# Silver(I) Oxide-mediated Syntheses of Four-membered Ring Platinalactones

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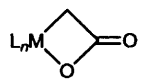
Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with an excess of dialkyl malonate in the presence of silver(I) oxide afforded the platinalactone complexes $[\overline{\mathrm{Pt\{OC(O)C}}\mathrm{H(CO_2R)\}(PPh_3)_2}]$ (R = Me or Et), *via* a novel cyclisation reaction. The platinalactone complexes have been fully characterised by NMR spectroscopy. Functionalised acetic acids containing activated hydrogens may also be used to synthesise four-membered ring platinalactones.

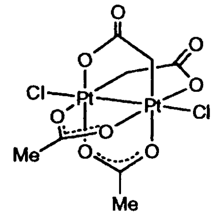
There is significant current interest in the chemistry of small-ring metallacycles, particularly four-membered rings.[1] Metallalactones **1** are one such ring system, and have been considered as intermediates in various transition-metal-mediated reactions involving the transformation or generation of lactones.[2] Examples of isolated metallalactones remain relatively rare however, and are largely limited to the platinum-group metals. Various methods have been employed for their synthesis in recent years, including the oxidative addition of the C–O bond of propiolactone (oxeten-2-one) to low-valent metal centres,[3] cyclometallation of functionalised benzoic and other unsaturated carboxylic acids,[4] and oxidative-coupling reactions of low-valent alkene complexes with carbon dioxide.[5] Metallalactones are not restricted to a single metal centre, however, and the dinuclear platinum(III) complex **2**[6] may be formulated as a diplatinalactone ring system.

Metallalactones are potentially important synthetic reagents, and recently a series of five- and six-membered ring nickelalactones **3**, synthesised from $[Ni(acac)_2]$ (acac = acetylacetonate), 2,2'-bipyridine (bipy), triethylaluminium and cyclic acid anhydrides, were found to be useful in $MnI_2$-catalysed cross-coupling reactions with alkyl iodides, yielding functionalised carboxylic acids.[7]

As part of a general study into methods for synthesising small-ring metallacycles we have recently demonstrated the utility of silver(I) oxide for the synthesis of a range of four-membered ring metallacycles of the type **4**.[8,9] Silver(I) oxide has previously been used to prepare a number of metal–alkyl complexes, from metal halide complexes and C–H acids, such as nitromethane, phenylacetylene, and acetone,[10] the role of the silver oxide being both as a halide-abstracting reagent and a strong base. As part of our studies we wished to extend this methodology to the synthesis of metallalactones, and in this paper report some studies on the synthesis of platinalactone complexes. In a recent communication[11] one of us (R. D. W. K.) reported that some related unsaturated platinalactone complexes **5** can be prepared using the silver(I) oxide-mediated reaction between *cis*-$[PtCl_2L_2]$ and 2-acetamidoacrylic acid.



**1**



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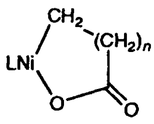
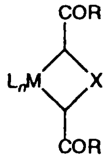


