Molecular Structures of Mixed-ligand Palladium(II) and Platinum(II) Alkyl Complexes, including Three Isomorphous Compounds *

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The crystal structures of the complexes [PdMe(β-dik)(PPh$_3$)] [β-dik = acetylacetonate (acac) or monothioacetylacetonate (sacac)] and [PtEt(β-dik)(PPh$_3$)] have been determined. All four complexes crystallize in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. They have a slightly distorted square-planar geometry. For the pair of acac complexes O(1)-Pd-O(2) 88.8(2), O(1)-Pt-O(2) 89.2(2), C(0)-Pd-P 88.3(2) and C(0)-Pt-P 92.7(2)°; Pd-C 2.003(9), Pt-C 2.013(9), Pd-P 2.209(2) and Pt-P 2.182(2) Å. For the two sacac complexes, S(1)-Pd-O(2) 91.35(9), S(1)-Pt-O(2) 91.59(9), C(0)-Pd-S(1) 86.4(2) and C(0)-Pt-S(1) 86.8(1)°; Pd-C 2.033(7), Pt-C 2.058(6) Å, Pd-P 2.274(1) and Pt-P 2.247(1) Å. Comparison of the M-C bonds in the structures shows a slight lengthening in complexes containing the sacac ligand, consistent with the previously observed enhanced carbonylation activity of the platinum sacac complex over that of the analogous acac compound. A comparison of M-P bonds reveals that those of Pt are consistently shorter than those of Pd, in agreement with proposed relative bond strengths.

Transition-metal alkyl complexes are believed to be intermediates in a variety of catalytic processes such as carbonylation and oligomerisation.[1] Palladium(II) and platinum(II) form a variety of alkyl complexes of varying stability and hence are often employed as model systems for studying important steps in these catalytic reactions. Ligands of the β-diketonate (β-dik) type e.g. *O,O′* chelates *O,S* chelates (monothio-β-diketonates) and *S,S* chelates (dithio-β-diketonates) have been extensively employed in catalysts based on various d^8 metal complexes.[2-5] In many of these catalyst systems evidence suggests that the chelate ligand remains associated with the active species and hence is able to influence reaction behaviour, and in each case it is believed that a metal alkyl species is formed as an active intermediate in the catalytic pathway. Little is known however about how the chelating ligand directs individual steps in the reaction pathways. In consideration of these problems we have been investigating a series of mixed-ligand alkyl and aryl complexes of Pd^{II} and Pt^{II} containing chelating ligands of the β-diketone and monothio-β-diketone type with a view to gaining some understanding of how the ligand modifies the catalytically important insertion and elimination reactions.

There has also been considerable recent interest in the role of chelating phosphine ligands in directing the mechanism for carbon monoxide insertion during the carbonylation of palladium- and platinum-hydrocarbyl complexes.[6-8] Our studies extend those on non-phosphine-based chelate systems.[9,10]

One aspect of our study has been to examine the metal-ligand bonding in a number of these complexes in an attempt to correlate structural parameters with ligand influences and complex reactivity. This study complements recent work undertaking detailed structural comparisons of palladium and platinum complexes containing metal-alkyl bonds.[11-13] Such comparisons have particular significance where isomorphous pairs exist.[11-14]

M = Pd or Pt, X = O or S

Accordingly, in this paper we report on an X-ray crystallographic study of the unusual set of mixed-ligand complexes [PdMe(acac)(PPh$_3$)] (acac = acetylacetonate), [PdMe(sacac)(PPh$_3$)] (sacac = monothioacetylacetonate), [PtEt(sacac)(PPh$_3$)] and [PtEt(acac)(PPh$_3$)], the first three of which are isomorphous. Crystal-packing influences can reasonably be assumed to be constant in comparing structural parameters for the isomorphous complexes and hence may be ignored. Thus, this study provides a valuable opportunity to investigate effects on structure arising from changes in the chelating ligand and in the metal centre. Prior to the present study we were unaware of any reports of structural studies on simple palladium and platinum alkyl complexes containing β-dik ligands, which is surprising considering the importance of such ligands in catalytic systems.

Experimental

Preparation of the Complexes.—Standard Schlenk techniques were employed throughout and all solvents were dried and purified by the usual methods. All other reagents were used as received. The complexes [PdMe(β-dik)(PPh$_3$)] were synthesised as previously described.[9] The platinum complexes were prepared by the following methods.

