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Preliminary communication

NEW SYNTHESES OF METALLACYCLOBUTAN-3-ONE (SLIPPED OXODIMETHYLENEMETHANE) COMPLEXES OF PLATINUM(II) AND THE X-RAY CRYSTAL STRUCTURE OF 2,4-DIACETYL-1,1-BIS(TRIPHENYLPHOSPHINE)PLATINACYCLOBUTAN-3-ONE; CH BOND ORIENTATION AND THE MAGNITUDE OF ^2J (PtH)

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Summary

Treatment of the carbonate complexes $[\mathrm{Pt(CO_3)L_2}]$ ($\mathrm{L = PPh_3, PMePh_2, PMe_2Ph}$, or $\mathrm{AsPh_3}$; $\mathrm{L_2 = Ph_2PCH_2CH_2PPh_2}$) with esters of 3-oxoglutaric acid $\mathrm{RCH_2COCH_2R}$ ($\mathrm{R = CO_2Me, CO_2Et}$, or $\mathrm{CO_2Pr^n}$) and with heptane-2,4,6-trione afford platinacyclobutan-3-one complexes, ^{1}H NMR studies indicating that the magnitudes of ^2J(PtH) and ^3J(PH) are dependant upon the orientation of the coupled hydrogen to the square planar metal function; the structure of $[\overline{\mathrm{Pt\{CH(COMe)COC}}\mathrm{H(COMe)\}(PPh_3)_2}]$ has been established by X-ray diffraction.

We have described how the fluxional metallacyclobutan-3-one complexes of the type $[\overline{\mathrm{M(CHRCOC}}\mathrm{HR)L_2}]$ (M = Pd or Pt; R = $\mathrm{CO_2Me}$; L = phosphorus donor ligand) can be prepared by the reaction of dimethyl 3-oxoglutarate with zerovalent complexes of palladium and platinum in the presence of dioxygen [1,2]. We now report that treatment of the carbonate complexes $[\mathrm{Pt(CO_3)L_2}]$ (L = phosphorus or arsenic donor ligand) [3,4] with esters of 3-oxoglutaric acid in refluxing ethanol affords a convenient, high yield synthesis of a variety of platinacyclobutan-3-one complexes (Ia—If). Similar reactions using heptane-2,4,6-trione in place of 3-oxoglutaric acid ester afford the complexes Ig and Ih.

The ^{1}H NMR spectra of several of these platinacyclobutan-3-one complexes, measured at low temperatures in $\mathrm{CD_2Cl_2}$, showed the expected features for the illustrated static structure (Table 1). The magnitude of the couplings of the CH protons on platinum in complex Ig to the *cis*- and *trans*-phosphorus

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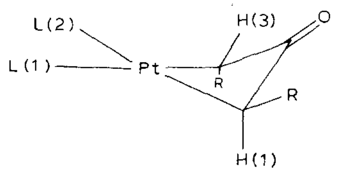
TABLE 1

LOW TEMPERATURE ^{1}H NMR DATA FOR SOME PLATINACYCLOBUTAN-3-ONES IN CD_2Cl_2 SOLUTION MEASURED AT 400 MHz [a]

Compound	Temperature (°C)	δ(H(1))	^3J(L(2)—H(1)) (Hz)	^2J(Pt—H(1)) (Hz)	δ(H(3))	^3J(L—H(3)) (Hz)	^2J(Pt—H(3)) (Hz)	δ(Me)
Ia	−95	4.05d	10.2	74.0	3.24t	4.7	23.8	3.16, 2.65
Id	−98	4.02	—	83.2	3.67	—	36.0	2.96, 2.67
Ig	−90	4.53d	8.0	49.9	3.80t	0.8	29	1.16, 0.98
Ih	−90	4.52	—	81.2	4.09	—	51.2	1.39, 1.06

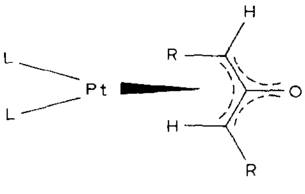
[a] Chemicals shifts in ppm relative to $SiMe_4$, coupling constants in Hz.

ligands suggest that the three-bond couplings (*cis*-P-PtCH) are under dihedral angle control as in the well-known Karplus relations for vicinal HCCH couplings[5]. Thus the signal at δ 3.80 ppm, assigned to the equatorial hydrogen H(3), couples to both the *cis*-phosphorus (P(2)—Pt—C—H(3) torsion angle 10(3)°) and *trans*-phosphorus ligands, but the signal at δ 4.53 ppm, assigned to the axial hydrogen H(1), showed no discernible coupling to its *cis*-phosphorus ligand (P(1)—Pt—C—H(1) torsion angle 100(3)°) and appeared as a doublet due to *trans*-phosphorus coupling only. Similar results have been obtained for other platinacyclobutan-3-ones (Table 1), the low frequency CH resonance being assigned to equatorial hydrogen since only this resonance exhibits coupling to both phosphorus ligands. Further evidence for these assignments is provided by the NMR data for the η^3-β-diketonato(2−) complexes of palladium(II) and platinum(II), recently described [6,7], which could also be formulated as puckered metallacyclobutan-3-one complexes $[\overline{M(CH_2COCH}R)L_2]$ (R = COMe or CO_2Et). Thus in these derivatives the equatorial CH hydrogens are more shielded than the axial CH hydrogens.



