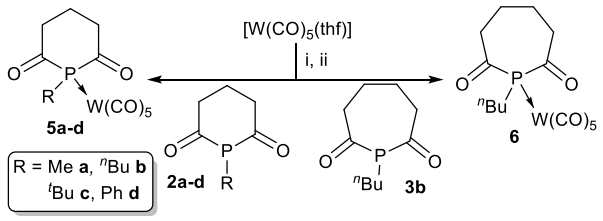


Fig 6 Molecular structure of **4** with hydrogen atoms omitted for clarity and displacement ellipsoids at 50 %.

Chemically, **2** and **3** are stable only under anaerobic conditions, decomposing instantaneously upon exposure to air, oxidation with H_2O_2 having similar effect, albeit more slowly. Though the break-down species remain unidentified, the formation of secondary phosphanes is obvious from ^{31}P NMR spectra, suggesting hydrolytic instability, as has been previously noted for phosphomides and acylphosphanes more generally. Surprisingly, **2** and **3** have proven relatively robust toward more controlled chemical oxidation, refluxing with both sulfur and selenium resulting only in recovery of the free heterocycles. This presumably reflects the influence of the flanking carbonyls, leading to some inductive stabilisation of the lone pair. This effect does not, however, preclude coordination to transition metals, as is illustrated in reaction of **2d** with $[Pt(PEt_3)Cl_2]_2$ to afford *cis*-[Pt(**2d**)$(PEt_3)Cl_2$] (**4**) the connectivity of which is illustrated in Figure 6, though the weakly diffracting nature of the crystal renders the metrics unreliable.

In seeking an assessment of the donor properties of these heterocycles, we sought to use the tungsten pentacarbonyl fragment as a reporter. Thus, complexes [$W(CO)_5$(**2**)] (**5a-d**) and [$W(CO)_5$(**3b**)] (**6**) were obtained by reaction of the respective heterocycles with *in situ* generated $W(CO)_5$(thf) (Scheme 3), and purified by sequential extraction into Et_2O and finally pentane (0 °C), to remove residual traces of $W(CO)_6$. The formation of **5a-d** results in a coordination shift for the phosphorus centre of ca 15 – 20 ppm to lower frequency, with a somewhat smaller change noted for **6** ($\Delta\delta_P$ = –9.7). This is in each case accompanied by the manifestation of tungsten satellites (^{183}W, I = ½, 14 %) confirming coordination of the phosphorus centre



Scheme 3. Synthesis of tungsten complexes **5** and **6**. *Reagents and Conditions:* i) thf, overnight; ii) ether/pentane

Table 3 Selected NMR Spectroscopic data for **5** and **6**.[a]

	δ_P ($^1J_{PW}$[c])	$\Delta\delta_P$[b]	δ_C(CO_{cis}) ($^1J_{CW}$[c])	δ_C(CO_{trans}) ($^1J_{CW}$[c])
5a	20.7 (203)	–16.2	195.4 (125)	197.9 (149)
5b	33.1 (202)	–14.6	195.4 (125)	197.9 (148)
5c	51.3 (207)	–16.9	196.0 (125)	197.2 (146)
5d	28.9 (214)	–20.3	195.7 (125)	197.8 (148)
6	39.2 (216)	–9.7	195.8 (125)	198.0 (147)

[a]as C_6D_6 solution. [b]coordination shift. [c]in Hz.

(Table 3). The magnitudes of the $^1J_{PW}$ couplings (200 – 216 Hz) are relatively low and essentially comparable to those for ligated PH_2R (R = H, Me, Et, Pr) and $PH(SiMe_3)_2$ (212 – 216 Hz),[27] but appreciably diminished relative to tertiary alkyl and aryl phosphanes more generally (e.g. PPh_3 244 Hz, PMe_3 230 Hz, P^tBu_3 232 Hz, P^iPr_3 233 Hz) and, indeed, phosphites ($P(OMe)_3$ 386.5 Hz, $P(O^iPr)_3$ 381 Hz, $P(OPh)_3$ 416 Hz).[28] Among the limited examples incorporating an α-carbonyl substituent only the phospholyl [{H_4C_4P(C(O)Me)}WCO_5] ($^1J_{PW}$ 215 Hz)[29] is comparable, while most others exhibit couplings in the range 230 – 280 Hz.[30] We note that the magnitude of $^1J_{PW}$ has been shown previously to have a positive correlation with the electronegativity of the α-substituents (greater electronegativity leading to enhanced s-character of the lone pair)[31] and/or the π-acidity of the ligand;[31,32] however, neither would appear applicable to these data.

Structural data for **5a**, **c** and **d** (Figure 7 and ESI S2 and S3; Table 4) are superficially in line with expectation and the wider range of similar tungsten pentacarbonyl derivatives. Notable are the P–W distances which appear shorter than for their respective tertiary phosphane analogues, viz. [$W(CO)_5(PMe_3)$] (2.516(2) Å),[33] [$W(CO)_5(P^tBu_3)$] (2.686(2) Å)[34] and [$W(CO)_5(PPh_3)$] (2.545(1) Å).[35] Though implicit of a more tightly bound ligand, contraction of the *trans* W–CO distances (relative to *cis*, and free $W(CO)_6$ (2.036–2.066 Å)[36]) suggest a lower *trans*-influence for **2** (relative to the respective PR_3) consistent with reduced σ-donor character. Indeed, this feature is also reflected in the associated values of δ_C and $^1J_{CW}$ for the trans carbonyl (*cf.* PPh_3 δ_C 199.2 (J_{CW} 144); PMe_3 δ_C 200.1 (J_{CW} 145)[37]). Moreover, there appears no evidence for appreciable π-acidity, with little variation in the *trans*-C–O distances relative to either the *cis*-ligands or the PR_3 analogues. The more sensitive

Table 4: Selected bond distances (Å) for compounds **5a**, **5c** and **5e**, with estimated standard uncertainties in parentheses.[a]

	5a	**5c**	**5d**
P1–C1	1.880(3)	1.879(5)	1.882(10)
P1–C5	1.881(4)	1.883(5)	1.889(12)
P1–C6	1.815(3)	1.882(5)	1.818(10)
C1–O1	1.202(4)	1.209(7)	1.212(13)
C5–O2	1.206(4)	1.203(6)	1.205(10)
W–P1	2.5065(7)	2.5149(10)	2.490(3)
W–CO_{trans}	1.998(3)	2.007(5)	2.009(11)
W–CO_{cis}	2.045(3)-2.064(4)	2.024(5)-2.060(5)	2.02(1)-2.05(1)
C≡O_{trans}	1.145(4)	1.147(6)	1.14(2)
C≡O_{cis}	1.133(5)-1.143(4)	1.133(6)-1.144(6)	1.13(1)-1.17(2)

[a]crystals grown by the slow evaporation of saturated benzene (**5a,c**) or dichloromethane (**5d**) solutions.