[PtEt(acac)(PPh$_3$)]. A solution of *trans*-[PtH(Cl)(PPh$_3$)$_2$][15] (0.14 g, 0.18 mmol) in acetone (*ca.* 15 cm^3) was treated with AgBF$_4$ (0.036 g, 0.18 mmol) in acetone (*ca.* 2 cm^3) to immediately precipitate AgCl. After stirring at room temperature for 0.5 h, ethylene was bubbled through the solution for *ca.* 1 h. Sodium acetylacetonate (0.022 g, 0.18 mmol) in MeOH (*ca.* 2 cm^3) was added. The mixture was stirred vigorously at room

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* *Supplementary data available:* See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

temperature overnight. The brown solid was filtered through a Celite column, and the colourless solution evaporated to dryness leaving a pale yellow oil which was crystallised from CH_2Cl_2–MeOH at − 5 °C. The cream solid was filtered off and dried in vacuum (yield: 0.096 g, 91%) (Found: C, 51.30; H, 5.00. Calc. for $C_{25}H_{27}O_2PPt$: C, 51.30; H, 4.65%). Mass spectrum: *m/z* 584, M^+; 556, $[M - C_2H_4]^+$, (high resolution) 584.133 (Calc. for $C_{25}H_{27}O_2P^{194}Pt$, 584.137). IR(KBr): 1580vs, 1520vs and 1480m cm^{-1} [ν(C=O) + ν(C=C)]. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 13.8 ($^1J_{PtP}$ = 4945 Hz).

[PtEt(sacac)(PPh_3)]. This complex was prepared as described for [PtEt(acac)(PPh_3)], and isolated as a green-yellow solid (yield: 89%) (Found: C, 49.90; H, 4.65. Calc. for $C_{25}H_{27}OPPtS$: C, 49.90; H, 4.50%). Mass spectrum: *m/z* 600, $[M]^+$; 571, $[M - Et]^+$; (high resolution) 600.115. (Calc. for $C_{25}H_{27}OP^{194}PtS$, 600.109). IR (KBr): 1560s and 1470vs cm^{-1} [ν(C=O) + ν(C=C) + ν(C=S)]. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 24.8 ($^1J_{PtP}$ = 3886 Hz).

Crystal-structure Determinations.—For each complex suitable crystals for crystallography were obtained by diffusing ether into a concentrated dichloromethane solution of the complex. Unique data sets were measured at ≈295 K within the specified $2\theta_{max}$ limit using Enraf-Nonius CAD-4 and Syntex $P2_1$ diffractometers (2θ–θ scan mode; monochromatic Mo-Kα radiation (λ = 0.710 73 Å); *N* independent reflections were obtained, N_o 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*| are quoted, 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 implemented by S. R. Hall;[17] neutral atom complex scattering factors were employed. Pertinent results are given in the Figures and Tables.

Crystal/refinement data. [PdMe(acac)(PPh_3)], $C_{24}H_{25}O_2PPd$, *M* = 482.8, triclinic, space group $P\bar{1}$, *a* = 12.759(3), *b* = 10.543(2), *c* = 8.889(2) Å, α = 83.29(2), β = 71.62(2), γ = 72.99(2)°, *U* = 1085 Å³, $D_c(Z = 2)$ = 1.47 g cm^{-3}, *F*(000) = 462, μ_{Mo} = 8.4 cm^{-1}, specimen 0.09 × 0.18 × 0.22 mm, $A^*_{min,max}$ = 1.07, 1.16, $2\theta_{max}$ = 50°, *N* = 3702, N_o = 2645, *R* = 0.044, *R'* = 0.045.

[PdMe(sacac)(PPh_3)], $C_{24}H_{25}OPPdS$, *M* = 498.9, triclinic, space group $P\bar{1}$, *a* = 13.192(5), *b* = 10.942(3), *c* = 8.783(1) Å, α = 87.13(2), β = 74.07(2), γ = 69.44(2)°, *U* = 1140 Å³, D_c (*Z* = 2) = 1.45 g cm^{-3}, *F*(000) = 508, μ_{Mo} = 8.9 cm^{-1}, specimen 0.12 × 0.23 × 0.65 mm, $A^*_{min,max}$ = 1.09, 1.28, $2\theta_{max}$ = 65°, *N* = 6820, N_o = 4428, *R* = 0.048, *R'* = 0.051.