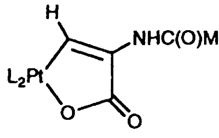
**3**

L = bipy or $Me_2NCH_2CH_2NMe_2$

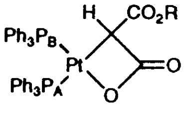


**4**

M = Pd or Pt;
X = CO, $SO_2$, or SO;
R = OMe or Ph



**5**



**6a** R = Me
**6b** R = Et
**6c** R = H

## Experimental

Melting points were measured in air on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin Elmer 580 spectrophotometer, $^1H$ and $^{13}C$-$\{^1H\}$ NMR in either $CDCl_3$ or $CD_2Cl_2$ and $^{31}P$-$\{^1H\}$ NMR spectra in either $CDCl_3$ or $CD_2Cl_2$–$CH_2Cl_2$ on either a Bruker ACP400 ($^1H$, 400.13; $^{31}P$, 162.00; $^{13}C$, 100.62 MHz), AC300 ($^{13}C$, 75.5 MHz) or on a JEOL JNM-FX60 spectrometer ($^{31}P$, 24.15 MHz). The NMR spectra were referenced relative to internal $SiMe_4$ ($^1H$ and $^{13}C$) or external 85% $H_3PO_4$ ($^{31}P$), with positive values of chemical shift, in ppm, being to high frequency (low field). Carbonyl assignments were confirmed by a long-range $^{13}C$–$^1H$ chemical shift correlation experiment[12] acquired with 4K data points in F2 and 128 increments in F1 with 256 scans per increment, the delays for defocusing and refocusing C–H multiplets being set to 62.5 and 31.25 ms respectively, *i.e.* arbitrarily optimised for $J$ = 8 Hz.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using dichloromethane solvent which was dried and distilled from calcium hydride under nitrogen prior to use. Light petroleum refers to the fraction boiling in the range 40–60 °C. The metal complexes were air-stable and were recrystallised in air. Dimethyl and diethyl malonates and dibenzoylmethane were used as supplied (Aldrich). The compounds $[PtCl_2(cod)]$[13] (cod = cycloocta-1,5-diene), and (phenylsulfonyl)acetic acid[14] were prepared by literature procedures.

*Preparations.*—$[Pt\{OC(O)CH(CO_2Me)\}(PPh_3)_2]$ **6a**. Triphenylphosphine (0.42 g, 1.605 mmol), dimethyl malonate (0.5 cm$^3$, excess) and silver(I) oxide (0.5 g, 2.16 mmol) were added in succession to a stirred solution of $[PtCl_2(cod)]$ (0.30 g, 0.802 mmol) in dichloromethane (50 cm$^3$), and the mixture was refluxed for 24 h. After filtration to remove silver salts, the filtrate was evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (*ca.* 3 cm$^3$) followed by addition of light petroleum (*ca.* 60 cm$^3$) gave a very pale yellow solid which was filtered off and dried *in vacuo* to give the product (0.642 g, 86%). Recrystallisation by addition of light petroleum to a dichloromethane solution gave colourless plates (Found: C, 54.3; H, 4.2. $C_{40}H_{34}O_4P_2Pt\cdot 0.5CH_2Cl_2\cdot H_2O$ requires C, 54.3; H, 4.2%), m.p. 188–192 °C (decomp.); IR $\nu$(C=O) at 1710vs (br) cm$^{-1}$. Fast atom bombardment (FAB) mass spectrum (positive-ion mode, *m*-nitrobenzyl alcohol matrix): $[M + H]^+$ at *m/z* 836. NMR: $^1$H (400 MHz, $CD_2Cl_2$), δ 7.6–7.2 (m, 30 H, Ph), 3.20 (s, 3 H, Me), 2.34 [dd, 1 H, Pt–CH, $^3J(PH)_{trans}$ 6.8, $^3J(PH)_{cis}$ 3.1, $^2J$(PtH) 53 Hz]; solvents of crystallisation identified by recording a spectrum in $CDCl_3$; $^{13}$C-{$^1$H} (100 MHz, $CD_2Cl_2$), δ 177.55 [dd, C=O lactone, $^3J$(PC) 4.9, 2.9, $^2J$(PtC) 127], 173.25 [dd, C=O ester, $^3J$(PC) 3.9, 1.5, $^2J$(PtC) 34], 50.81 (s, $CH_3$) and 33.79 [d, Pt–CH, $^2J$(PC) 69.9, $^1J$(PtC) 364]; a fully coupled $^{13}$C spectrum gave for Pt–CH carbon, $^1J$(CH) 146.6, $^2J(HCC_{lactone})$ 2.6 and for $CH_3$, $^1J$(CH) 146.0 Hz; $^{31}$P-{$^1$H} (24 MHz, $CDCl_3$), AB spin system, δ 18.10 [d, $P_A$, $^1J$(PtP) 2412, $^2J$(PP) 19.5] and 9.68 [d, $P_B$, $^1J$(PtP) 4219, $^2J$(PP) 19.5 Hz].

