Chemistry of Metallacyclobutanones. Part 4.† The Synthesis of 1,3-Diphenyl-substituted Oxodimethylenemethane Complexes of Platinum(II) and Palladium(II) *via* the Dianion $[PhCHC(O)CHPh]^{2-}$, and the *X*-Ray Crystal Structure of $[Pt\{\eta^3\text{-}CHPhC(O)CHPh\}(AsPh_3)_2]\cdot 2CH_2Cl_2$‡

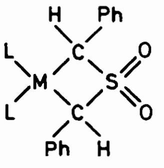
Kwok W. Chiu, William Henderson, Raymond D. W. Kemmitt,* Lesley J. S. Prouse, and David R. Russell
Department of Chemistry, The University, Leicester LE1 7RH

Treatment of the complexes *cis*-$[PtCl_2L_2]$ or *trans*-$[PdCl_2L_2]$ with the organopotassium reagent $K_2[PhCHC(O)CHPh]$ in tetrahydrofuran affords the η^3-oxodimethylenemethane (puckered metallacyclobutan-3-one) complexes $[M\{\eta^3\text{-}CHPhC(O)CHPh\}L_2]$ (M = Pt, L = $AsPh_3$ or PPh_3; L_2 = cyclo-octa-1,5-diene (cod); M = Pd, L = PPh_3 or PEt_3). *X*-Ray data indicate that these complexes contain highly non-planar metal–oxodimethylenemethane systems with both phenyl substituents adopting equatorial positions. In the synthesis of $[Pt\{\eta^3\text{-}CHPhC(O)CHPh\}(PPh_3)_2]$ a small amount of a *trans* diphenyl-substituted isomer is formed, along with the principal *cis* diequatorial isomer. N.m.r. data for the oxodimethylenemethane complexes are reported.

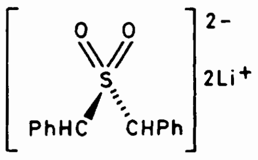
As part of our studies on four-membered metallacyclic complexes, we have shown that a range of metallathietane-3,3-dioxide complexes (**1**) may be prepared *via* the 1,3-dianion of dibenzyl sulphone (**2**).[1] The availability of the related 1,3-dianion of 1,3-diphenylacetone (**3**)[2] prompted us to investigate the use of this dianion in the synthesis of metallacyclobutan-3-one (η^3-oxodimethylenemethane) complexes (**4**), and in this paper we now describe the synthesis and properties of some 2,4-diphenyl-substituted metallacyclobutan-3-one complexes of platinum(II) and palladium(II). Previous studies on metallacyclobutan-3-one complexes of platinum(II),[3,4] palladium(II),[5] and iridium(III)[6] have established the presence of highly puckered metallacyclic rings (**4**) and it is clear that the η^3-allylic (oxodimethylenemethane) form (**5**) makes an important contribution to the bonding. Changes in the structural properties of such oxodimethylenemethane complexes have been related to variations in the metal, the ligand, and the ring substituents,[3–6] and the present studies have afforded the opportunity to study the effect of phenyl substituents upon the geometry of metal oxodimethylenemethane complexes.

Results and Discussion

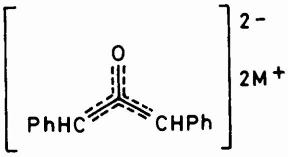
Treatment of either a suspension or solution of the complexes *cis*-$[PtCl_2L_2]$ (L = $AsPh_3$ or PPh_3; L_2 = cyclo-octa-1,5-diene, cod) or *trans*-$[PdCl_2L_2]$ (L = PPh_3 or PEt_3) with one equivalent of the organopotassium reagent $K_2[PhCHC(O)CHPh]$ (**3a**) in tetrahydrofuran (thf) at low temperature affords, in moderate to good yields, the oxodimethylenemethane complexes (**6a**)—(**6e**). Although the crude products were isolated as pale yellow to brownish solids, two recrystallisations yielded white to pale yellow microcrystalline solids. The complexes are air stable in the solid state; however, chloroform solutions exposed to the air decompose slowly. The labile cod ligand of (**6c**) may be readily displaced by either one mole of 1,2-bis(diphenylphosphino)ethane (dppe) or two moles of triphenylphosphine to afford complexes (**6f**) and (**6b**) respectively.



(**1**)

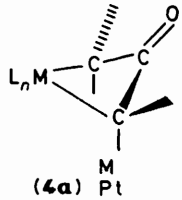


(**2**)



(**3a**) M = K

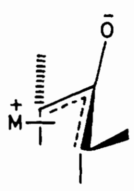
(**3b**) M = Li



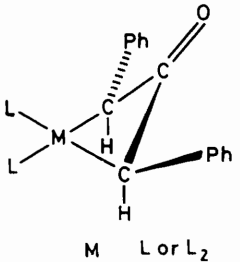
(**4a**) Pt

(**4b**) Pd

(**4c**) Ir



(**5**)



	M	L or L_2
(**6a**)	Pt	$AsPh_3$
(**6b**)	Pt	PPh_3
(**6c**)	Pt	cod
(**6d**)	Pd	PPh_3
(**6e**)	Pd	PEt_3
(**6f**)	Pt	dppe

---

† Part 3 is ref. 4.