[PtEt(acac)(PPh_3)], $C_{25}H_{27}O_2PPt$, *M* = 585.6, triclinic, space group $P\bar{1}$, *a* = 13.179(3), *b* = 10.968(4), *c* = 9.379(2) Å, α = 102.01(2), β = 101.88(2), γ = 112.93(2)°, *U* = 1158 Å³, D_c (*Z* = 2) = 1.68 g cm^{-3}, *F*(000) = 572, μ_{Mo} = 58.9 cm^{-1}, specimen 0.50 × 0.38 × 0.38 mm, $A^*_{min,max}$ = 3.1, 4.7, $2\theta_{max}$ = 65°, *N* = 8806, N_o = 7095, *R* = 0.054, *R'* = 0.061.

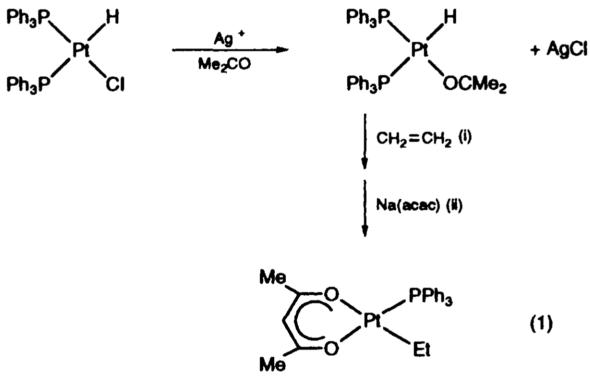
[PtEt(sacac)(PPh_3)], $C_{25}H_{27}OPPtS$, *M* = 601.6, triclinic, space group $P\bar{1}$, *a* = 13.189(2), *b* = 11.366(3), *c* = 8.875(1) Å, α = 88.78(2), β = 73.49(1), γ = 69.19(2)°, *U* = 1188 Å³, D_c (*Z* = 2) = 1.68 g cm^{-3}, *F*(000) = 588, μ_{Mo} = 58.1 cm^{-1}, specimen 0.13 × 0.25 × 0.48 mm, $A^*_{min,max}$ = 2.1, 6.0, $2\theta_{max}$ = 55°, *N* = 5414, N_o = 4557, *R* = 0.026, *R'* = 0.027.

To enhance the comparability of the molecular geometries, unit cells were calibrated for the four complexes under the same conditions on the same instrument on the same day; librational corrections to molecular geometries, although not applied, may reasonably be assumed to be similar throughout the series, in consequence of the isomorphism and the similarity in thermal parameters of pertinent atoms.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Preparation of the Complexes.—The complex [PdMe(acac)(PPh_3)] was synthesised from *trans*-[Pd(Me)I(PPh_3)$_2$] by a simple ligand-exchange reaction.[9] The complexes [PtEt(acac)(PPh_3)] and [PtEt(sacac)(PPh_3)] were prepared according to equation (1), in high yield in a one-pot multistep synthesis from



(1)

[PtH(Cl)(PPh_3)$_2$] using a method based on that developed by Clark and Kurosawa.[15] Removal of chloride with silver ions gave a solvated platinum hydride. Treatment with ethylene and then acetylacetonate leads to insertion of ethylene into the platinum–hydrogen bond and co-ordination of the chelate ligand to give the desired complex. The complexes appear air stable in the solid state, but in solution the palladium complexes slowly deposit palladium metal even under nitrogen.

Crystal Structures.—The mixed-ligand complexes [PdMe(acac)(PPh_3)], [PdMe(sacac)(PPh_3)], [PtEt(acac)(PPh_3)] and [PtEt(sacac)(PPh_3)] represent a unique set of closely related compounds. Within this set, three of which are isomorphous, the metal, the alkyl ligand and the chelating β-dik ligand are varied, providing a valuable opportunity to investigate metal–ligand bonding and possible correlation between structure and reactivity. Although [PtEt(acac)(PPh_3)] is not strictly isomorphous with the other three complexes, it is structurally very similar (Fig. 1) and hence it is considered useful to include it in the ensuing discussions and comparisons.

The crystal structures of the complexes show a packing of two molecules per unit cell. The cell dimensions along with other crystallographic details are given in the Experimental section and coordinates for the non-hydrogen atoms are in Table 1. Selected molecular structure data relating to the inner co-ordination sphere are shown in Table 2 and clearly illustrate the structural similarities and differences existing in these complexes. For comparison a list of metal–ligand bond distances in selected complexes of Pd^{II} and Pt^{II} is given in Table 3. Parameters of the essentially planar metal environments are given in Table 4.

