Synthesis and Carbonylation Reactions of Alkyl and Phenyl Complexes of Palladium- and Platinum-(II) containing β-Diketonate Type Ligands*

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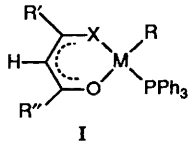
Methyl and phenyl complexes of the formula [MR(β-dik)(PPh_3)] (M = Pt or Pd, R = Me or Ph, β-dik = β-diketonate or monothio-β-diketonate ligand) have been prepared and fully characterized. Carbon monoxide readily inserts into the M–C bond to form the corresponding acyl complexes, and several of these complexes were isolated and characterized. Kinetic studies on the carbonylation of the palladium(II) complexes suggests that it is a pseudo-first order reaction with a rate that is sensitive to the nature of the β-diketonate ligand. Factors which influence the insertion process including the important role of the β-diketonate ligand in controlling the insertion step are discussed. The crystal structure of [Pt(COMe)(bzac)(PPh_3)] (bzac = 3-mercapto-1-phenylbut-2-en-1-onate) has been determined (R = 0.040 for 6198 observed reflections). Crystals are monoclinic, space group $P2_1/c$, a = 14.785(3), b = 10.654(8), c = 20.102(8) Å, β = 122.56(2)° and Z = 4. The complex has square planar co-ordination with the acyl group *trans* to the oxygen atom [Pt–S, –P, –O, –C 2.291(2), 2.267(2), 2.134(5), 1.974(9) Å]. The chelate ring forms an angle of 3.6(1)° with the PtSOPC co-ordination plane.

The insertion of small molecules such as carbon monoxide into four-co-ordinate d^8 metal–carbon bonds is an important process in homogeneous catalysis, and the influence of ligands on this process is a major consideration in catalyst design. There have been few studies on the mechanism of carbon monoxide insertion in complexes with chelating ligands,[1–3] and even fewer on complexes of the β-diketonate (β-dik) type ligands,[4]† which is surprising considering the significance of the ligands in various catalytic processes. These carbonylation studies also represent an important addition to the limited studies carried out on complexes containing chelating ligands with dissimilar co-ordinating atoms.[1d] It is important to attempt to correlate the nature of the chelate ligand with the carbonylation process, and both the co-ordinating atoms of the ligand and the alkyl or aryl groups on the chelate ring might be expected to influence the insertion reaction.

For carbonylation processes catalysed by d^8 metal complexes, several detailed mechanisms have been suggested for the important insertion steps.[1a,2] One involves an associative pathway, in which a five-co-ordinate carbonyl intermediate is formed. The second proposal involves a dissociative pathway, in which ligand dissociation occurs to allow co-ordination of carbon monoxide and formation of a four-co-ordinate carbonyl intermediate. For complexes containing chelating ligands the preferred insertion mechanism is particularly unclear, although it has been suggested that a weakly co-ordinating ligand is necessary to allow insertion.[2]

In a previous paper the preparation of methyl-platinum(II) and -palladium(II) complexes containing β-diketonate type ligands was reported.[5] It was found that for complexes of monothio-β-diketonate ligands there is a strong preference for the structure in which the sulfur is *trans* to the phosphine, and that it is only for the substituted monothio-β-diketonate ligand (bzsacac) complex that sulfur *trans* to $-CH_3$ is observed.

In this paper, the preparation and characterization of a number of phenyl-platinum(II) and -palladium(II) complexes of type **I** is described. The reactivity of these complexes, and that of the related methyl complexes, towards CO is reported. NMR based kinetic studies on the carbonylation of the palladium(II) complexes were undertaken, and the effects of changing the β-diketonate and the hydrocarbyl ligand on carbonylation rates are discussed. A number of acyl complexes were prepared and characterized by spectroscopic techniques, although only the platinum complexes were stable enough to be isolated.



I

M = Pd or Pt
X = O or S, R = Me or Ph
R', R'' = Me, CF_3 or Ph

Solid-state structural studies on d^8 metal–acyl complexes containing chelating ligands are limited, and none of the complexes contains β-diketonate type ligands.[2,3] Here we report the first detailed structural study of an acylplatinum(II) complex with a chelating β-diketonate ligand, [Pt(COMe)(sacac)(PPh_3)].

Experimental

Reagents.—Manipulations were generally carried out under dry, oxygen-free nitrogen by using standard Schlenk techniques. Solvents were dried and purified by standard methods and freshly distilled before use. Chemical reagents were used as received; *trans*-[PtPhI(PPh_3)$_2$], *trans*-[PtPhCl(PPh_3)$_2$] and *trans*-[Pt(COMe)Cl(PPh_3)$_2$] were prepared by literature methods.[1c,6] The salts Na(acac), Na(tfacac) and Na(sacac) were

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

† In this paper β-dik represents the monoanions of β-diketones such as pentane-2,4-dione (Hacac), 1,1,1-trifluoropentane-2,4-dione (Htfacac) or 1-benzoylacetone (Hbzac); or monothio-β-diketones, such as 3-mercapto-1-phenylbut-2-en-1-one (Hbzsac) or 4-mercaptopent-3-en-2-one (Hsacac).

prepared by reaction of NaOMe with the corresponding β-diketonates in MeOH and recrystallized from MeOH–diethyl ether.[7] Tl(bzsacac) was prepared by reaction of $Tl(O_2CMe)$ with Hbzsacac in methanol. The preparation of σ-methyl complexes of the type $[MMe(\beta\text{-dik})(PPh_3)]$ (M = Pd^{II} or Pt^{II}, β-dik = acac, tfac, bzac, sacac or bzsacac) has been described previously.[5]

Measurements.—Nuclear magnetic resonance spectra were recorded at 22 °C on a Bruker AM-300 spectrometer at 300.13 (^{1}H), 75.48 (^{13}C) and 121.50 MHz (^{31}P). Chemical shifts (δ) are reported in ppm relative to internal $SiMe_4$ (^{1}H, ^{13}C), or to external 85% H_3PO_4 (^{31}P). Coupling constants (*J*) are given in Hz and NMR peaks are given as singlet (s), doublet (d), triplet (t) and multiplet (m). Unlabelled NMR peaks can be assumed to be singlets.

Infrared spectra were recorded in absorbance units on a Digilab FTS 20E FT-IR spectrophotometer. Potassium bromide disks were used in the mid IR range (4000–500 cm^{-1}). Absorption bands (cm^{-1}) are described as strong (s), medium (m) or weak (w) in intensity.

Microanalyses were performed by the Central Science Laboratory, University of Tasmania, using a Carlo Erba CHNS-O EA1108 elemental analyser.