‡ (η^3-1,3-Diphenyl-2-oxopropane-1,3-diyl)bis(triphenylarsine)-platinum(II)–dichloromethane (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected intramolecular bond lengths (Å) and angles (°) in $[Pt\{\eta^3\text{-}CHPhC(O)CHPh\}(AsPh_3)_2]\cdot2CH_2Cl_2$ with estimated standard deviations in parentheses

Pt–As(1)	2.394(3)	Pt–C(2)	2.350(26)
Pt–As(2)	2.391(3)	Pt–C(3)	2.187(27)
Pt–C(1)	2.116(25)		
CHPhC(O)CHPh ligand		Triphenylarsine ligands	
C(1)–C(2)	1.50(4)	As(1)–C(51)	1.935(14)
C(2)–C(3)	1.47(4)	As(1)–C(61)	1.967(13)
C(2)–O	1.29(3)	As(1)–C(71)	1.926(14)
C(1)–C(11)	1.453(28)	As(2)–C(21)	1.898(13)
C(3)–C(01)	1.52(4)	As(2)–C(31)	1.918(13)
		As(2)–C(41)	1.909(15)
As(1)–Pt–As(2)	96.9(1)	As(1)–Pt–C(3)	96.4(8)
As(2)–Pt–C(1)	97.5(6)	C(1)–Pt–C(3)	69.2(10)
CHPhC(O)CHPh ligand		Triphenylarsine ligands	
C(1)–C(2)–C(3)	110.4(25)	Pt–As(1)–C(51)	114.2(6)
C(1)–C(2)–O	116(3)	Pt–As(1)–C(61)	124.0(5)
C(3)–C(2)–O	133(3)	Pt–As(1)–C(71)	109.0(6)
Pt–C(1)–C(2)	79.0(16)	C(51)–As(1)–C(61)	98.0(7)
Pt–C(1)–C(11)	125.0(14)	C(61)–As(1)–C(71)	101.5(8)
C(11)–C(1)–C(2)	122.3(23)	C(51)–As(1)–C(71)	108.7(9)
C(1)–C(11)–C(16)	119.7(12)	Pt–As(2)–C(21)	110.9(5)
C(1)–C(11)–C(12)	120.3(12)	Pt–As(2)–C(31)	115.2(6)
Pt–C(3)–C(2)	77.2(16)	Pt–As(2)–C(41)	120.9(5)
Pt–C(3)–C(01)	121.8(17)	C(21)–As(2)–C(31)	108.5(7)
C(2)–C(3)–C(01)	114(3)	C(31)–As(2)–C(41)	101.5(8)
C(3)–C(01)–C(02)	126.8(16)	C(21)–As(2)–C(41)	98.0(8)
C(3)–C(01)–C(06)	113.2(16)		
Pt–C(2)–O	133.2(21)		
Pt–C(2)–C(1)	62.1(13)		
Pt–C(2)–C(3)	65.2(14)		

A single-crystal *X*-ray diffraction study has been carried out on the triphenylarsine–platinum complex (**6a**), the results of which are shown in Tables 1 and 2. The molecular structure of (**6a**) is shown in the Figure; this depicts the characteristically non-planar metal–oxodimethylenemethane system.[3–6] If this system is considered as a metallacyclobutan-3-one, the fold angle (between the C–Pt–C and C–C–C planes) for the four-membered ring is 56.7°, and this angle is the largest yet observed for an oxodimethylenemethane metal complex. Previous studies on oxodimethylenemethane complexes of Pt[3,4] and Pd[5] have established fold angles in the ranges 48.0—50.4 and 51.3—53.3° respectively. This large degree of non-planarity results in a relatively short transannular Pt···C(2) distance in (**6a**) of 2.350(26) Å. Consistent with the description of (**6a**) as an oxo-

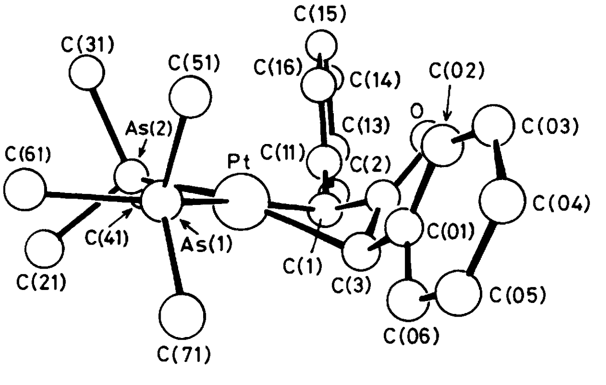


Figure. Molecular structure of (**6a**) showing the atom numbering scheme. Atoms are drawn as circles with arbitrary radii. For the triphenylarsine ligands, carbon atoms other than those bonded to As have been omitted. Phenyl and oxodimethylenemethane hydrogen atoms have also been omitted