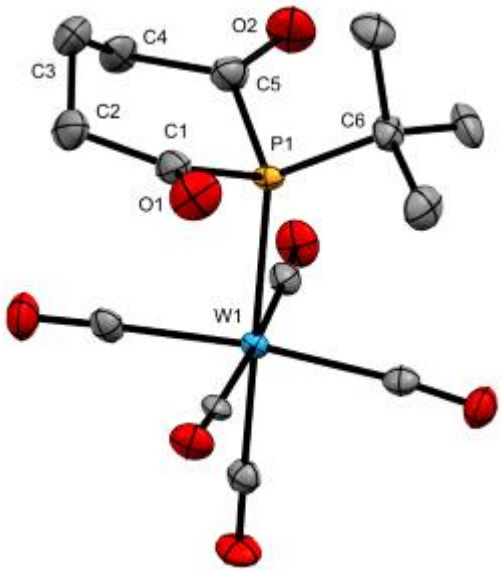


Fig. 7. Molecular structure of **5c** with hydrogen atoms omitted for clarity and ellipsoids at 50 %. **5a** and **5d** exhibit directly comparable geometries and are illustrated in ESI figures S2 and S3.

Table 5: Carbonyl stretch data for **5**, **6** and related analogues.

Compound	ν_{max} (CO) / cm^{-1}	
	CO_{trans}	CO_{cis}
$W(CO)_5(PMe_3)$[a,38]	2069	1976, 1942, 1932
$W(CO)_5(P^nBu_3)$[a,39]	2068	1932
$W(CO)_5(PPh_3)$[a,40]	2071	1976, 1940
5a[a]	2076	1946, 1933
5b[a]	2075	1953, 1950, 1942
5c[a]	2075	1955, 1940
5d[a]	2076	1949(br)
6[a]	2075	1951, 1946, 1938
$W(CO)_5(P\{OMe\}_3)$[28a]	2079	1962, 1948
$W(CO)_5(P\{OPh\}_3)$[b,40]	2083	1968, 1959

[a]as solution in thf; [b]as solution in hexane;

infrared data (ν_{CO}, Table 5), do illustrate a slight increase in the *trans*-carbonyl (pseudo-A_1) mode for **5a**, **b** and **d** relative to respective PR_3 complexes.[38,39] Indeed, those of **5a** and **5d** are intermediate between the respective PR_3 and $P(OR)_3$ analogues.[28a,40] This would appear commensurate with **2** and **3** being relatively weak σ-donors, while also lacking any appreciable π-acid character. We further note that there would seem to be little influence exerted by the nature of 'R', the series **5a-d** exhibiting (within bounds of uncertainty) negligible variations in both the 'A_1' stretch and the chemical shifts for the carbonyls (whether *cis* or *trans*).

Conclusions

In summary, we have reported the synthesis of the first examples of phosphinane- and phosphepane-α-diones through condensation of $RP(SiMe_3)_2$ and, respectively, glutaryl or adipoyl chlorides. These materials exhibit the characteristic hydrolytic sensitivity of acyl-phosphanes more generally and show no evidence of 'phosphomide' character. Indeed,

symmetric C=O stretches are noted to reduce in energy upon ligand coordination, precluding any possible delocalisation of the lone pair in the free pro-ligand.

A reluctance toward oxidation would suggest a relatively stabilised, and thus weakly donating, lone-pair, which is also reflected by data for the tungsten complexes, which place the phosphinane systems below tertiary phosphanes in the *trans*-influence series. Data also suggest a negligible level of π-acidity, placing these ligands apart from the classically weakly donating phosphites.

Experimental

General Methods

All manipulations were performed under anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under an atmosphere of dry argon or catalytically purified dinitrogen respectively. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å; DCM, THF, benzene, Et_2O) or potassium mirrors. General reagents were obtained from Sigma-Aldrich, Fisher or Fluorochem and purified by appropriate methodology prior to use. $W(CO)_5(THF)$ was prepared in accordance with literature procedures.[41] NMR spectra were recorded on a Varian VNMRS 400 (303 K, ^{1}H 399.5 MHz, ^{13}C 100.46 MHz, ^{31}P 161.71 MHz, ^{195}Pt 85.53 MHz) spectrometer and references to external Me_4Si, 85 % H_3PO_4 or $K_2[PtCl_6]$ as appropriate, at 303 K unless otherwise stated. Mass spectrometric data were recorded by Dr A. Abdul-Sada of the departmental service. Elemental analyses were performed by Mr S. Boyer of the London Metropolitan University Elemental Analytical Service.

X-ray diffraction studies

Single crystal X-ray diffraction data were recorded on an Agilent XCalibur EoS Gemini Ultra diffractometer with CCD plate detector using Cu-Kα (λ = 1.514184 Å) radiation. Structure solution and refinement were performed using SHELXT[42] and SHELXL[43] running under Olex2.[44]

Crystal data for $MesP(SiMe_3)_2$ (CCDC 1988266): For $2(C_{15}H_{29}PSi_2)$ (M = 593.06 g mol^{-1}): monoclinic, $P2_1/c$ (no. 14), a = 12.2774(2) Å, b = 24.2123(3) Å, c = 13.4741(2) Å, β = 113.140(2) °, V = 3683.12(11) Å^3, Z = 4, T = 100(2) K, μ(CuKα) = 2.430 mm^{-1}, D_c = 1.069 Mg m^{-3}, 7100 independent reflections, full matrix F^2 refinement, R_1 = 0.0331 on 6594 independent absorption corrected reflections [I > 2σ(I); $2\theta_{max}$ = 143.2 °), 343 parameters, wR_2 = 0.0895 (all data).

Crystal data for 2d (CCDC 1988260): For $C_{11}H_{11}O_2P$ (M = 206.17 g mol^{-1}): orthorhombic, $Pna2_1$ (no. 33), a = 14.2522(3) Å, b = 5.97643(12) Å, c = 12.0658(2) Å, V = 1027.73(3) Å^3, Z = 4, T = 173(2) K, μ(CuKα) = 2.134 mm^{-1}, D_c = 1.332 Mg m^{-3}, 1817 independent reflections, full matrix F^2 refinement, R_1 = 0.0588 on 1736 independent absorption corrected reflections [I > 2σ(I); $2\theta_{max}$ = 134.0 °), 127 parameters, wR_2 = 0.1635 (all data).