Structure Determination.—A unique data set was measured at ≈295 K within the limit $2\theta_{max} = 65°$ using an ENRAF-Nonius CAD-4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ = 0.7107$_3$ Å); 9409 independent reflections were obtained, 6198 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals *R*,*R*′ on |*F*| were 0.040, 0.044, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system[8] implemented by S. R. Hall; neutral-atom complex scattering factors were employed.[9]

Crystal data. $C_{30}H_{27}O_2PPtS$, *M* = 677.7, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), *a* = 14.785(3), *b* = 10.654(8), *c* = 20.102(8) Å, β = 122.56(2)°, *U* = 2669 Å^3, D_c (*Z* = 4) = 1.69, *F*(000) = 1328, μ_{Mo} = 52 cm^{-1}; specimen: 0.33 × 0.75 × 0.56 mm; $A^*_{min,max}$ = 4.2, 10.9.

Synthesis of Complexes.—[PdPh(acac)(PPh_3)] **5**. A solution of *trans*-[PdPhI(PPh_3)$_2$] (0.18 g, 0.22 mmol) in tetrahydrofuran (thf) (*ca.* 15 cm^3) was treated with $TlPF_6$ (0.075 g, 0.22 mmol) in thf (2 cm^3). Thallium iodide precipitated immediately. The mixture was stirred at room temperature for *ca.* 0.5 h. A solution of Na(acac) (0.03 g, 0.22 mmol) in MeOH (*ca.* 2 cm^3) was added to the mixture and further solid precipitated. The mixture was stirred at room temperature overnight. The solution was filtered through a Celite column, and the pale yellow filtrate was evaporated to dryness leaving an oily residue which was treated with MeOH at −5 °C to give a pale yellow solid. The solid was filtered off and crystallized from thf–MeOH to give a white solid (yield: 76%) (Found: C, 63.8; H, 5.1. Calc. for $C_{29}H_{27}O_2PPd$: C, 63.9; H, 5.0%). IR (KBr): 1580vs, 1560s and 1520vs cm^{-1} [ν(C=O) + ν(C=C)]. ^{31}P-{^{1}H} NMR (C_6D_6): δ 30.9.

[PdPh(tfacac)(PPh_3)] **6**. The complex was prepared as described for **5** and was obtained as a white solid (yield: 85%) (Found: C, 58.2; H, 4.3. Calc. for $C_{29}H_{24}F_3O_2PPd$: C, 58.15; H, 4.05%). IR (KBr): 1620vs, 1580m, 1520m, 1480s [ν(C=O) + ν(C=C)] and 1200–1100vs (br) cm^{-1} [ν(C–F)]. ^{31}P-{^{1}H} NMR ($CDCl_3$: two isomers, δ 30.0, 31.3.

[PdPh(sacac)(PPh_3)] **7**. Prepared as described for **5**, [PdPh(sacac)(PPh_3)] was obtained as a yellow solid (yield: 82%) (Found: C, 60.2; H, 5.1, S, 5.5. Calc. for $C_{29}H_{27}OPPdS$: C, 60.5; H, 4.9; S, 5.3%). IR (KBr): 1600s, 1580vs and 1480vs cm^{-1} [ν(C=O) + ν(C=C)].

[PdPh(bzsac)(PPh_3)] **8**. A thf solution (*ca.* 30 cm^3) of Tl(bzsac) (0.08 g, 0.22 mmol) was added in stages to a pale yellow solution of *trans*-[PdPhI(PPh_3)$_2$] (0.18 g, 0.22 mmol) in thf (15 cm^3). The mixture was stirred at room temperature overnight, and was filtered through a Celite column to remove TlI. The filtrate was evaporated to dryness leaving an orange oil which was treated with MeOH (1 cm^3) to precipitate a pale orange solid. This was recrystallized from thf–MeOH to give a pale orange crystalline solid (0.11 g, 79%) (Found: C, 64.9; H, 4.6. Calc. for $C_{34}H_{29}OPPdS$: C, 65.55; H, 4.70%). IR (KBr): 1600m, 1550vs and 1500s cm^{-1} [ν(C=O) + ν(C=C) + ν(C=S)]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 21.3.

[PtPh(acac)(PPh_3)] **1**. A solution of [PtPhCl(PPh_3)$_2$] (0.1 g, 0.12 mmol) in thf was treated with $AgBF_4$ (0.023 g, 0.12 mmol) at room temperature for 30 min to precipitate AgCl. A solution of Na(acac) (0.015 g, 0.12 mmol) in MeOH (0.5 cm^3) was added to the mixture which was stirred overnight. The solution was filtered through a Celite column and evaporated to dryness. The residue was crystallized from CH_2Cl_2–MeOH at −5 °C to give a white crystalline solid (yield: 75%) [Found: C, 52.2; H, 4.9. Calc. for $C_{29}H_{27}O_2PPt\cdot1.5H_2O$ (the presence of water in the molecule was detected from the IR spectrum of **1** in dried CH_2Cl_2): C, 52.75; H, 4.60%]. IR (KBr): 1580s and 1520s cm^{-1} [ν(C=O) + ν(C=C)]. ^{31}P-{^{1}H} NMR (C_6D_6): δ 9.63 ($^1J_{PtP}$ = 4791). Mass spectrum: *m*/*z* 632 [*M*]$^+$, 555 [*M* − Ph]$^+$ and 534 [*M* − (acac − H)]$^+$. High resolution mass spectrum: *m*/*z* 632.133. Calc. for $C_{29}H_{27}OP_2{}^{194}Pt$: 632.137.

[PtPh(tfacac)(PPh_3)] **2**. Prepared as described for **1**. The complex [PtPh(tfacac)(PPh_3)] was isolated as a white solid from CH_2Cl_2–MeOH, yield 69% (Found: C, 50.5; H, 3.8. Calc. for $C_{29}H_{24}F_3O_2PPt$: C, 50.65; H, 3.50%). IR (KBr): 1610vs, 1580m, 1520s [ν(C=O) + ν(C=C)] and 1000–1200vs cm^{-1} (br) [ν(C–F)]. ^{31}P-{^{1}H} NMR ($CDCl_3$): two isomers, δ 7.7 ($^1J_{PtP}$ = 4957), δ 9.52 (small amount, $^1J_{PtP}$ cannot be obtained unambiguously). Mass spectrum: *m*/*z* 687 [*M*]$^+$, 609 [*M* − Ph]$^+$ and 532 [*M* − (tfac − H)]$^+$. High resolution mass spectrum: *m*/*z* 686.112. Calc. for $C_{29}H_{24}F_3O_2P^{194}Pt$: 686.109.