(I)

(a: L(1), L(2) = PPh_3, R = CO_2Me;
b: L(1), L(2) = $PMePh_2$, R = CO_2Me;
c: L(1), L(2) = PMe_2Ph, R = CO_2Me;
d: L(1), L(2) = $AsPh_3$, R = CO_2Me;
e: L(1), L(2) = $(Ph_2PCH_2)_2$, R = CO_2Me;
f: L(1), L(2) = PPh_3, R = CO_2Et, CO_2Pr^n;
g: L(1), L(2) = PPh_3, R = COMe;
h: L(1), L(2) = $AsPh_3$, R = COMe)



(II)

^{1}H NMR data for platinacyclobutan-3-ones (Table 1) also reveal that 195-platinum axial hydrogen coupling is much larger than 195-platinum equatorial hydrogen coupling. In cyclic organophosphorus compounds $^2J(\mathrm{PH})$ is much larger when the coupled proton lies close to the orbital of the phosphorus(III) lone pair, and is quite small when remote [8]. Similar effects have been observed in imines, hydrazones, oximes, and aziridines, the magnitude of $^2J(^{15}\mathrm{NH})$ being enhanced if the nitrogen lone pair approaches the coupled hydrogen [9]. The location of the axial and equatorial hydrogens in the platinacyclobutan-3-one (Ig) by an X-ray study described below establishes that the $\mathrm{C{-}H_{axial}}$ vector is aligned with the vector on platinum (defined as the z direction) perpendicular to the C(1)PtC(3) plane, whereas the $\mathrm{C{-}H_{equatorial}}$ vector is not (the angles between the vector on platinum perpendicular to the C(1)PtC(3) plane and the C(1)—H(1) and C(3)—H(3) vectors are 13° and 126°, respectively). The axial hydrogen atom is also closer to the platinum (Pt—H(1) 2.53(3) Å, Pt—H(3) 2.79(2) Å). We therefore propose that the axial hydrogen experiences a greater coupling to the $^{195}\mathrm{Pt}$ nucleus than the equatorial hydrogen because the axial hydrogen lies closer to non-bonding electron density on platinum, possibly an electron pair in a $d_{z^2} + s + p_z$ hybrid orbital. This effect is also transmitted to the *trans*-phosphorus ligands since inspection of the data in Table 1 shows that the 3-bond couplings $^3J(\mathrm{P}_{trans}{-}\mathrm{H})$ are greater for axial than equatorial hydrogens. Similar arguments may account for the larger $^{195}\mathrm{Pt}$ coupling to *anti*-hydrogens than *syn*-hydrogens in static allyl complexes of platinum(II) [10].

Upon warming to room temperature the Me and CH ring signals in the $^1\mathrm{H}$ NMR spectra of platinacyclobutan-3-ones (I) undergo reversible changes. Thus for complex Ig the methyl resonances observed at δ 1.16 and 0.98 ppm at −90°C collapsed to a singlet at δ 1.33 ppm and the CH protons collapsed to the A part of an $\mathrm{A_2X_2}$ spin system ($\mathrm{X} = {}^{31}\mathrm{P}$). These results are consistent with an inversion of the ring through a planar structure. The free energy of activation, $\Delta G^{\ddagger}\,T_\mathrm{c}$, calculated for this process from the coalescence temperature is 37.3 kJ $\mathrm{mol^{-1}}$. The value of $\Delta G^{\ddagger}T_\mathrm{c}$ for Ia is 36.1 kJ $\mathrm{mol^{-1}}$. These energies are lower than found for analogous palladium complexes [2]. The low temperature (−115°C) $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectrum of Ia, measured at 146 MHz, exhibits two resonances at δ 16.71 (d, P(1), $^2J(\mathrm{P(2)P(1)})$ 11.3) and 14.38 ppm (d, P(2), $^2J(\mathrm{P(1)P(2)})$ 11.3 Hz), relative to external $[\mathrm{H_3PO_4}]$, consistent with the illustrated static structure. The $^1\mathrm{H}\text{-}\{^{31}\mathrm{P}\}$ broad band decoupled NMR spectrum of Ia, measured at 360 MHz, consisted of resonances at δ 3.14 and 2.63 ppm for the methyl protons and resonances for the CH groups at δ 4.01 (s, H(1), $^2J(\mathrm{PtH})$ 74 Hz) and 3.18 ppm (s, H(3), $^2J(\mathrm{PtH})$ not discernible). Irradiation of the P(2) resonance collapses the H(1) signal to a singlet, however, irradiation of the P(1) resonance leaves the H(1) signal as a doublet. On irradiation of either P(1) or P(2), the H(3) signals appears as a doublet ($^3J(\mathrm{PH})$ 4—5 Hz) which is partially obscured by one of the methyl signals. These results suggest that P(1), P(2) and H(3) can be treated as "first order" with similar P—H couplings.