Crystal data for 2e (CCDC 1988261): For $C_{14}H_{17}O_2P$ (M = 248.24 g mol^{-1}): monoclinic, $P2_1/c$ (no. 14), a = 10.8705(3) Å, b = 9.7423(2) Å, c = 11.9167(2) Å, β = 93.452(2), V = 1259.83(5) Å^3, Z = 4, T = 100(2) K, μ(CuKα) = 1.828 mm^{-1}, D_c = 1.309 Mg m^{-3}, 2407 independent reflections, full matrix F^2 refinement, R_1 = 0.0344 on 2237 independent absorption corrected reflections [I > 2σ(I); $2\theta_{max}$ = 143.4 °), 157 parameters, wR_2 = 0.0915 (all data).

Crystal data for 4 (CCDC 1988262): For $C_{17}H_{26}Cl_2O_2P_2Pt$ (M = 590.31 g mol^{-1}): orthorhombic, $P2_12_12_1$ (no. 19), a = 7.4569(9) Å, b = 10.591(2) Å, c = 26.251(4) Å, V = 2073.2(6) Å^3, Z = 4, T = 173(2) K, μ(CuKα) = 16.553 mm^{-1}, D_c = 1.891 Mg m^{-3}, 3724 independent reflections, full matrix F^2 refinement, R_1 = 0.1055 on 1793 independent absorption corrected reflections [I > 2σ(I); $2\theta_{max}$ = 136.4 °), 172 parameters, wR_2 = 0.3003 (all data).

Crystal data for 5a (CCDC 1988263): For $C_{11}H_9O_7PW$ (M = 460.00 g mol^{-1}): monoclinic, $P2_1/n$ (no. 14), a = 6.89715(9) Å, b = 12.94011(18) Å, c = 15.8307(2) Å, β = 101.0523(13) °, V = 1386.69(3) Å^3, Z = 4, T = 173(2) K, μ(CuKα) = 16.818 mm^{-1}, D_c = 2.242 Mg m^{-3}, 2671 independent reflections, full matrix F^2 refinement, R_1 = 0.0204 on 2620 independent absorption corrected reflections [I > 2σ(I); $2\theta_{max}$ = 143.2 °), 182 parameters, wR_2 = 0.0508 (all data).

Crystal data for 5c (CCDC 1988264): For $C_{14}H_{15}O_7PW$ (M = 510.08 g mol^{-1}): orthorhombic, Pbca (no. 61), a = 12.3442(2) Å, b = 12.5495(2) Å, c = 21.9424(4) Å, V = 3399.18(10) Å^3, Z = 8, T = 173(2) K, μ(CuKα) = 13.786 mm^{-1}, D_c = 1.993 Mg m^{-3}, 3219 independent reflections, full matrix F^2 refinement, R_1 = 0.0301 on 2866 independent absorption corrected reflections [I > 2σ(I); $2\theta_{max}$ = 143.4 °), 211 parameters, wR_2 = 0.0852 (all data).

Crystal data for 5d (CCDC 1988260): For $2(C_{16}H_{11}O_7PW)$ (M = 1060.13 g mol^{-1}): monoclinic, $P2_1/n$ (no. 14), a = 11.0044(3) Å, b = 9.7434(3) Å, c = 32.7494(10) Å, β = 91.882(3) °, V = 3509.51(18) Å^3, Z = 4, T = 100(2) K, μ(CuKα) = 13.364 mm^{-1}, D_c = 2.004 Mg m^{-3}, 6635 independent reflections, full matrix F^2 refinement, R_1 = 0.0672 on 5673 independent absorption corrected reflections [I > 2σ(I); $2\theta_{max}$ = 143.6 °), 463 parameters, wR_2 = 0.1678 (all data).

Syntheses

$HP(SiMe_3)_2$: Adapted from literature procedures,[45] neat $P(SiMe_3)_3$ (7.83 g, 31.3 mmol) was treated with MeOH (1.26 cm^3, 31.3 mmol) and the mixture stirred for 10 h. Purification by bulb-to-bulb distillation afforded $HP(SiMe_3)_2$ as a colourless liquid, the identity of which was confirmed by comparison to literature data. Yield: 3.88 g, 70 %. ^{1}H NMR (C_6D_6): δ_H 0.68 (d, PH, $^1J_{HP}$ = 187 Hz, 1H); 0.24 (d, $SiMe_3$, $^3J_{HP}$ = 4.2 Hz, 18H). ^{31}P NMR (C_6D_6): δ_P –236.8 (dm, J_{HP} 187 Hz, 4.4 Hz).

$MeP(SiMe_3)_2$: To a cooled (–78°C) solution of $HP(SiMe_3)_2$ (0.727 g, 4.08 mmol) in THF (10 cm^3) was added ^{n}BuLi (2.07 M, 2.0 cm^3, 4.08 mmol) dropwise over 5 min. The mixture was stirred at –78°C for 10 min. then allowed to warm slowly to ambient temperature over 45 min with continued stirring for a further 45 min. The mixture was cooled to –78 °C prior to dropwise addition of MeI (0.26 cm^3, 4.2 mmol) over 10 min, before allowing to warm to ambient temperature, resulting in formation of a white precipitate; the suspension was stirred for a further 4 h. The mixture was filtered and the THF removed from the filtrate under reduced pressure; the residue was extracted with pentane (2 x 10 cm^3), filtered and the solvent

removed under reduced pressure. The crude product was distilled to purity (2.12 mbar, 32 °C), affording $MeP(SiMe_3)_2$ as a colourless liquid, as confirmed by comparison of spectroscopic data with the literature.[46] Yield 0.633 g, 81 %. ^{1}H NMR (C_6D_6): δ_H 0.95 (d, PCH_3, $^2J_{HP}$ = 1.2 Hz, 3H); 0.19 (d, $SiMe_3$, $^3J_{HP}$ = 4.3 Hz, 18H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P –196 (s).

