

Reactions of Dimethyl 3-Oxoglutarate with Zerovalent Compounds of Palladium and Platinum. Preparation of 1-Metallacyclobutan-3-one Complexes and the X-Ray Crystal Structure of 2,4-Bis(methoxy-carbonyl)-1,1-bis(triphenylphosphine)platinacyclobutan-3-one

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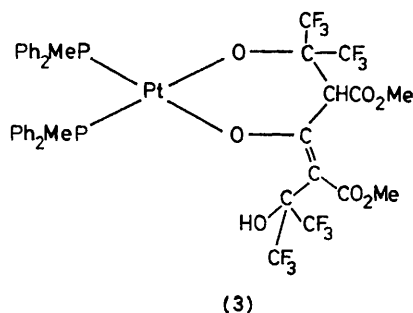
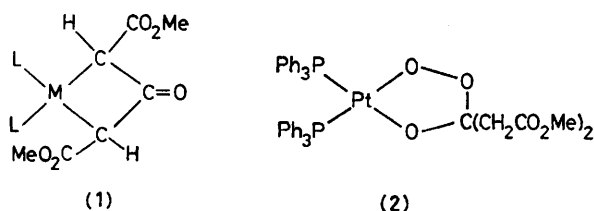
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Summary Dimethyl 3-oxoglutarate reacts with the zero-valent complexes $[ML_4]$ ($M = Pd, L = PPh_3; M = Pt, L = PPh_3, PMePh_2, PMe_2Ph$) in the presence of dioxygen to give the metallacyclobutan-3-one complexes (**1**); the X-ray crystal structure of the title compound (**1a**) establishes the presence of a highly puckered platinacyclobutanone ring.

CURRENT interest^{1,2} in the synthesis of metallacyclobutane complexes and the involvement of such species in alkene

disproportionation reactions³ prompts us to report a novel preparation of platinacyclobutanone derivatives *via* esters of 3-oxoglutaric acid.

Dimethyl 3-oxoglutarate ($MeO_2CCH_2COCH_2CO_2Me$) reacts at room temperature with the complexes $[Pt(PPh_3)_4]$ or $[Pt(trans\text{-stilbene})(PPh_3)_2]$ in benzene solution in the presence of dioxygen to afford (60–70%) a white micro-crystalline compound (**1a**) [m.p. 212–213 °C (decomp.)]. The ¹H n.m.r. spectrum ($CDCl_3$) of (**1a**) at room temperature showed signals at τ 2.76 (m, 30H, Ph), 6.12 [d, 2H, CH,



- a; M = Pt, L = PPh₃
 b; M = Pt, L = PMePh₂
 c; M = Pt, L = PMe₂Ph
 d; M = Pd, L = PPh₃

bond in (**1a**) is inclined by 12.5° out of the C(1), C(2), C(3) plane in the direction of the platinum atom. It is also interesting that (**1a**) is the *trans* isomer, with one of the methoxycarbonyl groups in a *pseudo-axial* position. It is not clear whether this represents the result of a stereoselective ring-closure, or is the sterically favoured isomer.

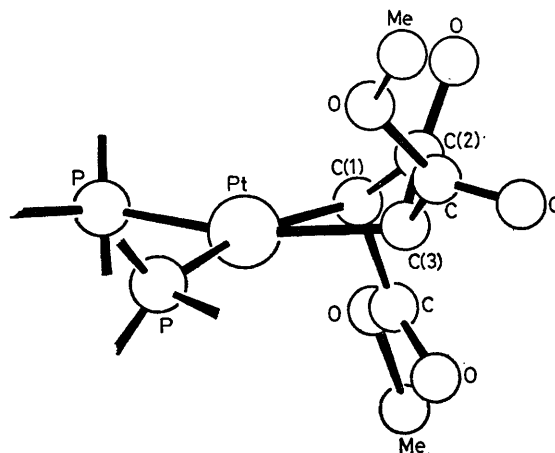


FIGURE. The molecular structure of $[\text{PtCH}(\text{CO}_2\text{Me})\text{COCH}(\text{CO}_2\text{Me})(\text{PPh}_3)_2]$; phenyl rings and hydrogen atoms have been omitted for clarity.

$J(\text{PH})$ 6; $J(\text{PtH})$ 52 Hz], and 7.00 (s, 6H, Me). In order to establish the molecular structure of (**1a**) a single crystal X-ray diffraction study was carried out.†

Crystal data: C₄₃H₃₈O₅P₂Pt, $M = 891.8$, triclinic, $a = 17.59$, $b = 12.74$, $c = 10.27$ Å, $\alpha = 118.2$, $\beta = 94.7$, $\gamma = 74.0^\circ$, $U = 1946.4$ Å³, $Z = 2$, $D_c = 1.53$ g cm⁻³. 7130 reflections with $I > 3\sigma(I)$ measured by a Stoe Weissenberg diffractometer (Mo-K α , $\lambda = 0.7107$ Å) have been refined to $R = 0.040$ by block diagonal least squares methods using anisotropic temperature factors for all non-hydrogen atoms.

The principal feature of interest in the structure of (**1a**) is the extent of non-planarity of the platinacyclobutanone ring (Figure). The ring is folded about the line C(1)–C(3) by 49.7°. As a consequence the Pt–C(2) distance is only 2.420(6) Å [Pt–C(1) and Pt–C(3) are 2.149(6) and 2.128(6) Å] which suggests an important Pt–C(2) bonding contribution in the 4-membered ring system. Such interactions have been invoked in platinacyclobutanes,⁴ where the fold angle ranges⁵ from 25 to 30°, and in a possible mechanism for the isomerisation of metallacyclobutane complexes.¹ Non-metallacyclobutanones are only slightly non-planar, *e.g.* in *cis*-1,3-di-*t*-butyl-1,3-dibromocyclobutan-2-one⁶ the fold angle is only 10°. The carbonyl

The reactions of dimethyl 3-oxoglutarate with $[\text{Pt}(\text{PMe}_2\text{Ph}_2)_4]$, $[\text{Pt}(\text{PMe}_2\text{Ph})_4]$, and $[\text{Pd}(\text{PPh}_3)_4]$ in the presence of dioxygen similarly yield metallacyclobutanone complexes (**1b**)–(**1d**) in yields ranging from 75 to 85%.

In the reactions of $[\text{Pt}(\text{PPh}_3)_4]$ with dimethyl 3-oxoglutarate the peroxo ring complex (**2**) can be detected in the early stages. This complex [m.p. 158–159 °C (decomp.)] can be isolated from the reaction of the ketone with $[\text{PtO}_2(\text{PPh}_3)_2]$, and appears to be involved in the formation of (**1a**) since further reaction of (**2**) with dimethyl 3-oxoglutarate and triphenylphosphine gives (**1a**).

Preliminary studies indicate that the platinacyclobutanone complexes undergo novel ring expansion reactions with hexafluoroacetone. Thus hexafluoroacetone reacts with a suspension of (**1b**) in diethyl ether at room temperature to afford (51%) the adduct (**3**), the structure of which was established by a single crystal X-ray structure determination.⁷

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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