Interligand angles about the metal centres show generally small but distinct deviations from 90° reaching a maximum of 95.6(1) and 93.48(9)° for the O(2)–Pd–P angles. The C(0)–M–X (X = O or S) interligand angles were consistently the smallest, ranging from 86.1(3) for the C(0)–Pt–O(1) angle to 87.4(3)° for the C(0)–Pd–O(1) angle.

Differences in bond lengths for the complexes discussed in this paper are often small, in many cases barely greater than twice the standard deviation. However, the direction of change is always consistent and distinctive trends are generally evident.

The M–(β-dik) bond distances are very similar in all complexes in this group (Table 3). A small difference in the M–O(1) distances for the Pd–acac and Pt–acac complexes is suggested, the Pd–O bond being longer [0.019(5) Å]. Similarly small differences in M–O(2) distances for pairs of metal complexes are also evident; for the two palladium complexes the difference is 0.017(6) Å and for the platinum complexes the difference is 0.018(4) Å. In both pairs the M–O(2) distance in

Table 1 Non-hydrogen atom parameters for [MR(β-dik)(PPh_3)] [β-dik = MeC(X)CHC(O)Me]

Atom	*x*	*y*	*z*	*x*	*y*	*z*
(*a*) R = Me, M = Pd, X = O				X = S		
Pd	0.247 21(5)	0.494 07(5)	0.331 78(6)	0.239 80(3)	0.508 10(3)	0.344 85(4)
C(0)	0.362 8(6)	0.581 2(7)	0.349 2(9)	0.354 0(5)	0.586 8(5)	0.366 6(7)
X(1)	0.153 3(4)	0.681 3(4)	0.275 9(5)	0.138 0(1)	0.713 0(1)	0.284 1(2)
C(1)	0.060 0(6)	0.703 9(7)	0.238 0(7)	0.029 7(4)	0.708 7(5)	0.217 7(6)
C(1′)	0.009 1(6)	0.849 8(7)	0.204 4(9)	−0.034 2(5)	0.839 2(6)	0.164 3(8)
C	0.004 6(6)	0.614 4(8)	0.228 6(9)	−0.005 3(4)	0.608 7(6)	0.211 6(6)
O(2)	0.125 6(4)	0.414 6(4)	0.297 6(5)	0.121 8(3)	0.432 4(3)	0.310 4(4)
C(2)	0.038 3(6)	0.478 3(8)	0.257 2(8)	0.037 8(4)	0.479 0(5)	0.258 0(5)
C(2′)	−0.034 1(7)	0.392 3(8)	0.240(1)	−0.021 2(5)	0.387 4(6)	0.243 5(7)
P	0.352 8(1)	0.304 2(2)	0.402 4(2)	0.349 12(9)	0.313 5(1)	0.413 6(1)
C(11)	0.329 9(5)	0.281 5(6)	0.615 7(7)	0.332 6(3)	0.299 0(4)	0.626 2(5)
C(12)	0.317 1(6)	0.161 9(6)	0.693 2(7)	0.333 5(4)	0.184 4(5)	0.699 1(5)
C(13)	0.295 5(6)	0.146 7(7)	0.854 8(8)	0.315 2(4)	0.178 2(5)	0.863 9(6)
C(14)	0.285 2(6)	0.250 2(8)	0.943 1(8)	0.296 4(4)	0.287 4(6)	0.951 8(6)
C(15)	0.298 7(6)	0.367 3(8)	0.868 3(8)	0.296 7(5)	0.401 1(6)	0.882 8(6)
C(16)	0.319 9(6)	0.383 8(7)	0.705 0(8)	0.313 9(4)	0.407 6(5)	0.719 0(5)
C(21)	0.507 2(5)	0.274 1(6)	0.316 1(7)	0.499 0(4)	0.270 1(4)	0.323 1(5)
