# Facile Syntheses of the Metallacyclic Rings Pt–C–P–C, Pt–N–P–N and Pt–N–S–N; Crystal Structures of [Pt{CH(COPh)P(O)(Ph)CH(COPh)}$(PPh_3)_2$] and [Pt{$C(CO_2Me)=C(CO_2Me)NHS(O)_2NH$}$(PMePh_2)_2$]

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Reaction of $PhCOCH_2P(O)(Ph)CH_2COPh$, RNHP(O)(Ph)NHR or $RNHS(O)_2NHR$ (R = H or Ph) with *cis*-[$PtCl_2L_2$] (L = $PPh_3$ or $PMePh_2$; $L_2$ = $Ph_2PCH_2CH_2PPh_2$ or cycloocta-1,5-diene) in the presence of silver(I) oxide gives metallacyclic complexes of the type [Pt{CH(COPh)P(O)(Ph)CH(COPh)}$L_2$], [Pt{NRP(O)(Ph)NR}$L_2$] or [Pt{$NRS(O)_2NR$}$L_2$] respectively; single crystal X-ray studies on [Pt{CH(COPh)P(O)(Ph)CH(COPh)}$(PPh_3)_2$] and the insertion product [Pt{$C(CO_2Me)=C(CO_2Me)NHS(O)_2NH$}$(PMePh_2)_2$] establish the presence of puckered metallacycles, the oxygen of the platinaphosphetane-3-oxide adopting an equatorial environment.

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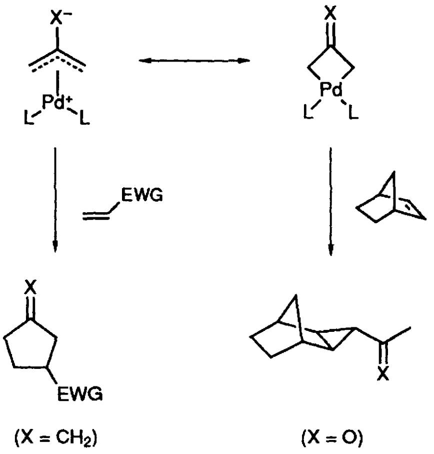
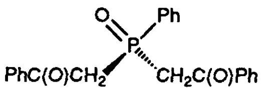
The use of the fragments trimethylenemethane[1,2] and oxodimethylenemethane[3] in metal assisted cycloaddition reactions (Scheme 1) led us to develop routes to complexes of derivatives of the fragment $CH_2S(O)_nCH_2$ ($n$ = 1 or 2).[4–6] Studies on the sulphoxide fragment PhCOCHS(O)CHCOPh showed that platinum complexes were obtained in quantitative yield by treatment of *cis*-[$PtCl_2L_2$] (L = tertiary phosphine donor) with the sulphoxide $PhCOCH_2S(O)CH_2COPh$ in the presence of silver(I) oxide.[5] Herein we report that the use of silver(I) oxide provides convenient synthetic routes to a range of metal complexes of fragments which contain the atom framework C–P–C, N–P–N or N–S–N.

Treatment of *cis*-[$PtCl_2L_2$] with the phosphine oxide **1** in the presence of an excess of silver(I) oxide in refluxing dichloromethane affords quantitative yields of the air-stable complexes **2**. Similarly, reactions of *cis*-[$PtCl_2L_2$] with the phenylphosphonic diamides **3** or the sulphamides **4** in the presence of excess of silver(I) oxide under analogous conditions gives the complexes **5** and **6** respectively.

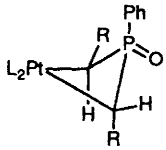
It is noteworthy that this synthetic technique allows isolation of cycloocta-1,5-diene (cod) derivatives, there being no indication of nucleophilic attack on, or displacement of, the diene.[7] We also find that by simply refluxing *cis*-[$PtCl_2(PPh_3)_2$] in acetone in the presence of silver(I) carbonate, a very convenient route to the $\eta^3$-oxodimethylenemethane complex [Pt{$\eta^3$-$CH_2C(O)CH_2$}$(PPh_3)_2$][8] can be achieved. Whether these reactions occur by initial displacement of chloride at platinum or proton removal from the other



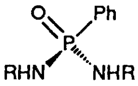
Scheme 1 EWG = electron-withdrawing group



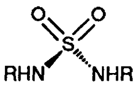
**1**



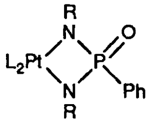
**2** R = COPh
**a**; L = PPh$_3$
**b**; L = PMePh$_2$
**c**; L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
**d**; L$_2$ = cod