^{n}BuP(SiMe$_3$)$_2$: To a cooled (–78°C) solution of $HP(SiMe_3)_2$ (3.992 g, 22.4 mmol) in Et_2O (40 cm^3) was added ^{n}BuLi (2.5 M, 9.0 cm^3, 22.5 mmol) dropwise over 5 min. The mixture was stirred at –78°C for 10 min. then allowed to warm slowly to ambient temperature and stir for a further 30 min. The mixture was cooled to –78 °C prior to dropwise addition of 1-chlorobutane (2.34 cm^3, 22.4 mmol) over 5 min, before allowing to warm to ambient temperature; the suspension was left to stir overnight. The mixture was filtered and the residue washed with Et_2O (2 x 5 cm^3); the filtrates were, combined, concentrated and then triply distilled (40 °C, 2x10^{-2} mbar) to afford ^{n}BuP(SiMe$_3$)$_2$ as a colourless liquid Yield 2.71 g, 52 %. ^{1}H NMR (C_6D_6): δ_H 1.57 (br, m, CH_2CH_2Et 4H); 1.40 (dt, CH_2CH_2Me, J_{HH} ~ 6 Hz, 2H); 0.88 (t, CH_3, J_{HH} = 6Hz); 0.24 (*d*, $SiMe_3$, $^3J_{HP}$ =4.2 Hz, 18H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P –176.1 (s).

^{t}BuP(SiMe$_3$)$_2$: To a cooled (–78°C) ethereal solution of ^{t}BuPH_2 (0.159 M, 82 cm^3, 13.04 mmol) was added ^{n}BuLi (2.5 M, 11.06 cm^3, 27.64 mmol) dropwise over 5 min. The mixture was stirred at –78°C for 10 min. then allowed to warm slowly to ambient temperature and stir for a further 2 h. The mixture was cooled to –78 °C prior to the addition of Me_3SiCl (3.7 cm^3, 29.0 mmol) over 5 min and stirred for a further 10 minutes before allowing to warm to ambient temperature; the suspension was left to stir overnight. The mixture was filtered and the residue washed with Et_2O (2 x 5 cm^3); the filtrates were, combined, concentrated and distilled (50-55 °C, 2.7 x 10^{-2} mbar) to afford ^{t}BuP(SiMe$_3$)$_2$ as a colourless liquid, as confirmed by comparison of spectroscopic data with the literature.[47] Yield 2.637 g, 86 %. ^{1}H NMR (C_6D_6): δ_H 1.31 (d, $C(CH_3)_3$, $^3J_{HP}$ 12 Hz, 9H); 0.31 (*d*, $SiMe_3$, $^3J_{HP}$ = 4 Hz, 18H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P –108.8 (s).

PhP(SiMe$_3$)$_2$: To a cooled (–78°C) solution of $PhPH_2.Et_2O$ (6 g, 32.6 mmol) in THF (25 cm^3) was added ^{n}BuLi (2.5 M, 27.6 cm^3, 69 mmol) dropwise over 10 min, resulting in formation of a yellow solution. After 10 min. the solution was allowed to warm to ambient temperature stir for a further 2 h. The mixture was then cooled to –78 °C prior to the addition of Me_3SiCl (9.2 cm^3, 72.4 mmol) over 10 min and stirred for a further 10 minutes before allowing to return to ambient temperature; the suspension was left to stir overnight. The resulting suspension was filtered, concentrated and then purified via bulb-to-bulb distillation to afford $PhP(SiMe_3)_2$ as a colourless liquid. as confirmed by comparison of spectroscopic data with the literature.[48] Yield 6.401 g, 77 %. ^{1}H NMR (C_6D_6): δ_H 7.59 (t, 7 Hz, 2H), 7.10 -7.01 (m, 3H), 0.25 (*d*, $SiMe_3$, $^3J_{HP}$ =5 Hz, 18H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P –137.0 (s).

MesP(SiMe$_3$)$_2$: To a cooled (–78°C) solution of $MesPH_2$ (4.05 g, 26.6 mmol) in Et_2O (80 cm^3) was added ^{n}BuLi (2.07 M, 27.3 cm^3, 56.42 mmol) dropwise over 10 min, resulting in formation of a yellow solution. After 10 min. the solution was allowed to warm to ambient temperature stir for a further 2 h. The mixture was then cooled to –78 °C prior to the addition of Me_3SiCl (7.5 cm^3, 59.1 mmol) over 5 min., resulting in formation of a yellow precipitate. The mixture was stirred for a further 10 minutes before allowing to return to ambient temperature and stir overnight. The resulting suspension was filtered and volatiles removed from the filtrate under reduced pressure; the product was triply distilled to purity, affording $MesP(SiMe_3)_2$ as a colourless liquid, as confirmed by comparison of spectroscopic data with the literature.[10c] Yield 3.235 g, 41 %. ^{1}H NMR (C_6D_6): δ_H 6.87 – 6.84 (m, 2H), 2.63 (s, CH_3, 6H), 2.09 (s, CH_3, 3H), 0.28 (*d*, $SiMe_3$, $^3J_{HP}$ = 5.8 Hz, 18H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P –162.6 (s).

1-Methylphosphinane-2,6-dione (2a). To a cooled (–78°C) solution of $MeP(SiMe_3)_2$ (1.01 g, 5.25 mmol) in Et_2O (5 cm^3) was added glutaryl chloride (0.7 cm^3, 5.25 mmol). After stirring for 30 minutes at this temperature, the mixture was allowed to warm to ambient temperature and stir for a further 16 hours. The mixture was filtered and the Et_2O removed from the filtrate under reduced pressure. The product was purified by distillation (60 °C, 5 x 10^{-3} mbar) affording **2a** a colourless liquid. Yield: 0.337 g, 45%. NMR ($CDCl_3$, 303 K): ^{1}H NMR: δ_H = 2.75 (br, CH_2, 4H, unresolved), 2.36 (br, CH*H*, 1 H, unresolved), 1.92 (br, C*H*H, 1 H, unresolved), 1.44 (s, CH_3, 3H). $^{13}C\{^1H\}$ NMR: δ_C = 220.6 (d, C(O), $^1J_{CP}$ = 42.6 Hz), 44.5 (d, CH_2, $^2J_{CP}$ = 29 Hz), 18.1 (d, CH_2, $^3J_{CP}$ = 2.6 Hz), 1.0 (d, CH_3, $^1J_{CP}$ = 9.3 Hz). ^{31}P NMR: δ_P = 39.5 (qnt, J_{PH} = 7.3 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6; 303 K): δ_P = 36.9. IR (THF): ν_{CO} 1739 (w), 1668 (s) cm^{-1}. NMR (C_7D_8): ^{1}H NMR (303 K): δ_H = 2.06 (br, CH_2, 4H, unresolved), 1.54 (br, CH*H*, 1 H, unresolved), 1.26 (s, CH_3, 3H), 1.00 (br, C*H*H, 1 H, unresolved). ^{1}H NMR (238 K): δ_H = 1.99 (m, CH_2, 2H), 1.86 (m, CH_2, 2H) , 1.38 (br, CH*H*, 1 H), 1.29 (s, CH_3, 3H), 0.80 (br, C*H*H, 1 H). $^{13}C\{^1H\}$ NMR (303 K): δ = 218.5 (d, C(O), $^1J_{CP}$ = 42.2 Hz), 44.0 (d, CH_2, J_{CH} = 29.2 Hz), 17.8 (d, CH_2, $^3J_{CP}$ = 2.9 Hz), 0.67 (d, CH_3, $^1J_{CP}$ = 9.4 Hz). $^{31}P\{^1H\}$ NMR (303 K): δ_P = 36.6 (s). EI HRMS (m/z): Calcd for $C_6H_9O_2P$ 144.0340 ([M]+). Found 144.0337 ([M]+).