$[Pt\{OC(O)CH(CO_2Et)\}(PPh_3)_2]$ **6b**. This compound was prepared in 88% yield in analogous fashion to **6a**, using diethyl malonate (Found: C, 55.4; H, 4.4. $C_{41}H_{36}O_4P_2Pt\cdot 0.5CH_2Cl_2\cdot H_2O$ requires C, 54.8; H, 4.3%), m.p. 127–131 °C; $\nu$(C=O) at 1712vs (br) cm$^{-1}$. NMR: $^1$H (400 MHz, $CD_2Cl_2$), δ 7.8–7.2 (m, 30 H, Ph), 3.86 [$ABX_3$ spin system, 1 H, dq, $CH_xH_y$, $J(H_xMe)$ 7.2, $J(H_xH_y)$ 10.7], 3.53 [$ABX_3$ spin system, 1 H, dq, $CH_xH_y$, $J(H_yMe)$ 7.2], 2.29 [dd, 1 H, Pt–CH, $^3J(PH)_{trans}$ 6.4, $^3J(PH)_{cis}$ 3.2, $^2J$(PtH) 47] and 1.02 [t, 3 H, Me, $J$(HH) 7.15 Hz]; $^{13}$C-{$^1$H} (100 MHz, $CD_2Cl_2$), δ 177.59 [dd, C=O lactone, $^3J$(PC) 4.8, 2.4, $^2J$(PtC) 126.9], 172.85 [d, C=O ester, $^3J$(PC) 4.31, $^2J$(PtC) 35.3], 59.62 (s, $CH_2$, ester), 34.25 [d, Pt–CH, $^2J$(PC) 69.68, $^1J$(PtC) 367 Hz] and 14.06 (s, $CH_3$); $^{31}$P-{$^1$H} (24 MHz, $CDCl_3$), AB spin system, δ 18.66 [d, $P_A$, $^1J$(PtP) 2393, $^2J$(PP) 14.7] and 8.98 [d, $P_B$, $^1J$(PtP) 4230, $^2J$(PP) 14.7 Hz].

*cis*-$[PtCl\{OC(O)CH_2SO_2Ph\}(PPh_3)_2]\cdot H_2O$ **8**. Triphenylphosphine (0.150 g, 0.573 mmol), (phenylsulfonyl)acetic acid (0.054 g, 0.270 mmol), and silver(I) oxide (0.4 g, 1.73 mmol) were added in succession to a stirred solution of $[PtCl_2(cod)]$ (0.10 g, 0.267 mmol) in dichloromethane (20 cm$^3$), and the mixture refluxed for 1 h. The silver salts were filtered off, and the filtrate evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (*ca.* 10 cm$^3$) followed by addition of light petroleum (*ca.* 30 cm$^3$) gave, on standing, a white microcrystalline solid which was filtered off and dried *in vacuo* to give complex **8** (0.188 g, 72%) (Found: C, 54.35; H, 4.0. $C_{44}H_{37}ClO_4P_2PtS\cdot H_2O$ requires C, 54.4; H, 4.0%), m.p. 207–208 °C (decomp.); $\nu_{max}$ at 1657vs, 1438s, 1373s (br), 1151s, 1099vs, 749s and 698vs cm$^{-1}$. NMR ($CDCl_3$): $^1$H (300 MHz), δ 8.05–7.09 (m, 35 H, Ph), 3.13 (s, 2 H, $CH_2$) and 1.83 (s, br, 2 H, $H_2O$); $^{31}$P-{$^1$H} (24 MHz), AB spin system, δ 18.35 [d, $P_B$, $^1J$(PtP) 3872, $^2J$(PP) 19.5] and 2.42 [d, $P_A$, $^1J$(PtP) 3682, $^2J$(PP) 19.5 Hz].

$[Pt\{OC(O)CH(SO_2Ph)\}(PPh_3)_2]$ **9**. An identical mixture of reactants to that above was refluxed in dichloromethane for 16 h, and then stirred for 72 h at room temperature. The mixture was filtered, and the brownish yellow filtrate evaporated to dryness under reduced pressure to afford a brown oil which was examined by $^{31}$P-{$^1$H} NMR spectroscopy and found to contain the complex **9** in about 50% yield, together with three other unidentified phosphorus-containing compounds. $^{31}$P-{$^1$H} NMR (24 MHz, $CDCl_3$): AB spin system, δ 16.54 [d, $P_A$, $^1J$(PtP) 2534, $^2J$(PP) 14.65] and 8.75 [d, $P_B$ $^1J$(PtP) 41.55, $^2J$(PP) 14.65 Hz].