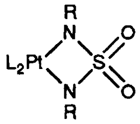
**3 a**; R = H
**b**; R = Ph



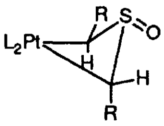
**4 a**; R = H
**b**; R = Ph



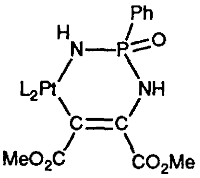
**5** R = H
**a**; L = PPh$_3$
**b**; L = PMePh$_2$
**c**; L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
**d**; L$_2$ = Ph$_2$P(CH$_2$)$_3$PPh$_2$
R = Ph
**e**; L = PPh$_3$
**f**; L = PMePh$_2$
**g**; L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
**h**; L$_2$ = cod



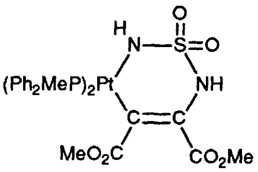
**6** R = H
**a**; L = PPh$_3$
**b**; L = PMePh$_2$
**c**; L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
**d**; L = PPh$_3$
R = Ph
**e**; L = PMePh$_2$
**f**; L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
**g**; L$_2$ = cod



**7 a**; L = PPh$_3$
**b**; L = PMePh$_2$
**c**; L = PMe$_2$Ph



**8 a**; L = PPh$_3$
**b**; L = PMePh$_2$
**c**; L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$
**d**; L$_2$ = Ph$_2$P(CH$_2$)$_3$PPh$_2$



**9**

substrate is not clear but we note that the sulphamide complexes $[\overline{\mathrm{Pt\{NHS(O)_2N}}\mathrm{H\}L_2}]$ (L = PPh$_3$, PMePh$_2$, PEt$_3$ or PMe$_2$Ph; L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$) have recently been obtained by reaction of *cis*-[PtCl$_2$L$_2$] with (NH$_2$)$_2$SO$_2$ in liquid ammonia which presumably proceed *via* initial deprotonation of the sulphamide ligand.[9,10]

Studies on platinathietane-3-oxides **7** have established the presence of puckered rings with the sulphinyl oxygen adopting an equatorial environment.[5,6] The availability of the first examples of 1-metalla-3-phenylphosphetane-3-oxide complexes **2** afforded the opportunity to investigate the conformation of this ring system and to determine the competing conformational requirements of a phenyl group and an oxygen atom in a metallaphosphetane ring. Accordingly a single crystal X-ray structure determination of **2a** was carried out.†

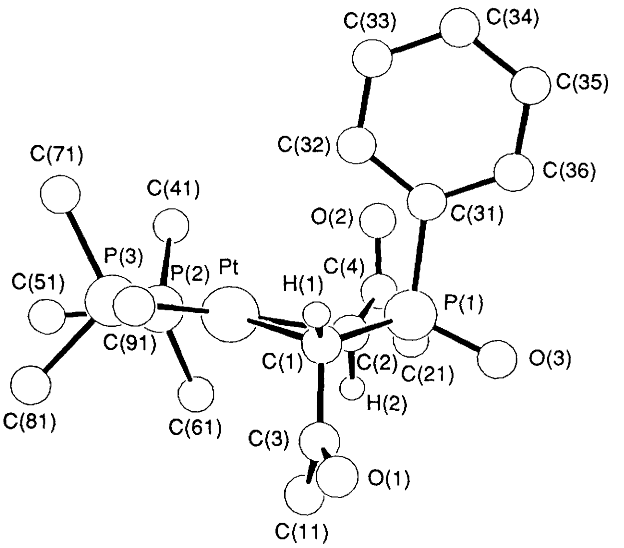


**Fig. 1** Molecular structure of $[\overline{\mathrm{Pt\{CH(COPh)P(O)(Ph)C}}\mathrm{H(COPh)\}(PPh_3)_2}]$ **2a** with phenyl carbons other than those directly bonded to P(2), P(3), C(3) and C(4), and H atoms of the remaining phenyl ring being omitted. Interatomic distances: Pt–P(2) 2.283(2), Pt–P(3) 2.301(2), Pt–C(1) 2.137(7), Pt–C(2) 2.162(7), Pt···P(1) 2.821(2), C(1)–P(1) 1.790(8), C(2)–P(1) 1.782(8), P(1)–O(3) 1.486(6) Å. Angles: P(2)–Pt–P(3) 98.3(1), C(1)–Pt–C(2) 74.9(3), C(1)–Pt–P(2) 92.9(2), C(2)–Pt–P(3) 93.7(2), C(1)–P(1)–C(2) 94.0(3)°