Table 2. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for $[Pt\{\eta^3\text{-}CHPhC(O)CHPh\}(AsPh_3)_2]$ (**6a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.639 04(4)	0.331 94(7)	0.637 76(9)	C(25)	0.648 5(6)	−0.017 3(12)	0.789 3(13)
As(1)	0.618 95(9)	0.348 95(20)	0.808 00(22)	C(26)	0.639 1(6)	0.063 1(12)	0.718 5(13)
As(2)	0.584 45(9)	0.197 26(18)	0.578 22(23)	C(32)	0.481 2(5)	0.167 1(16)	0.517 9(15)
O(1)	0.675 9(7)	0.523 6(16)	0.499 5(16)	C(33)	0.434 0(5)	0.200 3(16)	0.504 3(15)
C(1)	0.670 3(8)	0.343 6(17)	0.502 4(21)	C(34)	0.423 9(5)	0.301 7(16)	0.523 3(15)
C(2)	0.685 7(10)	0.442 8(20)	0.556(3)	C(35)	0.461 1(5)	0.370 0(16)	0.556 0(15)
C(01)	0.706 0(7)	0.522 0(14)	0.733 7(15)	C(36)	0.508 3(5)	0.336 9(16)	0.569 7(15)
C(02)	0.682 2(7)	0.613 5(14)	0.706 2(15)	C(42)	0.626 3(7)	0.050 2(14)	0.462 4(13)
C(3)	0.703 4(9)	0.426(3)	0.667 9(25)	C(43)	0.632 5(7)	−0.005 0(14)	0.374 1(13)
C(03)	0.689 6(7)	0.696 5(14)	0.774 1(15)	C(44)	0.602 0(7)	0.011 2(14)	0.279 0(13)
C(04)	0.720 8(7)	0.687 9(14)	0.869 5(15)	C(45)	0.565 3(7)	0.082 6(14)	0.272 1(13)
C(05)	0.744 6(7)	0.596 4(14)	0.896 9(15)	C(46)	0.559 1(7)	0.137 8(14)	0.360 4(13)
C(06)	0.737 2(7)	0.513 5(14)	0.829 0(15)	C(52)	0.581 4(6)	0.549 2(12)	0.751 4(15)
C(11)	0.644 4(6)	0.339 0(14)	0.395 7(11)	C(53)	0.558 5(6)	0.640 7(12)	0.765 7(15)
C(12)	0.661 6(6)	0.280 2(14)	0.321 3(11)	C(54)	0.543 6(6)	0.660 2(12)	0.860 3(15)
C(13)	0.636 9(6)	0.277 6(14)	0.218 5(11)	C(55)	0.551 5(6)	0.588 3(12)	0.940 4(15)
C(14)	0.595 0(6)	0.333 8(14)	0.190 2(11)	C(56)	0.574 4(6)	0.496 9(12)	0.926 1(15)
C(15)	0.577 8(6)	0.392 5(14)	0.264 7(11)	C(62)	0.591 5(6)	0.182 6(13)	0.934 9(14)
C(16)	0.602 5(6)	0.395 2(14)	0.367 5(11)	C(63)	0.559 6(6)	0.120 7(13)	0.976 2(14)
C(21)	0.592 2(6)	0.087 4(12)	0.674 5(13)	C(64)	0.510 5(6)	0.134 9(13)	0.945 8(14)
C(31)	0.518 4(5)	0.235 4(16)	0.550 6(15)	C(65)	0.493 3(6)	0.211 0(13)	0.874 1(14)
C(41)	0.589 6(7)	0.121 6(14)	0.455 5(13)	C(66)	0.525 2(6)	0.273 0(13)	0.832 9(14)
C(51)	0.589 3(6)	0.477 3(12)	0.831 5(15)	C(72)	0.684 5(5)	0.390 6(16)	1.003 1(14)
C(61)	0.574 2(6)	0.258 8(13)	0.863 3(14)	C(73)	0.725 6(5)	0.373 7(16)	1.077 1(14)
C(71)	0.675 9(5)	0.333 1(16)	0.911 5(14)	C(74)	0.758 3(5)	0.299 4(16)	1.059 4(14)
C(22)	0.554 5(6)	0.031 4(12)	0.7013 (13)	C(75)	0.749 8(5)	0.242 0(16)	0.967 7(14)
C(23)	0.563 8(6)	−0.048 9(12)	0.772 1(13)	C(76)	0.708 6(5)	0.258 9(16)	0.893 8(14)
C(24)	0.610 8(6)	−0.073 2(12)	0.816 1(13)				

dimethylenemethane complex, the Pt–C, C–C, and C–O bond distances are similar to those observed in other oxodimethylenemethane complexes of platinum(II).[3,4] The carbonyl C(2)–O bond of (**6a**) also shows the characteristic 'tipping' towards the platinum atom, the angle of inclination between the C(2)–O bond and the C(1)–C(2)–C(3) plane being 6.46°.

The most noteworthy feature in the structure of (**6a**) concerns the novel substitution of phenyl groups on the oxodimethylenemethane ligand, both phenyls adopting equatorial positions if (**6a**) is viewed as a metallacyclic complex. Ketone or ester 1,3-disubstituted oxodimethylenemethane complexes have been shown exclusively to exhibit axial–equatorial substitution;[3–5] this *trans* substitution is also favoured for 2,4-disubstituted metallacyclic complexes of the form $[\overline{\mathrm{M(CHRXC}}\mathrm{HR)L_2}]$ (R = COPh, X = SO_2, M = Pt or Pd;[1,7] X = SO, M = Pt[7]), which also contain puckered four-membered rings. The novel mode of substitution of phenyl groups on the oxodimethylenemethane ligand is probably best interpreted in terms of conjugation of the phenyl substituents with the π system of the (basically planar) oxodimethylenemethane ligand. With the oxodimethylenemethane ligand inclined at an angle of 56.7° to the plane containing Pt, C(1), and C(3), such conjugation is best achieved if the phenyl substituents adopt equatorial positions. This may be demonstrated by an examination of the torsion angles C(01)–C(3)–C(2)–O and C(11)–C(1)–C(2)–O, which indicates that the oxodimethylenemethane ligand and the attached carbon atoms of the phenyl substituents are approximately coplanar, the angles being 7.60 and $-2.64°$ respectively. Although the axially disposed oxodimethylenemethane hydrogens of (**6a**) could not be located in the *X*-ray study, the torsion angles H(1)–C(1)–C(2)–O and H(3)–C(3)–C(2)–O would be expected to be around 120—130°, *e.g.* the torsion angle COMe(axial)–C–C–O in the complex $[\mathrm{Pt\{\eta^3\text{-}MeC(O)CHC(O)CHC(O)Me\}(PPh_3)_2}]$[4] is 126.7°. Hence, little conjugation would be expected between an axially disposed phenyl substituent and the π system of the oxodimethylenemethane ligand in an axial–equatorial isomer. It is worth noting also that in η^3-allyl complexes containing substituents on the outer allyl carbons, these substituents generally occupy *syn* rather than *anti* positions, the *syn* and *anti* positions being analogous to the equatorial and axial positions respectively of an oxodimethylenemethane ligand.