Interestingly the η^3-β-diketonato(2−) complexes (or metallacyclobutan-3-ones), $[\overline{\mathrm{M(CH_2COC}}\mathrm{HR)L_2}]$ of palladium(II) or platinum(II) do not appear to undergo ring inversion in solution at room temperature on the NMR time scale [6,7], the acyl or ester substituent R occupying an axial site.

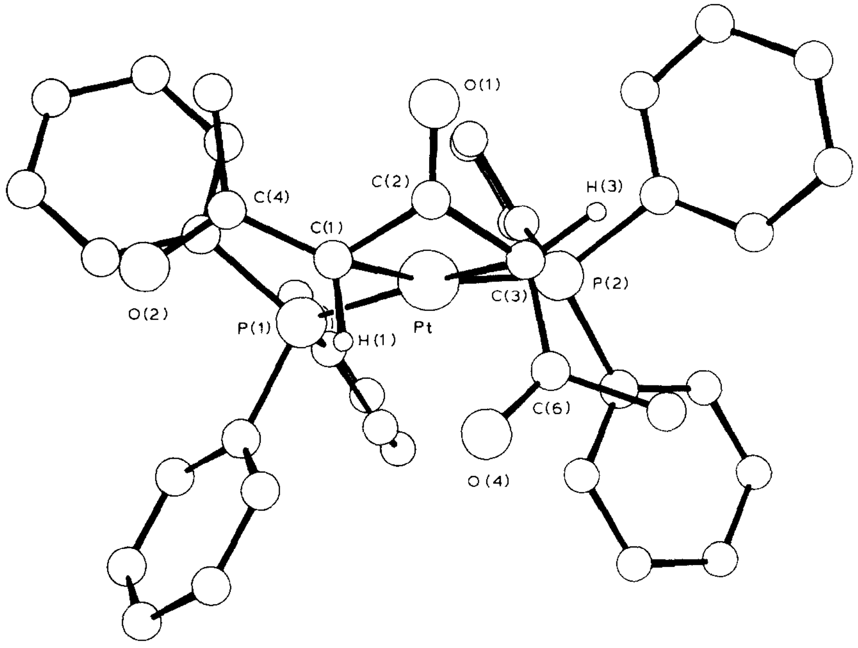


Fig. 1. Molecular structure of Ig, with H atoms of phenyl rings and methyl groups omitted. Interatomic distances: Pt—P(1) 2.309(1), Pt—P(2) 2.295(2), Pt—C(1) 2.183(7), Pt—C(2) 2.486(6), Pt—C(3) 2.153(5) Å. Angles: Pt—C(1)—C(2) 82.8(4), C(2)—C(1)—C(4) 121.0(5), Pt—C(3)—C(2) 84.0(3), C(2)—C(3)—C(6) 120.8(6), C(1)—C(2)—C(3), 107.2(4).

Crystal data: $C_{43}H_{38}O_3P_2Pt$, M = 859.8, triclinic, space group $P\bar{1}$, a 11.337(1), b 18.341(1), c 11.545(8) Å, α 111.8(1), β 123.6(1), γ 90.0(1)°, U = 179 Å^3, Z = 2, $F(000)$ = 856, Mo-K_α radiation ($\bar{\lambda}$ 0.71069 Å), μ(Mo-K_α) 38.63 cm^{-1}; current R 0.033 (R_w 0.034) for 8307 independant reflections [$I > 3\sigma(I)$] collected at 293 K on a Stöe STADI-2 Weissenberg diffractometer in the range $7° < 2\theta < 60°$. Hydrogen atom positions for H(1) and H(3) were located from a difference Fourier map. They were then refined subject to a weak constraint the corresponding C—H distances were 1.08 ± 0.05 Å, the angular orientation of the C—H vector was not constrained. The hydrogen atom temperature factors refined to reasonable values*.

The molecular geometry is shown in Fig. 1. As has previously been observed [1,2], the platinacyclobutan-3-one ring is highly non-planar (fold angle 48°) and it is apparent that a bonding description should include a contribution from the slipped oxodimethylenemethane structure (II). Details of the molecular structure are summarised in the caption.

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

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