Fig. 1 shows the geometry of the platina-3-phenylphosphetane-3-oxide ring which is folded about the line C(1)–C(2) by 31.1° and is slightly less puckered than the platinathietane-3-oxide ring in **7a** (fold angle = 36.7°).[5,6] The P=O oxygen in **2a** occupies an equatorial environment as observed in $\overline{\mathrm{C{-}C{-}C{-}P}}$(O)Ph rings providing there are no *cis*-3-methyl-1-phenyl interactions.[11] In **2a** 1,3-diaxial interactions will be minimised by the presence of a square planar platinum(II) function. Fold angles in $\overline{\mathrm{C{-}C{-}C{-}P}}$(O)Ph rings lie in the range 16–30°.[11]

The Pt···P(1) distance of 2.821(2) Å, just outside the sum of the covalent radii of 2.6 Å, indicates no significant transannular Pt···P interaction in **2a**. Furthermore the P=O distance is normal for phosphetane-1-oxides which occur in the range 1.47–1.48 Å.[11] The C–P ring bonds are slightly

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† *Crystal data*: Crystals of **2a** and **9** were grown slowly from chloroform–light petroleum and dichloromethane–light petroleum respectively. Data were collected at 293 K using Mo-K$\alpha$ X radiation, $\lambda$ = 0.7107 Å, on a Stöe STADI-2 Weissenberg diffractometer. **2a**, $\mathrm{C_{58}H_{47}O_3P_3Pt{\cdot}CHCl_3}$, $M$ = 1199.4, 0.39 × 0.48 × 0.84 mm, monoclinic, space group $P2_1/c$, $a$ = 12.370(5), $b$ = 17.74(3), $c$ = 23.98(5) Å, $\beta$ = 96.39(8)°, $U$ = 5228.3 Å$^3$, $Z$ = 4, $D_c$ = 1.523 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 28.30 cm$^{-1}$; final $R$ 0.048 ($R_w$ 0.049) for 6999 independent reflections [$I > 3\sigma(I)$] in the range $7 < 2\theta < 54°$. **9**, $\mathrm{C_{32}H_{34}N_2O_6P_2PtS}$, $M$ = 831.7, 0.40 × 0.41 × 0.21 mm, monoclinic, space group $P2_1/c$, $a$ = 16.330(27), $b$ = 11.114(19), $c$ = 18.728(9) Å, $\beta$ = 100.03(2)°, $U$ = 3347.1 Å$^3$, $Z$ = 4, $D_c$ = 1.663 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 42.0 cm$^{-1}$; an absorption correction was applied to the data with maximum and minimum transmission factors of 0.66 and 0.32; final $R$ 0.0698 ($R_w$ 0.0725) for 4250 independent reflections [$I > 3\sigma(I)$] in the range $7 < 2\theta < 54°$. The amino hydrogens were not found. Some residual electron density was found around the platinum atom. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

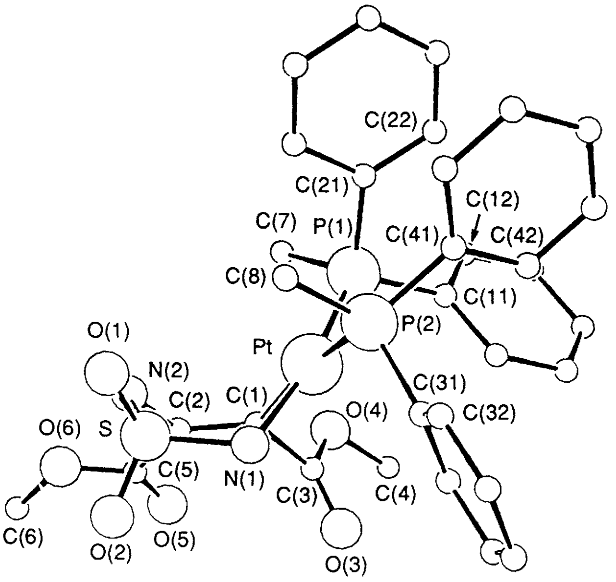

**Fig. 2** Molecular structure of [$\overline{Pt\{C(CO_2Me){=}C(CO_2Me)NH\text{-}S(O)_2NH\}}(PMePh_2)_2$] **9** with all hydrogens omitted. Interatomic distances: Pt–P(1) 2.183(5), Pt–P(2) 2.330(4), Pt–N(1) 2.03(1), Pt–C(1) 2.07(2), C(1)–C(3) 1.50(2), C(1)–C(2) 1.32(2), C(2)–C(5) 1.48(2), C(2)–N(2) 1.47(2), N(2)–S 1.66(1), S–O(1) 1.46(1), S–O(2) 1.43(1), S–N(1) 1.65(1) Å. Angles: P(2)–Pt–P(1) 101.6(2), C(1)–Pt–P(1) 92.9(6), C(1)–Pt–N(1) 82.7(6), P(2)–Pt–N(1) 83.4(3), Pt–C(1)–C(2) 120.3(1), C(1)–C(2)–N(2) 118.0(1), C(2)–N(2)–S 112.9(1), O(1)–S–O(2) 118.4(8), N(2)–S–N(1) 108.4(6), S–N(1)–Pt 113.6(6)°