[PtPh(sacac)(PPh_3)] **3**. Prepared as described for **1**. This complex [PtPh(sacac)(PPh_3)] was obtained as a yellow solid (yield: 78%) (Found: C, 53.9; H, 4.1. Calc. for $C_{29}H_{27}OPPtS$: C, 53.6; H, 4.2%). IR (KBr): 1570vs and 1480vs cm^{-1} [ν(C=O) + ν(C=C)]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 19.4 ($^1J_{PtP}$ = 3667). Mass spectrum: *m*/*z* 648 [*M*]$^+$ and 571 [*M* − Ph]$^+$. High resolution mass spectrum: *m*/*z* 648.110. Calc. for $C_{29}H_{27}OP^{194}PtS$: 648.115.

[PtPh(bzsac)(PPh_3)] **4**. Prepared as described for its palladium analogue **8**. The complex [PtPh(bzsac)(PPh_3)] was obtained as an orange crystalline solid (yield: 88%) [Found: C, 56.0; H, 4.5. Calc. for $C_{34}H_{29}OPPtS\cdot H_2O$ (the presence of water was detected from the IR spectrum in dry CH_2Cl_2): C, 56.0 H, 4.3%]. IR (KBr): 1570m and 1540vs cm^{-1} [ν(C=O) + ν(C=C) + ν(C=S)]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 19.8 ($^1J_{PtP}$ = 3661). Mass spectrum: *m*/*z* 710 [*M*]$^+$ and 633 [*M* − Ph]$^+$. High resolution mass spectrum: *m*/*z* 710.132. Calc. for $C_{34}H_{29}OP^{194}PtS$: 710.130.

[Pt(COMe)(bzsac)(PPh_3)] **9**. *Method* 1. Carbon monoxide was bubbled gently through a syringe into the solution of [PtMe(bzsac)] (0.08 g, 0.12 mmol) in benzene at room temperature overnight. After the orange solution was evaporated to dryness, the residue was crystallized from thf–light petroleum (b.p. 40–60 °C) to give a pale orange solid (yield: 0.05 g, 64%) (Found: C, 52.9; H, 4.3; S, 4.6. Calc. for $C_{30}H_{27}O_2PPtS$: C, 53.15; H, 4.00; S, 4.70%). IR (KBr): 1640vs cm^{-1} [ν(C=O)]. NMR: ^{1}H, δ 2.07 (s, CH_3) and 2.1 (s, $COCH_3$); ^{31}P-{^{1}H}, δ 18.1 ($^1J_{PtP}$ = 4047).

Method 2. A solution of *trans*-[Pt(COMe)Cl(PPh_3)$_2$] (0.12 g, 0.15 mmol) in thf (15 cm^3) was treated with Tl(bzsac) (0.6 g, 0.16 mmol) in thf (30 cm^3). The mixture was stirred at room temperature for 2 d. The precipitated solid was filtered off, the filtrate was evaporated to dryness. The residue was crystallized from MeOH–diethyl ether–light petroleum to give a yellow-

orange solid (0.077 g, yield 76%). The complex was characterized spectroscopically by comparison with that obtained from Method 1.

[Pt(COMe)(sacac)(PPh_3)] **10**. *Method* 1. Prepared as described for **9** (Method 1), complex **10** was obtained as a yellow solid by crystallization from thf–light petroleum (yield: 65%) (Found: C, 48.4; H, 4.2. Calc. for $C_{25}H_{25}O_2PPtS$: C, 48.8; H, 4.1%). ^{31}P-{^1H} NMR ($CDCl_3$): δ 19.3 (J_{PtP} = 3465).

Method 2. A solution of *trans*-[Pt(COMe)Cl(PPh_3)$_2$] (0.1 g, 0.13 mmol) in acetonitrile (15 cm^3) was treated with $AgBF_4$ (0.023 g, 0.13 mmol) immediately giving a white solid. To the solution was added Na(sacac) (0.02 g, 0.14 mmol) in MeOH (2 cm^3). The mixture was stirred at room temperature overnight. The black solid was filtered off, and the pale orange filtrate was evaporated to dryness leaving an orange oil. This was crystallized from CH_2Cl_2–Et_2O to give a yellow solid (0.053 g, 71%).

The complex was characterized spectroscopically by comparison with those obtained from Method 1.

[Pt(COMe)(tfac)(PPh_3)] **11**. A solution of [PtMe(tfacac)(PPh_3)] in CH_2Cl_2 was saturated with CO at room temperature by bubbling CO through the solution for *ca.* 30 min. The flask was then closed, and the solution was stirred overnight. After the solution was evaporated to dryness, the residue was extracted with CH_2Cl_2 (*ca.* 2 cm^3), diethyl ether was added to precipitate an unidentified yellow solid which was predominantly a carbonyl complex with a strong band at 2100 cm^{-1} in its IR spectrum. After filtration, the filtrate was worked up to give a second yellow solid. This was assigned spectroscopically as [Pt(COMe)(tfacac)(PPh_3)] (Table 4), yield 30–40% (Found: C, 46.6; H, 3.3. Calc. for $C_{25}H_{22}F_3O_3PPt$: C, 45.95; H, 3.40%).

[Pd(COMe)(acac)(PPh_3)] **15**. Carbon monoxide was bubbled through a solution of [PdMe(acac)(PPh_3)] (0.04 g, 0.08 mmol) in C_6D_6 for *ca.* 5 min. The NMR tube was fitted with a septum cap and secured with Teflon tape. The solution was then kept at room temperature for 5 h; NMR and IR spectra were recorded *in situ* (Table 4).

All other palladium acyl complexes were prepared and characterized in a similar manner.

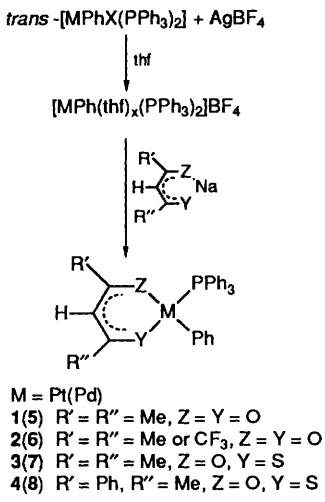
Kinetics.—The kinetics of the carbonylation of β-diketonate complexes of Pd^{II} was studied using ^1H NMR spectroscopy. The sample was prepared as follows: the solid was kept in a N_2 filled NMR tube (outside diameter 5 mm), and a CO flow passed continually over it for *ca.* 1 h, while $CDCl_3$, which was contaminated with a trace of grease, was added. The NMR tube was quickly fitted with a septum cap and secured with Teflon tape. The sample solution was made up to contain a concentration of 0.16–0.27 mol dm^{-3} of complex for each run.