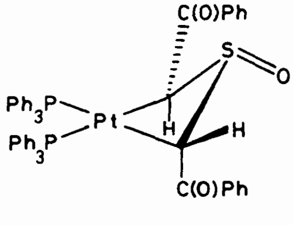
Overall, the geometry of (**6a**) bears a strong resemblance to the μ-2-oxo-1,3-diphenylpropanediylidene complex $[\mathrm{Pt_2\{\mu\text{-}CPhC(O)CPh\}(CNBu^t)_4}]$,[8] which may be considered as both a dimetallabicyclic complex, and a μ-η^3:$\eta^{3'}$-oxodimethylenemethane complex, displaying two equatorial (*syn*) phenyl substituents.

The n.m.r. spectroscopic properties of (**6a**)—(**6f**) are consistent with their formulation as oxodimethylenemethane complexes. Thus, the ^{31}P-{^{1}H} n.m.r. spectrum of (**6b**) displays a single resonance at δ 21.5 p.p.m., with coupling to platinum-195 [^1J(PtP) 3 152 Hz], this value being typical for triphenylphosphine ligands *trans* to an oxodimethylenemethane moiety. The ^{13}C-{^{1}H} n.m.r. spectra of (**6a**)—(**6c**) also show features characteristic of oxodimethylenemethane complexes. Hence, for the phosphine complex (**6b**) the Pt–CH carbons appear as the A part of a second-order AXX′ spin system (X = ^{31}P), due to the presence of chemically equivalent but magnetically non-equivalent ^{31}P nuclei, giving a second-order doublet of doublets, with a small central feature. Satellite features due to coupling to platinum-195 are also observed, the values of ^1J(PtC) increasing in the order PPh_3 < $AsPh_3$ < cod, consistent with the expected decrease in *trans* influence of these ligands. Thus, the values of ^1J(PtC) for (**6b**), (**6a**), and (**6c**) are 242.4, 308.4, and 351.7 Hz respectively. The central carbon resonance of the oxodimethylenemethane fragment of complex (**6b**) also shows coupling to both phosphorus-31 nuclei [J(PC) 5.5 Hz] to give a triplet with corresponding platinum-195 satellites [J(PtC) 155 Hz], these values being similar to those observed in related oxodimethylenemethane complexes.[3,4]

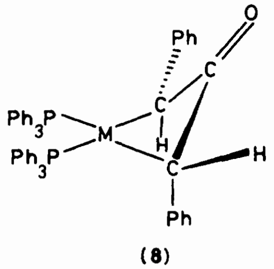
In contrast to *trans* disubstituted oxodimethylenemethane complexes which undergo inversion in solution,[3–5] the room temperature ^{1}H n.m.r. spectra of complexes (**6a**)—(**6f**) are consistent with the presence of a static, non-planar metal–oxodimethylenemethane system in solution, with both phenyl substituents adopting equatorial positions; although, it is also not possible to discount a rapid equilibrium between (**6**) and a small amount of a diaxially substituted isomer formed by inversion of the oxodimethylenemethane system. The oxodimethylenemethane hydrogens of the phosphine complexes (**6b**) and (**6d**)—(**6f**) appear as a simple doublet due to coupling to the *trans* ^{31}P atom only, with ^3J(PH) values in the range 9.45—11.1 Hz. Corresponding satellite features due to coupling to platinum-195 are observed for the complexes (**6a**)—(**6c**) and (**6f**). The absence of coupling of the oxodimethylenemethane hydrogens to their *cis* phosphines arises as a result of dihedral angle control of these three-bond *cis*-P–Pt–C–H couplings, as commonly described by the Karplus relations for vicinal H–C–C–H couplings.[9] Although the oxodimethylenemethane hydrogens could not be located in the *X*-ray study of (**6a**), the *cis*-P–Pt–C–H axial torsion angles for a number of axial–equatorial 1,3-disubstituted oxodimethylenemethane complexes of palladium and platinum lie in the range 80—100°.[3–5] No coupling is subsequently observed between an axial oxodimethylenemethane hydrogen and its *cis* phosphine, this being evidenced by low temperature ^{1}H n.m.r. studies on a range of 1,3-disubstituted oxodimethylenemethane complexes.[3–5] Furthermore, the large coupling constants between the oxodimethylenemethane hydrogens and the platinum-195 nuclei in (**6a**)—(**6c**) and (**6f**) are typical of their axial disposition, the values ranging from 84.2 (**6b**) to 104.4 Hz (**6c**), dependent upon the *trans* influence of the accompanying ligand.