1-^{n}Butylphosphinane-2,6-dione (2b). As for **2a** using ^{n}BuP(SiMe$_3$)$_2$ (0.25 g, 1.08 mmol) and 0.14 cm^3 (1.08 mmol) glutaryl chloride. Purified by distillation (85-90 °C, 1.3 x 10^{-2} mbar). Yield: 0.089 g, 44%. ^{1}H NMR (C_6D_6): δ_H = 2.08 (m, C*H*$_2$ Butyl 2H, overlapping CH_2 (ring) 4H), 1.57 (m, CH_2 (ring) 1H), 1.51 (m, CH_2 butyl, 2H), 1.31 (br. Unres, CH_2 (ring) 1H), 1.28 (sextet CH_2 (butyl), $^1J_{HH}$ = 7.40 Hz, 2H), 0.81 (t, CH_3, $^1J_{HH}$ = 7.40 Hz, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ_C = 219.3 (d, C(O), $^1J_{CP}$ = 42.4 Hz), 44.4 (d, CH_2 (ring), $^2J_{CP}$ = 29 Hz), 29.2 (d, CH_2 (butyl), $^1J_{CP}$ = 12.7 Hz), 24.3 (d, CH_2 (butyl), $^2J_{CP}$ = 11.9 Hz), 18.9 (d, CH_2 (butyl), $^3J_{CP}$ = 8.4 Hz), 17.8 (d, CH_2 ring, $^3J_{CP}$ = 2.5 Hz), 13.7 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P = 47.7 (s). IR (THF): ν_{CO} 1768 (w), 1660 (s) cm^{-1}. EI HRMS (m/z): Calcd for $C_9H_{15}O_2P$ 186.0810 ([M]+). Found 186.0818 ([M]+).

1-^{t}Butylphosphinane-2,6-dione (2c). As for **2a** using ^{t}BuP(SiMe$_3$)$_2$ (0.295 g, 1.26 mmol) and 0.16 cm^3 (1.26 mmol) glutaryl chloride. After removal of volatiles from the filtrate, the residue was washed with cold hexane (5 cm^3, 0 °C) and dried in vacuo, yielding **2c** as a wax-like white solid. Yield: 0.092 g, 40 %. ^{1}H NMR ($CDCl_3$): δ = 2.67 (q, CH_2, *J* = 6.2 Hz, 4H), 2.09 (br, CH_2, 2H), 1.34 (d, *J* = 13.6 Hz, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ_C = 218.8 (d, C(O) $^1J_{CP}$ = 48.3 Hz), 45.8 (d, CH_2, $^2J_{CP}$ = 27.1 Hz), 34.5 (d, $\underline{C}(CH_3)_3$, $^1J_{CP}$ = 12.1 Hz), 28.1 (d, CH_3, $^2J_{CP}$ = 7.6 Hz), 17.7 (d, CH_2, $^3J_{CP}$ = 2.5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P = 68.2 (s). IR (THF): ν_{CO} 1736 (w),

1655 (s) cm^{-1}. EI HRMS (m/z): Calcd for $C_9H_{15}O_2P$ 186.0810 ([M]+). Found 186.0795 ([M]+).

1-Phenylphosphinane-2,6-dione (2d). As for **2a** using $PhP(SiMe_3)_2$ (1.039 g, 4.1 mmol) and 0.52 cm^3 (4.1 mmol) glutaryl chloride. The solvent was removed under reduced pressure, affording a white solid, which was dried *in vacuo*. Yield: 0.750 g, 91 %. ^1H NMR (CD_2Cl_2): δ_H = 7.40-7.55 (m, aromatic, 5H), 2.86 (br, CH_2, 4H), 2.22 (br, CH_2, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ_C = 218.5 (d, CO, $^1J_{CP}$ = 44.1 Hz), 137.1 (d, C^o, $^2J_{CP}$ = 17.8 Hz), 131.7 (d, C^p, $^4J_{CP}$ = 2.5 Hz), 129.5 (d, C^m, $^3J_{CP}$ = 9.3 Hz), 126.9 (s, C^i), 45.6 (d, CH_2, $^2J_{CP}$ = 30.5 Hz), 18.4 (d, CH_2, $^3J_{CP}$ = 2.5 Hz). $^{31}P\{^1H\}$ NMR: $\delta_P(CD_2Cl_2)$ = 52.5 (s); $\delta_P(C_6D_6)$ = 49.2 (s). IR (THF): ν_{CO} 1737 (w), 1667 (s) cm^{-1}. EI HRMS (m/z): Calcd for $C_{11}H_{11}O_2P$ 206.0497 ([M]+). Found 206.0486 ([M]+).

1-Mesitylphosphinane-2,6-dione (2e). As for **2a** using $MesP(SiMe_3)_2$ (0.05 g, 0.169 mmol) and 0.021 cm^3 (0.169 mmol) glutaryl chloride. After removal of volatiles from the filtrate, the residue was extracted into pentane (3 x 10 cm^3), the extracts combined and the solvent removed under reduced pressure, affording **2e** as a colourless solid, dried in vacuo. Yield: 0.014 g, 33 %. ^1H NMR (C_6D_6): δ_H = 6.71 (br s, aromatic C-H, 2H), 2.27 (q, $CH_2CH_2CH_2$, $^1J_{HH}$ = 6.8 Hz, 4H), 2.22 (s, CH_3, 6H), 2.01 (s, CH_3, 3H), 1.41 (br m, $CH_2CH_2CH_2$, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ_C = 217.0 (d, C(O), $^1J_{CP}$ = 41.4 Hz), 145.8 (s, aromatic), 142.0 (d, aromatic, J_{CP} 2.4 Hz), 129.8 (d, aromatic, 6.7 Hz), 121.0 (aromatic, from HMBC), 45.2 (d, $CH_2CH_2CH_2$, $^2J_{CP}$ = 33.5 Hz), 23.9 (d, CH_3, $^3J_{CP}$ = 12.9 Hz), 21.2 (s, CH_3), 18.1 ($CH_2CH_2CH_2$, $^3J_{CP}$ = 1.8Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P = 31.3 (s). IR (THF): ν_{CO} 1738 (w), 1659 (s) cm^{-1}. EI HRMS (m/z): Calcd for $C_{14}H_{17}O_2P_1$ 248.0966 ([M]+). Found 248.0960 ([M]+).