The extent of conversion to the acyl complex was monitored by integration of the σ-methyl absorption of the methyl β-diketonate complexes (*ca.* δ 0.6) and the internal standard (grease, δ 0.2) whereas the rate of conversion of the phenyl β-diketonate complexes was calculated by integration of the methyl absorptions of the β-diketonate ligands in the newly formed acyl complexes. Each kinetic run consisted of four to eight points.

Results and Discussion

Preparation of [MPh(β-dik)(PPh_3)] (M = Pd^{II} *or* Pt^{II}).—Sodium β-diketonates and sodium monothio-β-diketonates readily react with [PtPh(thf)$_x$(PPh_3)$_2$]BF_4, to yield the β-diketonate complexes [PtPh(β-dik-*O*,*O*′)(PPh_3)] (**1** and **2**) and monothio-β-diketonate complexes [PtPh(β-dik-*O*,*S*)(PPh_3)] (**3** and **4**). The palladium(II) analogues (**5**–**8**) of these complexes were prepared by a similar method from *trans*-[PdPhI(PPh_3)$_2$] [equation (1)].

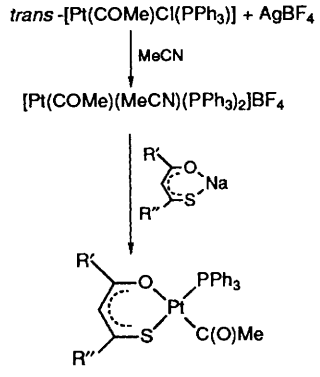
As was previously observed for the methyl analogues,[5] two regioisomers were obtained when an unsymmetrical β-diketonate, *e.g.* tfac, was used. For the β-diketonate-*O*,*S* complexes, one regioisomer predominated in which the PPh_3 ligand is *trans* to sulfur.



(1)

M = Pt(Pd)
1(5) R′ = R″ = Me, Z = Y = O
2(6) R′ = R″ = Me or CF_3, Z = Y = O
3(7) R′ = R″ = Me, Z = O, Y = S
4(8) R′ = Ph, R″ = Me, Z = O, Y = S

A similar ligand-exchange method can also be applied to generate the acyl complexes [M(COMe)(β-dik)(PPh_3)] from [M(COMe)Cl(PPh_3)] [equation (2)]. Decomposition occurs



(2)

9 R′ = Ph, R″ = Me
10 R′ = R″ = Me

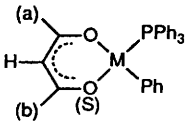
when M is Pd^{II}, but the complexes [Pt(COMe)(sacac)(PPh_3)] and [Pt(COMe)(bzsac)(PPh_3)] have been isolated as stable yellow-orange solids. However, interestingly, Na(acac), Na(tfacac) or Na(bzac), in the reaction with [Pt(COMe)(MeCN)(PPh_3)$_2$]BF_4, gave only a mixture of unidentified products rather than the expected acyl complexes. A spectroscopic investigation indicated that the main product was possibly [Pt(COMe)(dik)(PPh_3)] in which the β-diketonate ligand is monodentate. The IR spectrum showed a single, strong, broad band at 1500 cm^{-1} [very similar to that observed for Na(acac)] instead of the typical co-ordinated β-diketonate bands at around 1580 and 1420 cm^{-1}. A strong band observed at 1640 cm^{-1} is typical of the acyl carbonyl.

Characterization and Spectroscopic Properties of the β-*Diketonate Complexes.*—The ^1H NMR spectroscopic data for the phenyl complexes in $CDCl_3$ are summarized in Table 1.

The phenyl groups of these β-diketonate complexes normally appear in the region δ 6.3–7.1 as a complex multiplet in $CDCl_3$. The coupling constants for these protons with ^{31}P and ^{195}Pt could not be assigned unambiguously. In C_6D_6 solution, the phenyl group peaks in these complexes are masked by the triphenylphosphine resonances and could not be clearly observed.

An interesting solvent effect was observed in the ^1H NMR spectrum of the methyl β-diketonate complexes. In $CDCl_3$, C_6D_6, C_7D_8 and the polar mixture $CDCl_3$–CD_3OD(4:6), the room-temperature ^1H NMR spectrum of [PdMe(acac)(PPh_3)] shows two well separated, sharp peaks for the acac methyl groups. In [$^2H_5$]pyridine they form a broad singlet as a result of

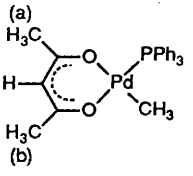
Table 1 Selected ^1H NMR spectroscopic data for the σ-phenyl β-diketonate complexes



Complex	β-Diketonate CH_3(a)	CH_3(b)	CH	M–Ph
M = Pt^{II}				
1 [PtPh(acac)(PPh_3)]	1.37 (s)	1.58 (s)	5.12 (s)	6.6 (m)
2 [PtPh(tfacac)(PPh_3)]*	1.69 (s)	CF_3	5.62 (s)	6.6–7.1 (m)
	CF_3	2.05 (s)		
3 [PtPh(sacac)(PPh_3)]	1.57 (s)	2.22 (s)	6.5 (s)	6.6 (m)
4 [PtPh(bzsac)(PPh_3)]	2.35 (s)	C_6H_5	—	6.6 (m)
M = Pd^{II}				
5 [PdPh(acac)(PPh_3)]	1.67 (s)	1.94 (s)	5.32 (s)	6.7 (m)
6 [PdPh(tfacac)(PPh_3)]	CF_3	2.08 (s)	5.96 (s)	
				6.6–7.1 (m)
	1.77 (s)	CF_3	5.70 (s)	
7 [PdPh(sacac)(PPh_3)]	1.74 (s)	2.35 (s)	6.4 (s)	6.7 (m)
8 [PdPh(bzsac)(PPh_3)]	2.51 (s)	C_6H_5	—	6.7 (m)

* Two isomers have been observed, but no effort has been made to distinguish them spectroscopically.