Low, and room temperature ^{1}H n.m.r. spectra for a number of platinum–oxodimethylenemethane complexes (**4a**)[3,4] and the platinathietane-3-oxide system (**7**),[7] respectively, have previously demonstrated that ^{195}Pt axial hydrogen coupling is larger than equatorial hydrogen coupling. Similarly, in η^3-allyl complexes of platinum(II), ^2J(PtH) coupling to the *anti* hydrogens is greater than to *syn* hydrogens.[10] Interestingly, no change in the ^{1}H n.m.r. spectrum of (**6b**) was observed on warming a [$^2H_8$]toluene solution to 80 °C, suggesting that a high barrier to inversion of the oxodimethylenemethane fragment may be operative. Such an inversion would presumably occur *via* a planar metallacyclobutanone form, to give an invertomer possessing two axial phenyl substituents, which would not possess any conjugation between the phenyl substituents and the π system of the oxodimethylenemethane moiety. Such an invertomer would also exhibit steric 1,3-diaxial interactions. An inversion of the isomer displaying two equatorial phenyl substituents would thus be an unfavoured process.

Both the CH and CH_2 groups of the cod ligand of (**6c**) appear as two resonances in the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra. For example, in the ^{1}H n.m.r. spectrum of (**6c**) the olefinic CH



(**7**)



(**8**)

Table 3. ^1J(PtP) values for a range of platinum–oxodimethylenemethane complexes [Pt{η^3-CHRC(O)CHR}$(PPh_3)_2$]

R	Substituent geometry	^1J(PtP)/Hz	Ref.
Ph	*cis*	3 152	This work
COMe	*trans*	3 130	4
H		3 085	6
CO_2Me	*trans*	3 081	3
Ph	*trans*	2 993	This work

groups appear as two resonances at 5.00 and 4.35 p.p.m., showing coupling to platinum of 56.1 and 49.2 Hz respectively.

Inspection of the ^1J(PtP) values for a range of platinum–oxodimethylenemethane complexes of the type [Pt{η^3-CHRC(O)CHR}$(PPh_3)_2$] (R = H, Ph, CO_2Me, or COMe) (Table 3) indicates that the *trans* influence of the oxodimethylenemethane ligands increases in the order *cis*-Ph < *trans*-COMe < H < *trans*-CO_2Me. The low *trans* influence of the diequatorial-diphenyl substituted oxodimethylenemethane moiety is presumably largely a result of steric effects.

In the synthesis of (**6a**) and (**6c**)—(**6e**) only a single *cis* diequatorial isomer was observed in the initially isolated products, however, complex (**6b**) was always initially contaminated with a variable amount, around 10—20%, of the *trans* disubstituted isomer (**8**), observed by ^{31}P-{^{1}H} and ^{1}H n.m.r. spectroscopy. Two recrystallisations from toluene–light petroleum afforded pure isomer (**6b**), and the complex (**8**) could not be isolated. The spectroscopic properties of (**8**) are consistent with a metal–oxodimethylenemethane system which is undergoing rapid inversion in solution at room temperature, as has been observed with other *trans* disubstituted oxodimethylenemethane complexes of platinum[3,4] and palladium.[5] Such inversion results in a rapid interconversion between axial and equatorial sites, and thus a single resonance for the PtCH protons is observed in the ^{1}H n.m.r. spectrum. The oxodimethylenemethane protons of (**8**) appear as the A part of an AA′XX′ spin system, due to the presence of chemically equivalent but magnetically non-equivalent ^{31}P (=X) nuclei, giving the characteristic second-order doublet of doublets. The type of substitution of phenyl groups on an oxodimethylenemethane fragment would thus appear to exert a large influence on the fluxionality of the 1,3-disubstituted complex. The *trans* diphenyl-substituted oxodimethylenemethane ligand in (**8**) displays, as expected, a greater *trans* influence than the *cis* diequatorial diphenyl ligand of (**6b**), but surprisingly also a greater *trans* influence than the ketone or ester substituted ligands (Table 3).

The i.r. spectra of the oxodimethylenemethane complexes (**6a**)—(**6f**) show the typically low values of ν(C=O) found in these systems,[3–6,11–14] the values for the platinum and palladium complexes (**6a**)—(**6f**) lying in the ranges 1 599—1 609 and 1 593—1 594 cm^{-1} respectively. The lowering of the carbonyl bond order may be attributed to a contribution from the η^3-allylic form (**5**) to the bonding in the oxodimethylenemethane metal complex. The values of ν(C=O) for the complexes (**6a**)—(**6f**) are only slightly higher than the value of ν(C=O) (1 550 cm^{-1}) for the dianion of 1,3-diphenylacetone (**3b**),[15] all these values being markedly lower than the value of ν(C=O) found for 1,3-diphenylacetone (1 720 cm^{-1}).[16] These data also suggest that the contribution from the allylic form (**5**) is significant. The value of ν(C=O) in (**6a**)—(**6f**) is dependent on the metal and the ligand, as found in other platinum,[3,4,13] palladium,[5,11,12] iridium,[6,14] and osmium[6] oxodimethylenemethane complexes. Thus, for (**6a**)—(**6f**), on changing the metal from platinum to palladium, there is an increase in the contribution of the allylic form (**5**), with a corresponding decrease in ν(C=O). Similarly, there is a decrease in ν(C=O) on increasing the *trans* influence of the ancillary ligands of the platinum complexes (**6a**)—(**6c**).

Experimental

Melting points were measured on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded on a Bruker Spectrospin WH400 spectrometer at 400.13 MHz, or on a Bruker AM300 spectrometer at 300.13 MHz, with $SiMe_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field), in [$^2H_1$]chloroform unless otherwise stated. Carbon-13, hydrogen-1 decoupled, n.m.r. spectra were recorded on a Bruker Spectrospin WH400 spectrometer at 100.62 MHz or on a Bruker AM300 spectrometer at 75.47 MHz with $SiMe_4$ (0.0 p.p.m.) as internal reference in [$^2H_1$]chloroform. Phosphorus-31, hydrogen-1 decoupled, n.m.r. spectra were recorded in [$^2H_1$]chloroform on a JEOL JNM-FX60 spectrometer at 24.15 MHz with $P(OH)_4^+$ in [$^2H_2$]water (0.0 p.p.m.) as external reference, and on a Bruker spectrospin WH400 spectrometer at 162 MHz with H_3PO_4 in [$^2H_2$]water as external reference.