$[Pt\{OCPhCHCPhO\}(PPh_3)_2]PF_6$ **10**. Triphenylphosphine (0.15 g, 0.573 mmol), dibenzoylmethane (0.060 g, 0.267 mmol), potassium hexafluorophosphate (0.3 g, excess), and silver(I) oxide (0.4 g, excess) were added in succession to a stirred solution of $[PtCl_2(cod)]$ (0.10 g, 0.267 mmol) in dichloromethane (30 cm$^3$) and the mixture was refluxed for 16 h. After filtration to remove silver salts and the excess of $KPF_6$, the yellow filtrate was reduced in volume to *ca.* 5 cm$^3$ and addition of light petroleum (*ca.* 40 cm$^3$) gave pale yellow plates (0.241 g, 83%), which were recrystallised from the same solvent mixture (Found: C, 55.7; H, 3.9. $C_{51}H_{41}F_6O_2P_3Pt$ requires C, 56.3; H, 3.8%), m.p. >230 °C (decomp.). NMR ($CDCl_3$): $^{31}$P-{$^1$H} (24 MHz), δ 8.67 [s, $^1J$(PtP) 3882] and −144.0 [hpt, $PF_6^-$, $^1J$(PF) 712.9]; $^{13}$C-{$^1$H} (75.5 MHz), δ 179.54 (s, PtOCPh), 136.7–121.7 (m, Ph) and 96.7 [s, CPh*C*H, $^2J$(PtC) *ca.* 27 Hz].

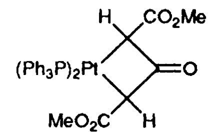
*Attempted Reaction of Compound* **6a** *with Iodomethane.*—A solution of compound **6a** (0.070 g) in dichloromethane (20 cm$^3$) with iodomethane (1 cm$^3$, large excess) was refluxed for 10.5 h. Evaporation to dryness under reduced pressure gave a white solid which was identified as unreacted **6a** by $^{31}$P-{$^1$H} NMR spectroscopy.

## Results and Discussion

The prolonged reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with an excess of both dimethyl malonate and silver(I) oxide in refluxing dichloromethane somewhat unexpectedly affords a high yield of the platinalactone complex **6a** by a novel cyclisation reaction. The ethyl ester analogue **6b** can similarly be prepared starting from diethyl malonate. Complex **6a** has been fully characterised by $^{31}$P, $^{13}$C and $^1$H NMR spectroscopy, and by IR and mass spectroscopy and elemental analysis. The free acid analogue **6c**, R = H, has previously been synthesised by a markedly different route starting from the dioxygen complex $[Pt(O_2)(PPh_3)_2]$ and ketene.[15] Complex **6c** was structurally characterised and found to contain an almost planar (fold angle 15°) four-membered lactone ring system,[15] although no NMR data appear to have been reported.

The $^{31}$P-{$^1$H} NMR spectrum of complex **6a** shows two distinct $PPh_3$ resonances at δ 18.1 and 9.7, the values of $^1J$(PtP) of 2412 and 4219 Hz indicating that these phosphines are respectively *trans* to high and low *trans*-influence alkyl and carboxylato ligands respectively. These coupling constants are comparable to those observed for the related complexes *cis*-$[Pt\{OC(O)CH_2SO_2Ph\}_2(PPh_3)_2]$[16] (3877 Hz), *cis*-$[PtMe_2(PPh_3)_2]$[17] (1852 Hz), *cis*-$[PtMe(Cl)(PEt_3)_2]$ [$^1J$(PtP) *trans* to C, 1719; *trans* to Cl, 4179 Hz][18] and the platinacyclic ring systems $[Pt\{OC(O)O\}\{P(C_6H_{11})_3\}_2]$[17] (3567 Hz) and $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2]$[8] (2817 Hz). Unfortunately, there do not appear to be any NMR data reported for platinalactones, with which a direct comparison may be made.