Table 2 Proton NMR spectroscopic data for [PdMe(acac)(PPh_3)] in different solvents



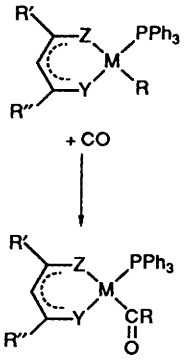
Solvent	δ CH_3(a)	δ CH_3(b)	δ Pd–CH_3 (*J*/Hz)
$CDCl_3$	1.59 (s)	2.02 (s)	0.56 (d, 2.3)
C_6D_6	1.60 (s)	1.93 (s)	1.06 (d, 2.7)
[$^2H_8$]Toluene	1.61(s)	1.93 (s)	0.98 (d, 2.7)
[$^2H_5$]Pyridine	1.91 (s, br)		0.96 (s, br)

time averaging of the two methyl groups. On cooling the pyridine solution, the singlet broadens further and finally separates into two peaks. Also in pyridine the expected doublet due to the σ-methyl group becomes a broad singlet (Table 2).

Similar behaviour has been described before for pyridine solutions of mixed-ligand complexes containing acac, triphenylphosphine and alkyl ligands.[10] After an extensive investigation of this phenomenon it was proposed that reversible dissociation of the acac, the phosphine and in one case the alkyl group was occurring owing to co-ordination of the pyridine.[10] It is likely that similar processes are occurring here: equilibration of the acac-methyls due to dissociation of one arm of the acac ligand and the broad singlet of the σ-methyl group due to dissociation of the phosphine.

Equilibration of the chelate methyl groups is not observed in complexes containing monothio-β-diketonate ligands. The methyl groups in [PdMe(sacac)(PPh_3)] appears as two sharp singlets in all solvents including [$^2H_5$]pyridine. However the expected doublet for the σ-methyl again appears as a broad singlet in pyridine. These results indicate that the sacac ligand is probably more strongly bound to palladium than is acac in these complexes. This conclusion is not surprising as sulfur tends to form stronger bonds to the 'soft' palladium(II) than does oxygen, probably due to back bonding from the metal to the sulfur atoms.[11]

Reaction of β-Diketonate Complexes with CO.—The β-diketonate complexes of Pd^{II} react readily with CO at room temperature in benzene or chloroform to form the corresponding acyl complexes **12–17** [equation (3)].



(3)

9(12) M = Pt(Pd), R = Me, R' = Ph, R'' = Me, Z = O, Y = S
10(13) M = Pt(Pd), R = Me, R' = Me, R'' = Me, Z = O, Y = S
11(14) M = Pt(Pd), R = Me, R', R'' = CF_3 or Me, Z = Y = O
15 M = Pd, R = Me, R' = R'' = Me, Z = Y = O
16 M = Pd, R = Ph, R' = R'' = Me, Z = Y = O
17 M = Pd, R = Ph, R' = R'' = Me, Z = O, Y = S

The acylpalladium complexes are not stable in solution at room temperature and decompose slowly even under CO to precipitate palladium black. Attempts to isolate these acyl complexes so far have resulted in impure products.

In contrast, carbonylation of β-diketonate complexes of platinum(II) is relatively slow, requiring about 10 h at room temperature to complete the reaction. Platinum acyl complexes **9–11** have been isolated as stable, pale cream to yellow orange solids.

Carbon monoxide also inserts quite readily into the Pt–Ph bond of complexes **1–4** to form the expected acyl complexes. However, no further efforts have been made to isolate these complexes as the acyl protons in the resulting complexes are masked by the multiplet peaks of PPh_3 which limits further spectroscopic studies on the complexes.

Selected spectroscopic data for the acyl complexes are summarized in Table 3.

All of the metal acyl complexes show a typical strong IR band in the region of 1640–1700 cm^{-1} due to ν(C=O) of the acyl group. In general the ν(C=O) band appears slightly higher for palladium complexes than those of platinum complexes.

The ^1H NMR spectrum of [Pt(COMe)(sacac)(PPh_3)] **10** shows two sharp singlets at δ 1.62 and 2.30 due to the two methyl groups of the sacac ligand; the acyl methyl group appears as a sharp singlet at δ 1.9, which is within the region for typical σ-acyl complexes. Similar ^1H NMR spectra have been observed for palladium acyl complexes (Table 3), and unambiguously identifies the complexes.

The reaction of the metal–hydrocarbyl compounds with CO clearly demonstrates the influence of the β-diketonate ligand. The ease of the CO insertion reaction depends markedly on the β-diketonate ligand present. For example, [Pt(COMe)(sacac)(PPh_3)] **10** was readily formed in benzene within 6 h by treating [PtMe(sacac)(PPh_3)] with CO. In contrast, under the same conditions, no acyl complex was observed in the reaction of [PtMe(acac)(PPh_3)] with CO, even after a prolonged reaction time. However, a small amount of the acyl complex [Pt(COMe)(bzac)(PPh_3)] was observed under these reaction conditions, and [Pt(COMe)(tfacac)(PPh_3)] **11** has been isolated by treating [PtMe(tfacac)(PPh_3)] with CO. It would therefore appear that carbonylation is favoured by electron-withdrawing groups on the β-diketonate ligand, *i.e.* groups that would be expected to weaken the metal–chelate bonding.

Table 3 Selected spectroscopic data for the metal acyl complexes

Acyl complex	^{1}H NMR (δ)	IR (KBr)[a]/cm^{-1}
11 [Pt(COMe)(tfacac)(PPh_3)]	1.76, 2.04 (CH_3), 5.78, 5.79 (=CH), 2.08, 2.09 (COMe)	1650vs, 1630s [ν(C=O)]
10 [Pt(COMe)(sacac)(PPh_3)]	1.62, 2.30 (CH_3), 6.4 (=CH), 1.86 (COMe)	1640vs [ν(C=O)]
9 [Pt(COMe)(bzsac)(PPh_3)]	2.07 (CH_3), 2.1 (COMe)	1640vs [ν(C=O)]
15 [Pd(COMe)(acac)(PPh_3)]	1.71, 1.94 (CH_3), 2.1 (COMe), 5.4 (=CH)	1700vs [ν(C=O)]
14 [Pd(COMe)(tfacac)(PPh_3)][b]	2.23, 2.24 (CH_3), 2.14 (COMe), 5.7 (=CH)	1700vs [ν(C=O)]
13 [Pd(COMe)(sacac)(PPh_3)]	1.79, 2.03 (CH_3), 2.40 (COMe)	1680vs [ν(C=O)]
12 [Pd(COMe)(bzsac)(PPh_3)]	2.30 (CH_3), 2.15 (COMe)	1690vs [ν(C=O)]
16 [Pd(COPh)(acac)(PPh_3)]	1.63, 1.67 (CH_3)	1680s [ν(C=O)]
17 [Pd(COPh)(sacac)(PPh_3)]	1.82, 2.34 (CH_3)	1660s [ν(C=O)]

[a] Bands due to acyl group only. [b] Two isomers.