Experiments were carried out under a dry, oxygen-free, dinitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to the fraction boiling in the range 40—60 °C. The oxodimethylenemethane complexes were recrystallised in air, although chloroform solutions were found to decompose slowly. The compounds *cis*-[$PtCl_2(AsPh_3)_2$],[17] *cis*-[$PtCl_2(PPh_3)_2$],[18] [$PtCl_2$(cod)],[19] *trans*-[$PdCl_2(PPh_3)_2$],[20] and [$PdCl_2(NCPh)_2$][21] were prepared as described in the literature.

The compound K_2[PhCHC(O)CHPh] was prepared in liquid ammonia solution as described in the literature.[2] The ammonia was allowed to boil away, and the residual red solid dissolved in thf to give a solution of approximately 0.2 mol dm^{-3}, which was estimated for total base content by hydrolysis of a 5.0 cm^3 aliquot in water (*ca.* 20 cm^3), followed by titration of the liberated hydroxide with hydrochloric acid, using phenolphthalein as indicator.

Preparation of Oxodimethylenemethane Complexes.—General method. One molar equivalent of K_2[PhCHC(O)CHPh] was added to a stirred suspension or solution of *cis*-[$PtCl_2L_2$] (L = $AsPh_3$ or PPh_3; L_2 = cod) or *trans*-[$PdCl_2L_2$] (L = PPh_3 or PEt_3) in thf (*ca.* 40 cm^3) at −78 °C. The mixture was stirred for 10 min at −78 °C, allowed to warm to room temperature and stirred for 14 h to give a clear yellow-brown to brown solution. Evaporation to dryness under reduced pressure gave an oil which was extracted into toluene (*ca.* 30 cm^3), and the solution filtered. The volume of the filtrate was reduced to *ca.* 2—3 cm^3, and light petroleum (*ca.* 60 cm^3) added to precipitate out the complex as an off-white to yellowish brown solid which was filtered off, dried, and examined by ^{31}P-{^{1}H} and/or ^{1}H n.m.r. spectroscopy. Two recrystallisations from either toluene–light petroleum and/or dichloromethane–light petroleum afforded microcrystalline solids which were filtered off and dried *in vacuo* (*ca.* 0.4 mmHg, *ca.* 53 Pa) to give pure samples of the oxodimethylenemethane complexes (**6a**)—(**6e**).

[Pt{η^3-CHPhC(O)CHPh}$(AsPh_3)_2$]·PhMe. The compound *cis*-[$PtCl_2(AsPh_3)_2$] (0.40 g, 0.46 mmol) gave a yellowish solid which, after two recrystallisations from toluene–light petroleum at −20 °C yielded white microcrystals of (**6a**)·PhMe (0.21 g, 42%) (Found: C, 63.2; H, 4.7. $C_{51}H_{42}As_2OPt{\cdot}C_7H_8$ requires C, 62.9; H, 4.6%), m.p. 210—212 °C (decomp.); ν(C=O) at 1 602s cm^{-1}. N.m.r.: ^{1}H (400 MHz), δ 7.28—6.57 (m, 45 H, Ph), 4.14 [s, 2 H, Pt–CH, ^2J(PtH) 100.29], and 2.35 p.p.m. (s, 3 H, Me, toluene); ^{13}C-{^{1}H} (100 MHz), δ 174.39 [s, CO, ^2J(PtC) not discernible], 140.71—123.74 (m, Ph), 61.52 [s, Pt–CH, ^1J(PtC) 308.4], and 21.3 p.p.m. (s, Me, toluene).

[Pt{η^3-CHPhC(O)CHPh}(PPh$_3$)$_2$]·PhMe. The compound *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.40 g, 0.506 mmol) gave a pale yellow solid (0.48 g, *ca.* 93%) from toluene–light petroleum, which was shown to be a mixture of (**6b**) (*ca.* 80—90%) and (**8**) (10—20%, varying from reaction to reaction) by ^{31}P-{^{1}H} and ^{1}H n.m.r. spectroscopy. Two recrystallisations from toluene–light petroleum yielded white microcrystals of pure (**6b**)·PhMe (0.238 g, 46%). Isomer (**6b**) (Found: C, 67.5; H, 5.0. $C_{51}H_{42}OP_2Pt{\cdot}C_7H_8$ requires C, 68.2; H, 4.9%), m.p. 210—212 °C (decomp.); ν(C=O) at 1 600s cm^{-1}. Nm.r.: ^{1}H (400 MHz), δ 7.4—6.6 (m, 45 H, Ph), 4.01 [d, 2 H, Pt–CH, ^3J(PH) 10.26, ^2J(PtH) 84.2], and 2.35 p.p.m. (s, 3 H, Me, toluene); ^{1}H (300 MHz, 80 °C, [^{2}H$_8$]-toluene), oxodimethylenemethane spectral features identical to room temperature spectrum; ^{13}C-{^{1}H} (300 MHz), δ 173.2 [t, CO, ^3J(PC) 5.5, ^2J(PtC) 155], 140.2—123.2 (m, Ph), 67.07 [dd, second-order, Pt–CH, $|^2J(\text{PC})_{trans} + {}^2J(\text{PC})_{cis}|$ 57.83, ^1J(PtC) 242.4], and 20.2 p.p.m. (s, Me, toluene); ^{31}P-{^{1}H} (162 MHz), δ 21.50 p.p.m. [s, ^1J(PtP) 3 152]. Isomer (**8**); selected n.m.r. spectroscopic data: ^{1}H (400 MHz), δ 4.32 p.p.m. [dd, second-order, Pt–CH, $|^3J(\text{PH})_{trans} + {}^3J(\text{PH})_{cis}|$ 4.5, ^2J(PtH) 50.0]; ^{31}P-{^{1}H} (162 MHz), δ 20.33 p.p.m. [s, ^1J(PtP) 2 993].