1-Methylphosphepane-2,7-dione (3a). To a cooled (–78°C) solution of $MeP(SiMe_3)_2$ (0.199 g, 1.03 mmol) in Et_2O (5 cm^3) was added adipoyl chloride (0.15 cm^3, 1.03 mmol). After stirring for 30 minutes at this temperature, the mixture was allowed to warm to ambient temperature and stir for a further 16 hours. The mixture was filtered through an alumina plug, washing with Et_2O (5 x 5 cm^3), then concentrated under reduced pressure to afford **3a** as a colourless oil. Yield: 0.019 g, 12%. ^1H NMR ($CDCl_3$): δ_H = 2.81 (br, CH_2, 4H), 1.61 (br, CH_2, 4H), 1.53 (d, CH_3, $^2J_{HP}$ = 2.0 Hz, 3H). ^1H NMR (C_6D_6): δ_H = 2.26 (br, CH_2, 4H), 1.50 (br, CH_2, 2H), 1.36 (d, CH_3, $^2J_{HP}$ = 1.95 Hz, 3H), 1.30 (br, CH_2, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ_C = 217.3 (d, C(O), $^1J_{CP}$ = 48 Hz), 48.0 (d, 2 x CH_2, $^2J_{CP}$ = 35 Hz), 22.5 (d, 2 x CH_2, $^3J_{CP}$ = 2.5 Hz), 1.8 (d, CH_3, $^1J_{CP}$ = 6 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P = 39.7 (s). IR (THF): ν_{CO} 1659 (s) cm^{-1} (symm not observed) EI HRMS (m/z): Calcd for $C_7H_{11}O_2P$ 158.0497 ([M]+). Found 158.0495 ([M]+).

1-^{n}Butylphosphepane-2,7-dione (3b). As for **3a**, using $^nBuP(SiMe_3)_2$ (0.376 g, 1.4 mmol) and 0.2 cm^3 (1.4 mmol) adipoyl chloride. Yield: 0.088 g, 31%. ^1H NMR (C_6D_6): δ_H = 2.27 (br, CH_2 (ring), 4H), 2.16 (m, CH_2 (butyl), 2H), 1.51 (m, CH_2 (butyl), 2H), 1.40 (br. Unres, CH_2 (ring), 4H), 1.33 (sextet, CH_2 (butyl), J = 7.2 Hz, 2H), 0.83 (t, CH_3, $^1J_{HH}$ 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ_C = 218. 5 (d, C(O), $^1J_{CP}$ = 47.5 Hz), 47.7 (d,CH_2 ring, $^2J_{CP}$ = 32 Hz), 28.7 (d, CH_2, $^1J_{CP}$ = 15.0 Hz), 24.4 (d, CH_2, $^2J_{CP}$ = 12.5 Hz), 22.4 (d, CH_2 ring, $^3J_{CP}$ = 2.5 Hz), 19.3 (d, CH_2, $^3J_{CP}$ = 6.5 Hz), 13.9 (s, CH_3). ^{31}P NMR (C_6D_6): δ_P = 48.9 (apparent nonet, J_{PH} = 5.9 Hz). IR (THF): ν_{CO} 1736 (w), 1657 (s) cm^{-1} EI HRMS (m/z): Calcd for $C_{10}H_{17}O_2P$ 200.0966 ([M]+). Found 200.0980 ([M]+).

1-^{t}Butylphosphepane-2,7-dione (3c). As for **3a**, using $^tBuP(SiMe_3)_2$ (0.330 g, 1.4 mmol) and 0.2 cm^3 (1.40 mmol) adipoyl chloride. After stirring overnight, the mixture was filtered and the solvent removed under reduced pressure. The crude product was extracted into cold hexane (10 cm^3) and the extracts stripped of volatiles then dried in vacuo, affording **3c** as a colourless solid. Yield: 0.114 g, 40 %. ^1H NMR ($CDCl_3$): δ_H = 2.74 (br, CH_2, 4H), 2.08 (br, CH_2, 4H), 1.29 (d, $^2J_{HP}$ = 13.24 Hz, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C = 221.7 (d, C(O), $^1J_{CP}$ = 50.0 Hz), 48.0 (d, CH_2, $^2J_{CP}$ = 27.1 Hz), 34.5 (d, $C(CH_3)_3$, $^1J_{CP}$ = 12.7 Hz), 27.8 (d, $C(CH_3)_3$, $^2J_{CP}$ = 8.5 Hz), 22.6 (d, CH_2 $^3J_{CP}$ = 4.2 Hz). $^{31}P\{^1H\}$ NMR: $\delta_P(CDCl_3)$ = 62.3 (s). $\delta_P(C_6D_6)$ = 60.9. IR (THF): ν_{CO} 1736 (w), 1652 (s) cm^{-1}. HRMS (m/z): Calcd for $C_{10}H_{17}O_2P$ 200.0966 ([M]+). Found 200.0863 ([M]+).

1-Phenylphosphepane-2,7-dione (3d). As for **3c**, using $PhP(SiMe_3)_2$ (0.272 g, 1.07 mmol) and 0.15 cm^3 (1.07 mmol) adipoyl chloride. Yield: 0.025 g, 11%. ^1H NMR ($CDCl_3$): δ = 7.57-7.35 (m, aromatic, 5H), 2.93 (br, CH_2, 4H), 2.20 (br, CH_2, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C = 218.3 (d, C(O), $^1J_{CP}$ = 46.6 Hz), 137.0 (d, C^i, $^1J_{CP}$ = 18.7 Hz), 131.1 (d, C^m, $^3J_{CP}$ = 2.5 Hz), 128.9 (d, C^o, $^2J_{CP}$ = 9.3 Hz), 127.5 (s, C^p), 47.6 (d, CH_2, $^2J_{CP}$ = 34 Hz), 22.8 (d, CH_2, $^3J_{CP}$ = 3.9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P = 52.2 (s); $\delta_P(C_6D_6)$ = 49.0. IR (THF): ν_{CO} 1735 (w), 1665 (s) cm^{-1}. HRMS (m/z): Calcd for $C_{12}H_{13}O_2P$ 220.0653 ([M]+). Found 220.0650 ([M]+).