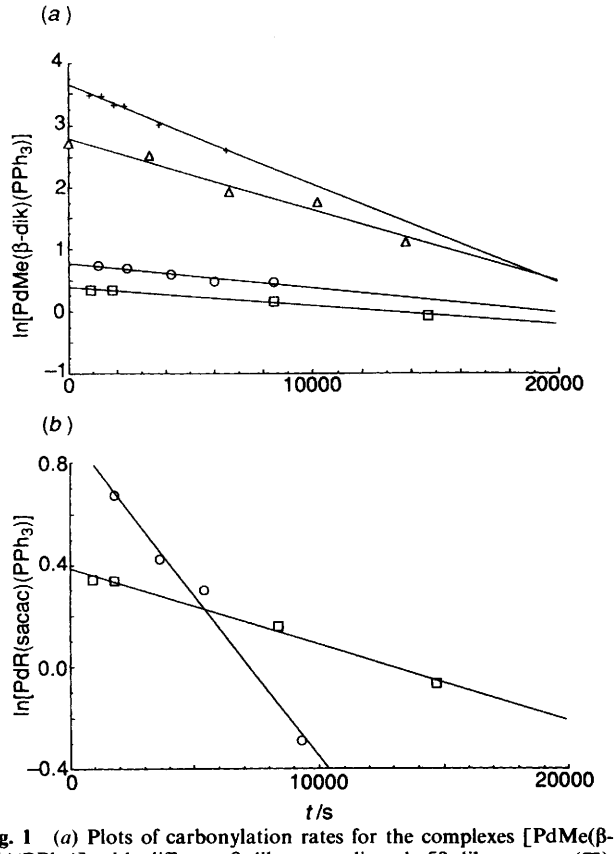


Fig. 1 (*a*) Plots of carbonylation rates for the complexes [PdMe(β-dik)(PPh_3)] with different β-diketonate ligands [β-dik = sacac (□); acac (○); tfac (△) or bzsacac (+)]; (*b*) for the complexes [PdR(sacac)(PPh_3)] [R = Me (□) or Ph (○)]

Table 4 The reaction rate of the carbonylation of the σ-methyl and σ-phenyl complexes of Pd^{II}

Complex	Reaction rate (10^4k/s)	$t_{\frac{1}{2}}$/s
[PdMe(acac)(PPh_3)]	0.40	17 325
[PdMe(tfacac)(PPh_3)]	1.2	5 775
[PdMe(bzsac)(PPh_3)]	1.6	4 331
[PdMe(sacac)(PPh_3)]	0.30	23 100
[PdPh(sacac)(PPh_3)]	1.3	5 331
[PdPh(acac)(PPh_3)]	3.1	2 235

To compare the effects of the β-diketonate ligand and substituents on the β-diketonate backbone, the kinetics of carbonylation has been studied by NMR spectroscopy. Pseudo-first-order conditions were applied, *i.e.* reactions were carried out under a large excesss of carbon monoxide. Plots of ln[starting complex] *versus* time, shown in Fig. 1(*a*) and 1(*b*), gave straight lines from which rate constants could be calculated. Results are presented in Table 4 and Fig. 1(*a*) and 1(*b*).

Consistent with the observations above, the rate of carbonylation increases markedly when electron-withdrawing moieties are attached to the β-diketonate backbone, *e.g.* a three-fold increase in rate was observed in going from acac to tfac [Fig. 1(*a*)]. Interestingly, a similar increase in the rate of carbonylation was observed when the σ-R group attached to the palladium centre was changed from Me to Ph [Fig. 1(*b*)].

There is a smaller but consistent change in the rate of carbonylation when the β-diketonate ligands are exchanged in the palladium complexes; in the order acac > sacac (Table 4). These results are in agreement with the proposal that the sacac ligand is more firmly bound than acac to palladium(II) and they are also consistent with the suggestion that a weakly co-ordinated ligand is required for carbonylation.[2] In turn, these observations lend support to a dissociative carbonylation mechanism for the palladium complexes. In contrast relative carbonylation rates for the platinum complexes follow the order sacac > acac. This may indicate that different mechanisms apply for carbonylation at the Pd and Pt centre or it may reflect different bonding strengths of sacac and acac with Pt and Pd.

There are two likely intermediates which could be involved in the carbonylation of a square-planar complex, [PtX(R)L_2] (R = alkyl or aryl, L = monodentate ligand), *i.e.* a five-co-ordinated complex [PtXR(CO)L_2] (associative route) or a complex in which CO initially substitutes for L (dissociative route). The route followed is thought to depend on the base strength of the ligands.[2] Where the mechanism proposed is a dissociative one, it generally involves displacement of a tertiary phosphine. This proposal for dissociation of L is supported by the inability of organoplatinum complexes containing bidentate phosphine ligands to undergo carbonylation.[1d,12] However, the associative route may occur in several cases, which probably then proceed by a ligand migration, from a species with a trigonal-bipyramidal configuration.[1d,13] Few complexes of [PtR(A–A)L], where A–A is a bidentate monoanionic ligand and L is a neutral two electron-donor ligand, have been reported to undergo the CO insertion, and little is known about the mechanism.

The *in situ* ^{1}H NMR spectra of carbonylation of [PtMe(tfacac)(PPh_3)], [PdMe(acac)(PPh_3)] and [PdMe(sacac)(PPh_3)] indicate that displacement of PPh_3 does not occur, at least within the NMR time-scale, as the coupling between ^{31}P and σ-methyl protons in these complexes was observed until all the starting complex was consumed. Nor was there any evidence of free PPh_3 in the ^{31}P-{^{1}H}NMR spectra. This parallels a previous study which showed that the exchange rate of acac ligand in [NiMe(acac)(PPh_3)] is much faster than that of PPh_3.[12]

Displacement of the acac ligand by CO appears more likely. Two sharp singlets at δ 1.59 and 2.02 in [PdMe(acac)(PPh_3)] due to the acac methyl groups became much broader during the