[Pt{η^3-CHPhC(O)CHPh}(cod)]. The compound [PtCl$_2$(cod)] (0.25 g, 0.67 mmol) gave a yellowish solid which was recrystallised firstly from toluene–light petroleum and then from dichloromethane–light petroleum to give white microcrystals of (**6c**) (0.16 g, 47%) (Found: C, 53.6; H, 4.8. $C_{23}H_{24}OPt$ requires C, 54.0; H, 4.7%), decomposes at 185—195 °C to black solid; ν(C=O) at 1 609vs cm^{-1}. N.m.r.: ^{1}H (300 MHz), δ 7.58—7.08 (m, 10 H, Ph), 5.00 [m, 2 H, C=CH, cod, J(PtH) 56.1], 4.35 [m, 2 H, C=CH, cod, J(PtH) 49.2], 3.99 [s, 2 H, Pt–CH, ^2J(PtH) 104.4], 2.35—2.20 (m, 4 H, CH$_2$, cod), and 2.20—2.01 p.p.m. (m, 4 H, CH$_2$, cod); ^{13}C-{^{1}H} (75.5 MHz), δ 178.36 [s, CO, ^2J(PtC) not discernible], 141.74—125.55 (m, Ph), 104.30 [s, C=C, cod, ^1J(PtC) 99.4], 98.34 [s, C=C, cod, ^1J(PtC) 78.0], 63.28 [s, Pt-*C*HPh, ^1J(PtC) 351.7], 30.27 (s, CH$_2$, cod), and 29.45 p.p.m. (s, CH$_2$, cod).

[Pd{η^3-CHPhC(O)CHPh}(PPh$_3$)$_2$]·0.5CH$_2$Cl$_2$. The compound *trans*-[PdCl$_2$(PPh$_3$)$_2$] (0.38 g, 0.54 mmol) gave a brownish solid which was recrystallised from toluene–light petroleum and then dichloromethane–light petroleum to give pale yellow microcrystals of (**6d**)·0.5CH$_2$Cl$_2$ (0.28 g, 56%) (Found: C, 69.8; H, 5.0. $C_{51}H_{42}OP_2Pd{\cdot}0.5CH_2Cl_2$ requires C, 70.2; H, 4.9%), m.p. 138—140 °C (decomp.); ν(C=O) at 1 594s cm^{-1}. N.m.r.: ^{1}H (400 MHz), δ 7.71—6.52 (m, 40 H, Ph), 5.22 (s, 1 H, CH$_2$Cl$_2$), and 4.15 p.p.m. [d, 2 H, Pd–CH, ^3J(PH) 9.45]; ^{31}P-{^{1}H} (162 MHz), δ 29.65 p.p.m. (s).

[Pd{η^3-CHPhC(O)CHPh}(PEt$_3$)$_2$]. Triethylphosphine (0.15 g, 1.26 mmol) was added to a stirred suspension of [PdCl$_2$(NCPh)$_2$] (0.217 g, 0.566 mmol) in toluene (20 cm^3), and the mixture stirred for 1 h. Evaporation to dryness under reduced pressure gave a pale yellow oil which was stirred with light petroleum (*ca.* 10 cm^3), to give a pale yellow solid. This solid, on addition of one equivalent of K$_2$[PhCHC(O)CHPh], gave a yellowish brown solid which was recrystallised from toluene–light petroleum and then from dichloromethane–light petroleum to give pale yellow microcrystals of (**6e**) (0.215 g, 69%) (Found: C, 58.8; H, 7.7. $C_{27}H_{42}OP_2Pd$ requires C, 58.9; H, 7.7%), m.p. 162—164 °C (decomp.); ν(C=O) at 1 593s cm^{-1}. Nm.r.: ^{1}H (400 MHz, [^{2}H$_2$]dichloromethane), δ 7.27—7.14 (m, 10 H, Ph), 3.87 [d, 2 H, Pd–CH, ^3J(PH) 9.64], 1.40—1.11 (m, 12 H, CH$_2$, PEt$_3$), and 1.02—0.94 p.p.m. (m, 18 H, CH$_3$, PEt$_3$); ^{31}P-{^{1}H} (162 MHz, [^{2}H$_2$]dichloromethane), δ 15.62 p.p.m. (s).

Reaction of (**6c**) *with Triphenylphosphine.*—A solution of (**6c**) (0.10 g, 0.196 mmol) and triphenylphosphine (0.105 g, 0.40 mmol) in dichloromethane (20 cm^3) was stirred for 1 h. Evaporation to dryness under reduced pressure afforded a white solid which was washed with light petroleum (5 cm^3) and identified as (**6b**) from its ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra.