***cis*-[PtCl$_2$(Ph)P{C(O)(CH$_2$)$_3$C(O)}] (4).** Dichloromethane solutions (5 cm^3) of **2d** (20 mg, 0.049 mmol) and $[Pt(PEt_3)Cl_2]_2$ (37 mg, 0.049 mol) were combined and stirred for 16 h. The resulting yellow solution was concentrated under reduced pressure, affording a yellow solid that was recrystallised from DCM/pentane. Yield: 24 mg, 83 % yield. ^1H NMR (CD_2Cl_2): δ_H = 7.72 (m, aromatic, 2H), 7.64 (m, aromatic, 1H), 7.54 (dt, aromatic, J_{HH} = 7.40 Hz, 2H), 3.47 (m, CH_2 (ring) 2H), 2.80 (m, CH_2 (ring) + $CH\underline{H}$, 3H), 1.90 (m, $C\underline{H}H$, 1 H), 1.81 (dq, CH_2 (PEt_3), J_{PH} 10.2 Hz, J_{HH} 7.7 Hz, 6H), (dt, CH_3 (PEt_3), J_{PH} 18.1 Hz, $^1J_{HH}$ = 7.7 Hz, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ_C = 208.8 (dd, C(O), $^1J_{CP}$ = 6 Hz, 1 Hz), 136.1 (d, C^m, $^3J_{CP}$ = 10 Hz, J_{PtC} 33 Hz), 133.9 (d, C^p, $^4J_{CP}$ = 3 Hz), 129.6 (d, C^o, $^2J_{CP}$ = 11 Hz), 121.0 (d, C^i, $^1J_{CP}$ = 55 Hz), 45.7 (d, CH_2, $^2J_{CP}$ = 38 Hz), 18.1 (d, J_{CP} = 1.6 Hz, CHH), 16.1 (d, CH_2 (PEt_3), $^1J_{CP}$ = 40.0 Hz, J_{PtC} 35 Hz), 8.5 (d, CH_3 (PEt_3), $^2J_{CP}$ = 3.4 Hz, J_{PtC} 25 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 26.8 (d, $R_2Ph\underline{P}Pt$, $^2J_{PP}$ = 14.9 Hz, J_{PtP} = 3413 Hz), 9.0 (d, $Pt\underline{P}Et_3$, $^2J_{PP}$ = 15 Hz, $J_{(PtP)}$ = 3166 Hz). ^{195}Pt NMR (CD_2Cl_2): δ_P = –4432 (dd,$^1J_{PtP}$ = 3410, 3164 Hz). IR (THF): ν_{CO} 1717, 1694 cm^{-1}. Anal. Calc. for $C_{17}H_{26}Cl_2O_2P_2Pt$: C, 34.59; H, 4.44. Found: C, 34.62; H, 4.49.

[W(CO)$_5$(L)]. In a typical procedure, a THF solution (2 cm^3) of **2a** (20 mg, 0.14 mmol) was combined with excess of $[W(CO)_5(THF)]$ (ca 0.1 M, 2.8 cm^3, ca. 0.28 mmol) and the mixture stirred for 16 h. The volatiles were removed under reduced pressure and the crude product extracted first into Et_2O (5 cm^3) then, following concentration of the extract, into cold pentane (5 cm^3, 0 °C). Removal of the solvent afforded **5a** as a pale yellow solid. Yield: 23 mg, 35 %. ^1H NMR (C_6D_6): δ_H = 2.40 (ddd, CH_2, $^2J_{CP}$ = 16.2 Hz, 12.2, 4.8 Hz, 2H), 1.97 (tdd, CH_2, $^2J_{CP}$ = 15,3, 5.7, 3.4 Hz, 2H), 1.40 (d, CH_3, $^1J_{CP}$ = 8 Hz, 3H), 1.18 (m, CH_2, 1H), 0.62 (m, CH_2, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ_C = 214.8

(d, C(O), $^{1}J_{CP}$ = 3.4 Hz), 197.9 (d, W(CO)$_{trans}$,$^{2}J_{CP}$ = 21.5 Hz, $^{1}J_{CW}$ = 149 Hz), 195.4 (d, W(CO)$_{cis}$, $^{2}J_{CP}$ = 5.7 Hz, $^{1}J_{WC}$ = 125 Hz), 42.3 (d, CH_2, $^{2}J_{CP}$ = 35.6 Hz), 17.8 (d, CH_2, $^{3}J_{CP}$ = 2.5 Hz), 9.0 (d, CH_3, $^{1}J_{CP}$ = 29.1 Hz). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P = 20.7 (s, $^{1}J_{WP}$ = 202 Hz). IR(THF) ν/cm^{-1}: 2076, 1946, 1933 [WCO], 1702, 1685 [CO]. Anal. Calc. for $C_{11}H_9O_7PW$: C, 28.23; H, 1.94. Found: C, 28.55; H, 2.17.

5b. From **2b** (13 mg, 0.07 mmol). Obtained as a yellow oil. Yield: 18 mg, 50 %. ^{1}H NMR (C_6D_6): δ_H = 2.34 (ddd, CH_2(ring), J = 16.3, 12.09, 4.2 Hz, 2H), 2.06 – 1.96 (m x 2, CH_2 (butyl) + CH_2 (ring), 4H), 1.25 (m, CH_2 (butyl), 2H), 1,22 (m, CH*H*, 1H), 1.01 (sextet, CH_2, $^{2}J_{HH}$ = 7.47 Hz, 2H), 0.79 (m, CH*H*, 1H), 0.67 (t, CH_3, $^{2}J_{HH}$ = 7.36 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C = 214.8 (d, C(O), $^{1}J_{CP}$ = 3.8 Hz), 197.9 (d, WCO$_{trans}$, $^{1}J_{CP}$ = 20.8 Hz, J_{WP} = 148 Hz), 195.4 (d, WCO$_{cis}$, $^{2}J_{CP}$ = 5.7 Hz, $^{1}J_{WC}$ = 125 Hz), 43.1 (d, CH_2 (ring), $^{2}J_{CP}$ = 33.0 Hz), 28.9 (d, CH_2 (butyl), $^{3}J_{CP}$ = 6.5 Hz), 26.3 (d, CH_2 (butyl), $^{1}J_{CP}$ = 23.1 Hz), 24.2 (d, CH_2 (butyl), $^{2}J_{CP}$ = 12.5 Hz), 17.6 (d, CH_2 (ring), $^{3}J_{CP}$ = 2.7 Hz), 13.4 (s, CH_3). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P = 33.1 (s, $^{1}J_{WP}$ = 202.0 Hz). IR(THF) ν/cm^{-1}: 2075, 1953, 1950, 1942 [WCO], 1683, 1660 [CO]. Anal. Calc. for $C_{14}H_{15}O_7PW$: C, 32.97; H, 2.96. Found: C, 33.15; H, 3.17.