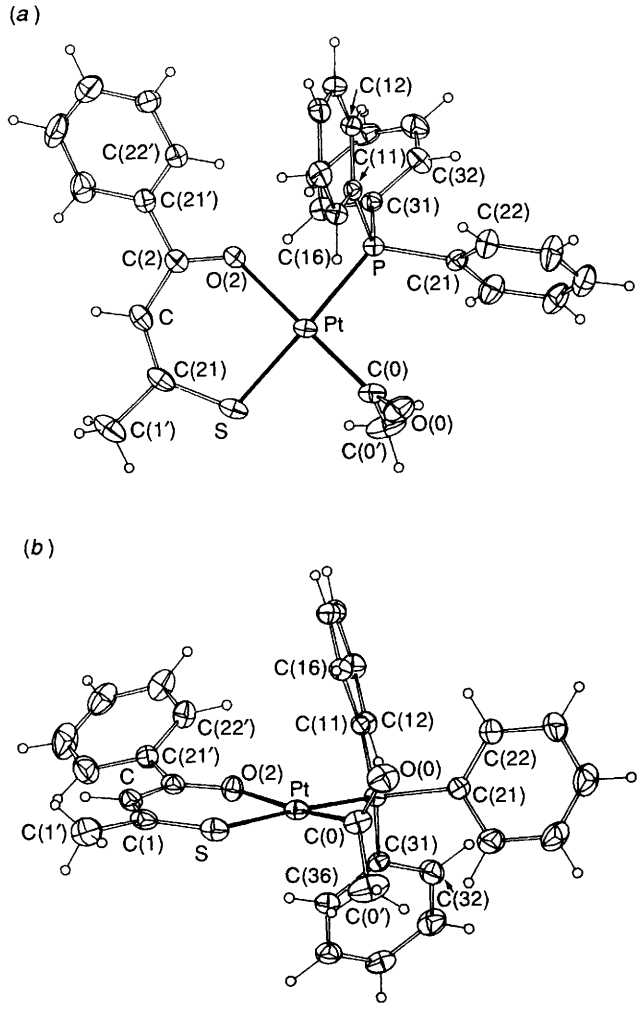


Fig. 2 (*a*) View of the complex [Pt(COMe)(bzsac)(PPh_3)] projected normal to the co-ordination plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms and hydrogen atoms have been given an arbitrary radius of 0.1 Å. (*b*) A second view, showing more clearly the relatively close approach of the protons on C(16) and C(36) to the metal

Table 5 Co-ordination geometry (distances in Å, angles in °) for the platinum atom in [Pt(COMe)(bzsac)(PPh_3)] **9**

Pt–C(0)	1.974(9)	Pt–O(2)	2.314(5)
Pt–S	2.291(2)	Pt–P	2.267(2)
C(0)–Pt–S	88.4(2)	P–Pt–C(0), O(2)	93.7(2)
S–Pt–O(2)	93.1(1)	C(0)–Pt–O(2)	175.4(2)
O(2)–Pt–P	85.2(1)	P–Pt–S	175.78(5)

Deviation (Å) of atoms from PCSO plane*

Pt	−0.027(1)	O(2)	−0.061(6)
C(0)	−0.146(9)	P	0.040(2)
S	0.059(2)		

* Angle chelate ligand is bent from PtCSOP plane is 3.6(1)°; the mean plane has $\chi^2 = 2112$.

carbonylation reaction until they were finally replaced by two sharp resonances at δ 1.71 and 1.94 due to the insertion product [Pd(COMe)(acac)(PPh_3)] **15**.

However there is no evidence that displacement of the sacac ligand by CO occurs, for example no band broadening of the

Table 6 Non-hydrogen positional parameters for complex **9**

Atom	*x*	*y*	*z*
Pt	0.803 92(2)	0.544 68(2)	0.360 44(1)
C(0)	0.883 6(5)	0.633 3(6)	0.321 3(4)
O(0)	0.842 4(4)	0.709 4(4)	0.268 8(3)
C(0′)	1.001 4(6)	0.612 6(8)	0.363 1(6)
S	0.880 1(1)	0.678 5(1)	0.466 3(1)
C(1)	0.829 9(5)	0.651 2(6)	0.522 8(3)
C(1′)	0.875 9(6)	0.735 0(8)	0.594 9(4)
C	0.752 0(5)	0.568 4(6)	0.511 9(3)
O(2)	0.706 4(3)	0.455 7(3)	0.395 2(2)
C(2)	0.692 7(5)	0.479 2(5)	0.450 3(3)
C(21′)	0.602 8(5)	0.408 8(5)	0.446 2(3)
C(22′)	0.516 5(5)	0.371 9(6)	0.373 3(4)
C(23′)	0.428 7(6)	0.312 4(6)	0.365 5(5)
C(24′)	0.426 5(8)	0.283 7(7)	0.430 1(6)
C(25′)	0.510 0(9)	0.316 5(8)	0.502 8(6)
C(26′)	0.598 3(7)	0.381 4(7)	0.512 1(4)
P	0.734 5(1)	0.400 4(1)	0.262 09(8)
C(11)	0.590 4(4)	0.388 0(5)	0.217 1(3)
C(12)	0.536 2(4)	0.274 2(5)	0.199 3(3)
C(13)	0.426 0(5)	0.271 9(6)	0.165 1(3)
C(14)	0.369 2(4)	0.383 2(7)	0.148 9(3)
C(15)	0.422 8(5)	0.496 2(6)	0.167 0(3)
C(16)	0.532 0(5)	0.498 5(5)	0.201 1(3)
C(21)	0.749 3(5)	0.420 0(5)	0.178 1(3)
C(22)	0.666 5(6)	0.451 4(6)	0.105 2(4)
C(23)	0.679 8(7)	0.462 0(9)	0.042 2(4)
C(24)	0.778 0(8)	0.443 2(8)	0.054 4(5)
C(25)	0.863 3(7)	0.413 3(8)	0.127 0(6)
C(26)	0.850 8(5)	0.402 9(8)	0.190 1(4)
C(31)	0.787 5(4)	0.243 6(5)	0.297 8(3)
C(32)	0.777 9(5)	0.148 4(6)	0.247 3(3)
C(33)	0.817 3(6)	0.028 6(6)	0.276 8(5)
C(34)	0.868 2(5)	0.005 0(6)	0.355 7(5)
C(35)	0.878 3(5)	0.096 4(6)	0.405 9(4)
C(36)	0.839 5(5)	0.217 2(6)	0.377 7(3)

sharp singlets attributed to the methyl groups of the sacac ligand in the complexes [PtMe(sacac)(PPh_3)] (δ 1.60, 2.20) and [PdMe(sacac)(PPh_3)] (δ 1.80, 2.40) is apparent. The sharp signals smoothly diminish as the alkyl complexes are consumed and sharp new signals due to the acyl complexes grow in proportion. This again supports previous observations that sacac ligand appears to co-ordinate more firmly than acac to Pd.

In conclusion the results and observations reported here support a dissociative carbonylation mechanism in which one arm of the chelating β-diketonate ligand dissociates to allow co-ordination of the CO prior to insertion.