Reaction of (**6c**) *with Dppe.*—A solution of (**6c**) (0.053 g, 0.10 mmol) and dppe (0.090 g, 0.23 mmol) in dichloromethane (20 cm^3) was stirred for 1 h. Evaporation to dryness under reduced pressure afforded a white solid which was recrystallised from dichloromethane–diethyl ether, and dried *in vacuo* to give white microcrystals of (**6f**)·CH$_2$Cl$_2$ (0.065 g, 71%) (Found: C, 57.0; H, 4.6. $C_{41}H_{36}OP_2Pt{\cdot}CH_2Cl_2$ requires C, 56.9; H, 4.3%), m.p. 236—239 °C (decomp.); ν(C=O) at 1 599s cm^{-1}. ^{1}H N.m.r. (300 MHz), δ 7.64—6.72 (m, 30 H, Ph), 5.32 (s, 2 H, CH$_2$Cl$_2$), 3.99 [d, 2 H, Pt–CH, ^3J(PH) 11.1, ^2J(PtH) 85], and 2.38—1.94 p.p.m. (m, 4 H, CH$_2$, dppe).

X-Ray Crystal-structure Determination.—*X*-Ray quality crystals of (**6a**)·2CH$_2$Cl$_2$ were grown from dichloromethane–light petroleum. A crystal of approximate dimensions 0.03 × 0.20 × 0.25 mm was mounted in a glass capillary under a nitrogen atmosphere of saturated dichloromethane–light petroleum. The unit-cell dimensions of the crystal were determined from an oscillation photograph for the *c* rotation axis and from the refined data of zero layer reflections for axes *a* and *b*, on a Weissenberg diffractometer. The intensities of 2 797 unique reflections having $(I) \geqslant 3\sigma(I)$ were measured in the range $7 \leqslant 2\theta \leqslant 45°$, on a Stoe STADI-2 Weissenberg diffractometer with graphite-monochromated Mo-K_α radiation using an ω-scan technique. All subsequent computations were carried out using the computer program SHELX.[22]

The structure was solved by Patterson and difference Fourier techniques. The hydrogen atoms of the phenyl groups were treated as rigid groups with C–H fixed at 1.08 Å, and the thermal parameters of these atoms were refined with two related values for each group. All other atoms were refined anisotropically. Final cycles employed a weighting parameter *g* (0.003 728) $\{w \propto [1/\sigma^2 F + gF^2]\}$ and gave the final residual indices $R\{= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ 0.0755 and $R'\{= \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ 0.0807.

Crystal data. $C_{51}H_{42}As_2OPt{\cdot}2CH_2Cl_2$, $M = 1\,185.74$, monoclinic, space group $P2_1/n$, $a = 28.477(1)$, $b = 13.141(1)$, $c = 13.01(3)$ Å, $\beta = 100.3(1)°$, $U = 4\,788.90$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, $F(000) = 2\,463.7$, λ(Mo-K_α) = 0.710 69 Å, $\mu = 43.85$ cm^{-1}.

Acknowledgements

We thank the S.E.R.C. for financial support, and for provision of high field n.m.r. facilities, Johnson Matthey plc for the generous loan of platinum metal salts, and Dr. O. W. Howarth (University of Warwick) and Miss M. Robinson (University of Leicester) for high field n.m.r. measurements.

References

1 K. W. Chiu, J. Fawcett, W. Henderson, R. D. W. Kemmitt, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1986, 41.
2 C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, 1959, **81**, 1154.
3 D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, P. McKenna, D. R. Russell, M. D. Schilling, and L. J. S. Sherry, *J. Chem. Soc., Dalton Trans.*, 1984, 1993.
4 A. Imran, R. D. W. Kemmitt, A. J. W. Markwick, P. McKenna, D. R. Russell, and L. J. S. Sherry, *J. Chem. Soc., Dalton Trans.*, 1985, 549.
5 R. D. W. Kemmitt, P. McKenna, D. R. Russell, and L. J. S. Sherry, *J. Chem. Soc., Dalton Trans.*, 1985, 259.
6 M. D. Jones, R. D. W. Kemmitt, J. Fawcett, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1986, 427.
7 W. Henderson, R. D. W. Kemmitt, J. Fawcett, L. J. S. Prouse, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1986, 1791.

8 W. E. Carroll, M. Green, J. A. K. Howard, M. Pfeffer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1472.

9 D. H. Williams and I. Fleming, 'Spectroscopic methods in organic chemistry,' 3rd edn., McGraw-Hill, London, 1980, p. 100.

10 See, for example, N. M. Boag, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1200.

11 N. Yanase, Y. Nakamura, and S. Kawaguchi, *Inorg. Chem.*, 1980, **19**, 1575.

12 Y. Otani, Y. Nakamura, S. Kawaguchi, S. Okeya, and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1467.

13 S. Okeya, Y. Nakamura, S. Kawaguchi, and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 477.

14 T. H. Tulip and D. L. Thorn, *J. Am. Chem. Soc.*, 1981, **103**, 2448.

15 D. Wilhelm, T. Clark, and P. von Ragué Schleyer, *J. Chem. Soc., Perkin Trans. 2*, 1984, 915.

16 C. J. Pouchert, 'The Aldrich Library of Infrared Spectra,' Aldrich, Milwaukee, 1970, p. 627.

17 K. J. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 225.

18 J. C. Bailar, jun., and H. Itatani, *Inorg. Chem.*, 1965, **4**, 1618.

19 J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

20 H. Itatani and J. C. Bailar, jun., *J. Am. Oil Chem. Soc.*, 1967, **44**, 147.

21 J. R. Doyle, P. E. Slade, and H. B. Jonassen, *Inorg. Synth.*, 1960, **6**, 218.

22 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.

Received 9th February 1987; *Paper* 7/235