The $^{13}$C-{$^1$H} NMR spectrum of the carbonyl region of complex **6a** at 400 MHz shows the presence of two distinct carbonyl resonances at δ 177.55 and 173.25. The first appears as a doublet of doublets, due to coupling to the two $^{31}$P nuclei of 4.9 and 2.9 Hz, and is assigned as the ring lactone carbonyl. Satellites due to coupling to $^{195}$Pt are also observed, with $^1J$(PtC) 127 Hz. The second resonance, assigned to the ester substituent, also appears as a doublet of doublets, with coupling to the two P nuclei of 3.9 and 1.5 Hz. These assignments were



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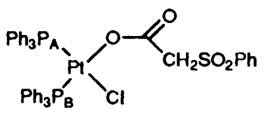

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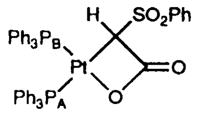

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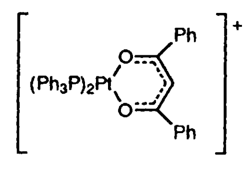

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confirmed by means of a long-range $^{13}C$–$^{1}H$ chemical shift correlation experiment. Of particular note, the value of $^{2}J$(PtC) for this carbonyl, 34 Hz, is markedly smaller than that of the lactone carbonyl. This rules out acyclic structures of the type $PtCH(CO_2R)CO_2R'$, since due to expected free rotation about the Pt–C bond both carbonyls might be expected to show very similar two-bond couplings to platinum. In the related platinacyclobutan-3-one (oxodimethylenemethane) complex **7** it has been observed that the ring carbonyl group also shows a substantially greater value of $^{2}J$(PtC) (175.5 Hz) compared with the ester ring substituent carbonyls (35.1 Hz).[9] The relative magnitudes of these platinum couplings are conclusive evidence for the formulation of complexes **6** as platinalactones. The Pt–CH ring carbon appears as a simple doublet with $^{2}J(PC)_{trans}$ 69.9 and $^{1}J$(PtC) 364 Hz, with no discernible coupling to the *cis* phosphine.

Proton NMR spectroscopy was also consistent with the presence of the platinalactone ring system. The Pt–CH ring protons of complexes **6** appear as a doublet of doublets, with corresponding broadened satellites due to $^{195}Pt$ coupling of 53 Hz. Assignment of the *cis* and *trans* $^{3}J$(PH) couplings was accomplished by selective decoupling of the P nuclei, with the value of $^{3}J(PH)_{trans}$ of 6.42 Hz as expected being larger than $^{3}J(PH)_{cis}$ (3.24 Hz). This is in accord with observations made for a number of square-planar complexes of platinum(II)[19] The $^{1}H$ resonances for the ester methylene protons in the ethyl ester analogue **6b** provide further corroboratory evidence for the platinalactone ring system. As a result of the chiral Pt–CH centre, these $CH_2$ protons are diastereotopic, yielding an $ABX_3$ spin system as two doublets of quartets.

All attempts directed towards growing a single crystal of complexes **6** suitable for an X-ray crystallographic study have to date been unsuccessful. Compound **6** was therefore further characterised by FAB mass spectrometry which showed a positive ion for $[M + H]^+$ at *m/z* 836. The calculated isotopomer distribution compared very favourably with that expected for $C_{40}H_{35}O_4P_2Pt$.

The mechanism of formation of these platinalactones is not clear, and we are not aware of any related examples of this type. The cyclisation reaction may involve initial formation of a platinum C-malonato species of the type $[PtCl\{CH(CO_2R)_2\}L_2]$. Related σ-alkyl complexes of platinum(II) have been observed previously in silver(I) oxide-mediated reactions of platinum halide complexes with CH 'acidic' hydrocarbons such as phenylacetylene, nitromethane, and acetone.[10] An attempt to monitor the progress of the reaction by $^{31}P$-{$^{1}H$} NMR spectroscopy indicated the presence of a complex mixture of intermediates. On prolonged refluxing, this mixture slowly transformed into the pure platinalactone **6a**. An alternative mechanism may involve initial oxide-promoted hydrolysis of one of the ester groups of the dialkyl malonate, followed by platinum carboxylate formation, and then cyclisation. If such a mechanism is operative, then protection of the platinalactone ester group towards hydrolysis, by the steric bulk of the $PPh_3$ ligands, must be invoked to account for the isolation of the observed platinalactone.

We have also briefly investigated the synthesis of platinalactones *via* alternative precursors. Whereas the synthesis of platinalactones from dialkyl malonates was somewhat unexpected, we reasoned that reaction of suitably functionalised acetic acids, $RCH_2CO_2H$ (R = electron-withdrawing group) with *cis*-$[PtCl_2(PPh_3)_2]$, mediated by silver(I) oxide would provide another route for the synthesis of metallalactone complexes. In this regard we note that the diplatinalactone complex **2** was prepared, albeit in low yield, from a related reaction of $K_2[PtCl_4]$ with silver(I) acetate in aqueous acetic acid, although the mechanism of formation of **2** under these conditions is not clear.[6] Both this diplatinalactone, and the platinalactones reported in this paper, may be considered to contain doubly metallated acetate ligands.

Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with 1 equivalent of (phenylsulfonyl)acetic acid, $PhSO_2CH_2CO_2H$, and an excess of silver(I) oxide in refluxing dichloromethane for 1 h gives the monocarboxylato complex **8**, characterised by NMR spectroscopy and elemental analysis. Thus, the $^{31}P$-{$^{1}H$} NMR spectrum shows two inequivalent triphenylphosphine ligands, showing $^{1}J$(PtP) couplings of 3682 and 3872 Hz. These values are characteristic for phosphines *trans* to chloride and carboxylate groups respectively, by comparison with the $^{31}P$-{$^{1}H$} NMR data for *cis*-$[PtCl_2(PPh_3)_2]$[19] [$^{1}J$(PtP) 3676 Hz] and *cis*-$[Pt\{OC(O)CH_2SO_2Ph\}_2(PPh_3)_2]$[16] [$^{1}J$(PtP) 3877 Hz] respectively. On refluxing the above mixture for 16 h followed by stirring at room temperature, $^{31}P$-{$^{1}H$} NMR spectroscopy indicated a *ca.* 50% yield of the platinalactone complex **9** together with three unidentified phosphorus-containing species. No attempt has yet been made to optimise the yield of **9**. It was readily identified as a platinalactone by comparison of NMR spectral properties with those of **6a** and **6b**. Thus, the $^{31}P$-{$^{1}H$} NMR spectrum showed two inequivalent triphenylphosphine ligands at δ 8.75 and 16.54 showing $^{1}J$(PtP) values of 4155 and 2534 Hz respectively.

In order to try and determine the general applicability of silver(I) oxide in metallalactone synthesis, we have attempted to prepare analogous complexes using either different ligands (CH acids) or metals. However, the reaction of either $[PdCl_2(PPh_3)_2]$ with diethyl malonate or *cis*-$[PtCl_2(PPh_3)_2]$ with ethyl-acetoacetate, pentane-2,4-dione, cyanoacetic acid, triethylphosphonioacetate, or with diethyl succinate leads to complex mixtures of products (as evidenced by $^{31}P$ NMR spectroscopy) from which no pure complexes could be isolated. However the nature of the substituent on the CH acid employed bears a major influence on the product formed in these silver oxide-mediated metallacyclisations. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with dibenzoylmethane and an excess of silver oxide does not lead to platinum–carbon bond formation, but instead yields the dibenzoylmethanato-*O,O'*-complex **10**, which was isolated as its hexafluorophosphate salt. The $^{31}P$-{$^{1}H$} NMR spectrum showed a single resonance with $^{1}J$(PtP) 3882 Hz, characteristic for phosphine ligands *trans* to a chelating β-diketonate ligand.[20] We have observed identical behaviour previously in the reaction of pentane-1,3,5-trione with *cis*-$[PtCl_2(PPh_3)_2]$ and silver oxide, which afforded an analogous β-diketonate complex rather than a metallacyclobutan-3-one ($\eta^3$-oxodimethylenemethane) four membered ring.[8] Presumably the driving force in both these reactions is the phenyl-induced formation of an extensively π-delocalised ligand–metal system.

A brief investigation into the chemistry of the platinalactones **6** suggests that they are relatively unreactive. Alkylation of the metallalactone ring oxygen by alkyl iodides giving cyclic ester complexes has been demonstrated to be a common mode of reactivity of many four-membered ring pallada- and five-membered ring rhoda- and irida-lactones,[4] although a related osmalactone is reported to be unreactive towards alkyl iodides.[4] This reactivity has been exploited in cross-coupling reactions of nickelalactones with alkyl iodides, giving functionalised carboxylic acids on work-up.[5] However, we find that attempted reaction of **6a** with an excess of iodomethane in refluxing dichloromethane leads only to recovery of unreacted starting material.

Investigations into the synthesis of metallalactones using organolithium reagents are in progress.

## Acknowledgements

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