Our results for the series of palladium–methyl complexes show that the rate of CO insertion depends primarily on the co-ordinating ability or relative nucleophilicity of the chelating ligands.[1d] Electron-withdrawing moieties on the ligand increase the rate of carbonylation, and replacement of an O by the more strongly bonding S as the donor atom decreases the carbonylation rate.[11] The following qualitative order of reactivity for the palladium–methyl complexes is observed; bzsacac > tfac > acac > sacac. The relative lability of the acac and tfac ligands in these complexes is also clearly demonstrated by the ^1H NMR studies. No corresponding evidence for dissociation of PPh_3 was observed.

For the series of platinum complexes mechanistic evidence is more indirect. The observation that carbonylation does not occur for the complex [PtMe(acac)(PPh_3)], but does occur where the acac ligand contains electron-withdrawing moieties, is consistent with a dissociative mechanism in which a weakly co-ordinated (less nucleophilic) ligand is required. The greater reactivity of the platinum–sacac complex over the platinum–acac complex is more difficult to reconcile. However, this

Table 7 Pt–L Distances in some selected platinum(II) complexes

Complex	Bond type	Bond distance/Å	Ref.
trans-[PtCl(COCOPh)(PPh_3)$_2$]	Pt–C	2.018(1)	13
	Pt–P	2.307(3), 2.306(3)	
cis-[Pt(CO_2Me)(COPh)(PPh_3)$_2$]	Pt–C (CO_2Me)	2.031(4)	13
	Pt–C (COPh)	2.047(4)	
	Pt–P (*trans* to CO_2Me)	2.313(1)	
	Pt–P (*trans* to COPh)	2.359(4)	
trans-[PtCl(COC_3H_7)(PPh_3)$_2$]	Pt–C	2.002(19)	14
	Pt–P	2.317(6)	
trans-[PtCl(COC_6H_{13})(PPh_3)$_2$]	Pt–P	2.302(3), 2.301(3)	15
	Pt–C	2.02(1)	
[Pt(CS_2)(PPh_3)$_2$]	Pt–P (*trans* to C)	2.346(10)	16
	Pt–P (*trans* to S)	2.240(15)	
	Pt–C	2.063(46)	
	Pt–S	2.328(16)	
[PtCl(PEt_3){$C(PPh_2S)_3$}]	Pt–P (*trans* to C)	2.254(4)	17
	Pt–P (*trans* to S)	2.351(4)	
[Pt(S_2CNEt_2)Cl(PPh_3)]	Pt–P (*trans* to S)	2.253(7)	18
	Pt–S (*trans* to P)	2.349(7)	
[Pt_2(acac)$_2$(CH_2=$CHCH_2$)$_2$]	Pt–C (alkyl)	2.13(3), 2.09(5)	19
	Pt–C (alkyl)	1.97(3)	
	Pt–O (*trans* to alkyl)	2.07(2)	
	Pt–O (*trans* to alkene)	1.98(2)	

variability in behaviour of the platinum complexes suggests that they do not carbonylate *via* an associative mechanism. It is difficult to envisage that the various 'active' platinum complexes are able to form a five-co-ordinate intermediate prior to insertion, whereas only [PtMe(acac)(PPh_3)] is not. It also appears unlikely, assuming a dissociative mechanism applies, that the dissociating ligand is the phosphine. The stronger Pt–P bond mitigates against such a route.

Solid-state Structure of [Pt(COMe)(bzsac)(PPh_3)].—Selected bond distances and angles are provided in Table 5 and a projection normal to the co-ordination plane is given in Fig. 2. Co-ordinates for the non-hydrogen atoms are given in Table 6.

Although the metal atom environment in the complex is essentially planar, small but significant deviations from the PtCOPS plane are observed [χ^2 = 2112; δ Pt, C, O, P, S are −0.027(1), −0.146(9), −0.061(6), 0.040(2), 0.059(2) Å], concomitant with *trans* angles deviating notably from 180° [C–Pt–O 175.4(2), 175.78(5)°] in spite of an angle sum in the plane of 360.4°. For the non-hydrogen skeleton of the β-diketonate ligand (excluding peripheral Ph atoms), χ^2 is 550 [δ S(1), O(2), C, C(1), C(1′), C(2), C(21′): −0.011(2), 0.065(6), 0.041(8), 0.048(7), 0.059(11), 0.013(7), −0.142(8) Å]. The angle between the pendant C_6 ring and the ligand is 29.0(3)°, while the PtCOPS/C(0)C(0′)O(0) interplanar dihedral angle is 77.8(3)°, with Pt lying 0.15(4) Å out of the second plane. The wrinkling of the co-ordination plane is suggestive of a snug disposition of the ligand substituents, an impression confirmed by Fig. 2, and also the large Pt–P–C(21) angle [120.4(2)°, *cf.* Pt–P–C(11), Pt–P–C(31), 110.1(2), 112.4(2)°]; in association with the disposition of the latter we find Pt ··· H(16) and Pt ··· H(36) approaches of 3.14 and 2.93 Å to either side of the plane.

Apart from the Pt–O bond of the sacac ligand, metal–ligand distances appear short, although comparisons are difficult as so few acyl complexes have been structurally characterised (Table 7), *e.g.* the Pt–C bond distance for the acyl ligand [1.974(9) Å] is 0.03–0.33 Å shorter than values for related complexes,[13–15] although the variation in reported Pt–C (acyl) distances is markedly affected by the group *trans* to the acyl group. Likewise, both the Pt–P [2.267(2) Å] and Pt–S [2.291(2) Å] bond distances are generally shorter than reported values (Table 7). However the related complex,[PtEt(sacac)(PPh_3)], which has phosphorus *trans* to sulfur, has Pt–P [2.247(1) Å] and Pt–S [2.296(1) Å] distances similar to those of the present complex.*

A notable feature of the structure of [Pt(COMe)(bzsac)(PPh_3)] is the long Pt–O bond [2.314(5) Å] compared with the related complex [PtEt(sacac)(PPh_3)] which has a Pt–O distance of 2.105(4) Å.[20] Both complexes have the O *trans* to C, however in the former case an acyl carbon and in the latter an alkyl carbon. The difference [Δ(Pt–O) 0.209(5) Å] is consistent with a comparatively large *trans* effect of the acyl group which has a sp^2 hybridized carbon.

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* The crystal structures of [PtEt(acac)(PPh_3)], [PtEt(sacac)(PPh_3)], [PdMe(acac)(PPh_3) and [PdMe(sacac)(PPh_3)] have been determined.[20]

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