5c. From **2c** (35 mg, 0.19 mmol). Yield: 60 mg, 62 %. ^{1}H NMR (C_6D_6): δ_H = 2.29 (ddd, CH_2 J = 16.5, 11.5, 4.3 Hz, 2H), 1.95 (dddd, CH_2, J = 16.6, 9.9, 6.7. 3.4 Hz, 2H), 1.15 (m, CH_2, 1H), 1.14 (d, C(C<u>H</u>$_3$)$_3$, J = 15.3 Hz, 9H), 0.90 (m, CH_2, 1H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C = 215.8 (d, C(O), $^{1}J_{CP}$ = 8.1 Hz), 197.2 (d, WCO$_{trans}$, $^{2}J_{CP}$ = 22 Hz, J_{PW} 146 Hz), 196.0 (d, WCO$_{cis}$, $^{2}J_{CP}$ = 5.7 Hz, $^{1}J_{WC}$ = 125 Hz), 44.1 (d, CH_2, $^{2}J_{CP}$ = 29.8 Hz), 37.9 (d, <u>C</u>(CH$_3$)$_3$, $^{1}J_{CP}$ = 13.6 Hz), 27.6 (d, C(<u>C</u>H$_3$)$_3$, $^{2}J_{CP}$ = 2.2 Hz)), 16.9 (d, CH_2, $^{3}J_{CP}$ = 3.4 Hz). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P = 51.3 (s, $^{1}J_{WP}$ = 207.0 Hz). IR(THF) ν/cm^{-1}: 2075, 1942, 1934 [WCO], 1676, 1655 [CO]. Anal. Calc. for $C_{14}H_{15}O_7PW$: C, 32.97; H, 2.96. Found: C, 32.84; H, 3.15.

5d. From **2d** (31 mg, 0.15 mmol). Yield: 20 mg, 25%. ^{1}H NMR (C_6D_6): δ_H = 7.58 (m, Ph, 2H), 6.97 (m, Ph, 3H), 2.35 (ddd, CH_2, J = 16.5, 11, 4 Hz, 2H), 2.03 (dddd, CH_2, J = 16.5, 11, 7, 3.5 Hz, 2H), 1.19 (m, CH*H*, 1H), 0.87 (dtt, CH*H*, J = 14, 11, 3.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C = 213.2 (d, C(O), $^{1}J_{CP}$ = 4.6 Hz), 197.8 (d, W<u>C</u>(O)$_{trans}$, $^{1}J_{CP}$ = 22.5 Hz, , $^{1}J_{WC}$ = 148 Hz), 195. 7 (d, W<u>C</u>O$_{cis}$, $^{1}J_{CP}$ = 5.7 Hz, $^{1}J_{WC}$ = 125 Hz), 133.1 (d, C^{o}, $^{2}J_{CP}$ = 10.2 Hz), Hz), 131.5 (d, C^{p}, $^{4}J_{CP}$ = 2.5 Hz), 129.3 (d, C^{m}, $^{3}J_{CP}$ = 10.2 Hz), 127.2 (d, C^{i}, $^{1}J_{CP}$ = 39.8 Hz), 43.2 (d, CH_2, $^{2}J_{CP}$ = 33.9 Hz), 17.1 (d, CH_2, $^{3}J_{CP}$ = 2.5 Hz). ^{31}P $\{^{1}H\}$ NMR (C_6D_6): δ_P = 28.9 ($^{1}J_{PW}$ = 213.9 Hz). IR(THF) ν/cm^{-1}: 2076, 1949 (br) [WCO], 1688 (br) [CO] cm^{-1}. Anal. Calc. for $C_{16}H_{11}O_7PW$: C, 36.25; H, 2.09. Found: C, 36.02; H, 1.87.

[W(CO)$_5$(3b)] (6). A THF solution (2 cm^3) of **3b** (15 mg, 0.075 mmol) was combined with excess of [W(CO)$_5$(THF)] (ca 0.1 M, 3.0 cm^3, ca. 0.30 mmol) and the mixture stirred for 16 h. The volatiles were removed under reduced pressure and the crude product extracted into Et_2O (5 cm^3); the extract was passed sequentially through four plugs of Celite®, then the solvent removed under reduced pressure to afford **6** as a pale yellow solid. Yield: 3 mg, 13 %. ^{1}H NMR (C_6D_6): δ_H = 2.54 (br m, CH_2 (ring), 2H), 2.09 (br m, CH_2 (ring), 2H), 2.01 (m, P<u>C</u>H$_2$, 2H), 1.32 (m, CH_2 (ring), 2H), 1.30 (m, CH_2 (butyl), 2H), 1.14 (br m, CH_2 (ring), 2H), 1.06 (Sextet, -CH_2C<u>H</u>$_2$$CH_3$, $^{1}J_{HH}$ = 7.40 Hz, 2H), 0.70 (t, CH_3, $^{1}J_{HH}$ = 7.40 Hz). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C = 215.7 (d, C(O), $^{1}J_{CP}$ = 3.2 Hz), 198.0 (d, W<u>C</u>(O), $^{1}J_{CP}$ = 22.5 Hz, $^{1}J_{CW}$ 147 Hz), 195.8 (d, W<u>C</u>O, $^{1}J_{CP}$ = 6Hz, $^{1}J_{WC}$ = 125 Hz), 44.2 (d, CH_2 $^{2}J_{CP}$ = 36.5 Hz), 27.8 (d, CH_2, $^{3}J_{CP}$ = 3.4 Hz), 27.6 (d, CH_2, $^{1}J_{CP}$ = 22.0 Hz), 24.2 (d, CH_2, $^{2}J_{CP}$ = 12.7 Hz), 24.0 (s, CH_2), 13. 4 (s, CH_3). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P = 39.2 (s, $^{1}J_{WP}$ = 215.7 Hz). IR(THF) ν/cm^{-1}: 2075, 1951, 1946, 1938 [WCO], 1691, 1678 [CO]. EI MS [M]$^+$ Calcd for $C_{15}H_{17}O_7PW$ 522 (77), 523 (55), 524 (100), 525 (17), 526 (85), 527 (15); Found 522 (70), 523 (47), 524 (100), 525 (21), 526 (83), 527 (15).

Conflicts of interest

There are no conflicts to declare.

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