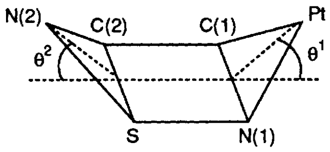

**Fig. 3** Fold angles $\theta^1$ and $\theta^2$ in **9** using the best plane through the atoms N(1)–S–C(2)–C(1): $\theta^1$ = 51.28°, $\theta^2$ = 43.95°

shorter than expected, C–P distances occurring in the range 1.80–1.91 Å for 3-phenyiphosphetane-3-oxide rings.[11] Similar C–S bond shortening has been observed in $\overline{Pt{-}C{-}S(O)_n{-}C}$ ($n$ = 1 or 2) rings.[4,6] It is noteworthy that the CPC bond angle of 94.0° in **2a** is significantly larger than the angle found in $\overline{C{-}C{-}C{-}P}(O)Ph$ rings (range 79–82°),[11] showing that the presence of a large platinum atom significantly reduces ring strain. We also note that **2a** is a *trans*-isomer with one of the benzoyl groups in a pseudo-axial environment, as found in metallathietane-3-oxides[4,5] and -3,3-dioxides[6] of platinum(II) and several metallacyclobutan-3-ones.[12–14]

The $^{31}P$-{$^1H$} NMR spectrum of **2a** exhibits three sets of resonances, each resonance appearing as a doublet of doublets with accompanying $^{195}Pt$ satellites. The $^1H$ NMR spectrum is consistent with the static structure shown. The magnitudes of the three-bond couplings (*Jcis*-P–Pt–C–H) for the axial and equatorial ring protons are under dihedral angle control as has been observed in highly puckered metallacyclobutan-3-one[12–14] and metallathietane-3-oxide complexes.[4,5] Thus $H(2)_{ax}$ exhibits coupling to the ring phosphorus and the *trans*-phosphorus ligand, with no discernible coupling to the *cis*-phosphorus ligand [*cis*-P–Pt–C–H(2) torsion angle 61.6°] and appears as a doublet of doublets with $^{195}Pt$ satellites. In contrast, $H(1)_{eq}$ exhibits coupling to the ring phosphorus and both the *cis*-phosphorus [*cis*-P–Pt–C–H(1) torsion angle −35.0°] and *trans*-phosphorus ligands. It is also noteworthy that the magnitude of the two-bond couplings [P(1)–C–H] is also under dihedral angle control with respect to the P=O moiety. Thus, for H(2), $^2J$[P(1)H(2)] = 17 Hz, [H(2)–C–P–O torsion angle 29.4°], while for H(1), $^2J$[P(1)H(1)] = 7 Hz, [H(1)–C–P–O torsion angle 83.9°].[15]

Preliminary studies show that some of the complexes readily undergo insertion reactions. Thus, treatment of **5a–d** or **6b** with an excess of dimethyl acetylenedicarboxylate in dichloromethane at room temperature affords the insertion products **8a–d** and **9** respectively. Interestingly, the one-pot reaction of *cis*-[$PtCl_2(PPh_3)_2$], **3a**, dimethyl acetylenedicarboxylate and an excess of silver(I) oxide in refluxing dichloromethane also leads to formation of **8a**. Complex **9** was characterised by an X-ray diffraction study, and the geometry of the molecule is shown in Fig. 2. The six-membered ring exists in a pseudo-boat conformation, with the fold angles between the best planes N(1)–S–C(2)–C(1), C(1)–Pt–N(1) and S–N(2)–C(2) being depicted in Fig. 3. The plane N(1)–S–C(2)–C(1) possesses a slight twist element, the torsion angle from planarity being 8.8°. The S=O bond distances are comparable to those reported for **6b**[9] but the N–S distances are slightly longer in **9**. Interestingly, the non-bonded contact distances Pt···S and Pt···N(2) are equal in **9** at 3.092 Å. The boat conformation found for **9** may be preferred over the half-chair conformation normally found in cyclohexenes since in the half-chair conformation there will be unfavourable steric interactions between the phosphine ligand *cis* to the $C(CO_2Me)$ ester group. These insertion reactions are inhibited by *N*-phenyl substituents, since analogous reactions with [$\overline{Pt\{NPhS(O)_2NPh\}}L_2$] do not take place.

We thank the SERC for support and Johnson Matthey plc for the generous loan of platinum metal salts.

*Received, 9th July 1990; Com. 0/03086D*

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