C(22)	0.584 0(6)	0.214 0(7)	0.398 8(7)	0.579 2(4)	0.199 7(5)	0.397 8(5)
C(23)	0.699 9(6)	0.191 8(8)	0.326 9(9)	0.693 2(4)	0.163 8(6)	0.320 3(7)
C(24)	0.740 6(6)	0.229 0(9)	0.172(1)	0.726 8(5)	0.199 5(6)	0.169 0(7)
C(25)	0.665 0(7)	0.288 1(8)	0.086 6(8)	0.647 7(5)	0.269 4(6)	0.091 9(6)
C(26)	0.549 5(6)	0.310 5(7)	0.157 9(8)	0.534 3(4)	0.306 0(5)	0.168 2(6)
C(31)	0.323 8(6)	0.161 1(6)	0.346 5(7)	0.320 0(4)	0.173 7(4)	0.357 8(5)
C(32)	0.407 0(6)	0.063 4(7)	0.251 0(8)	0.400 6(4)	0.072 9(4)	0.254 3(5)
C(33)	0.379 2(7)	−0.041 8(7)	0.209 4(8)	0.373 3(5)	−0.028 4(5)	0.207 3(6)
C(34)	0.268 5(8)	−0.052 2(7)	0.261 3(9)	0.266 2(6)	−0.028 5(5)	0.265 0(7)
C(35)	0.185 6(7)	0.043 9(8)	0.357 9(9)	0.184 8(5)	0.069 9(6)	0.369 4(7)
C(36)	0.211 4(6)	0.149 5(7)	0.399 7(7)	0.211 9(4)	0.171 0(5)	0.416 6(5)
(*b*) R = Et, M = Pt, X = O				X = S		
Pt	0.194 86(2)	0.420 72(3)	0.299 48(3)	0.247 89(1)	0.491 26(2)	0.353 30(2)
C(0)	0.227 0(6)	0.377 1(7)	0.099 1(9)	0.360 7(4)	0.562 0(4)	0.399 2(6)
C(0′)	0.293 7(9)	0.286(1)	0.096(1)	0.427 5(5)	0.609 8(5)	0.256 7(8)
X(1)	0.085 4(4)	0.209 7(5)	0.234 4(6)	0.154 6(1)	0.690 6(1)	0.293 4(2)
C(1)	0.025 1(6)	0.148 0(8)	0.310(1)	0.044 7(4)	0.693 9(5)	0.226 6(6)
C(1′)	−0.046 2(8)	−0.003 1(9)	0.238(1)	−0.015 6(4)	0.821 7(5)	0.175 2(8)
C	0.021 7(6)	0.211 5(9)	0.452(1)	0.005 9(4)	0.599 7(5)	0.215 2(6)
O(2)	0.153 9(5)	0.448 0(5)	0.503 6(6)	0.129 5(2)	0.424 2(3)	0.305 8(3)
C(2)	0.082 3(6)	0.352 0(9)	0.541 3(9)	0.045 8(3)	0.474 2(5)	0.255 4(5)
C(2′)	0.066 5(9)	0.401(1)	0.691(1)	−0.015 6(4)	0.389 4(5)	0.234 4(7)
P	0.308 4(1)	0.643 7(2)	0.361 0(2)	0.345 37(9)	0.301 5(1)	0.419 0(1)
C(11)	0.248 0(6)	0.736 1(7)	0.259 3(8)	0.321 2(3)	0.289 0(4)	0.631 1(4)
C(12)	0.285 9(7)	0.879 3(9)	0.321(1)	0.328 4(4)	0.174 4(5)	0.695 2(5)
C(13)	0.233 8(9)	0.944 0(9)	0.240(1)	0.311 0(4)	0.166 8(5)	0.855 8(6)
C(14)	0.148 4(8)	0.869(1)	0.100(1)	0.286 7(4)	0.271 7(6)	0.953 1(6)
C(15)	0.112 6(7)	0.730(1)	0.037 8(9)	0.279 4(4)	0.384 7(5)	0.891 4(6)
C(16)	0.160 6(6)	0.663 3(8)	0.118 9(8)	0.295 9(3)	0.395 0(4)	0.730 5(5)
C(21)	0.451 5(5)	0.688 7(7)	0.338 6(8)	0.499 6(3)	0.249 2(4)	0.337 4(5)
C(22)	0.512 8(6)	0.805 8(8)	0.301(1)	0.573 3(4)	0.183 0(4)	0.419 6(5)
C(23)	0.624 1(8)	0.835(1)	0.295(1)	0.689 7(4)	0.145 5(5)	0.353 6(7)
C(24)	0.674 5(7)	0.753(1)	0.329(1)	0.732 3(4)	0.175 6(6)	0.204 8(7)
C(25)	0.614 2(7)	0.638(1)	0.369(1)	0.660 2(5)	0.240 7(6)	0.119 3(6)
C(26)	0.503 6(6)	0.606 2(9)	0.371(1)	0.544 0(4)	0.278 5(5)	0.184 6(5)
C(31)	0.338 5(6)	0.733 3(7)	0.563 1(8)	0.312 2(4)	0.170 3(4)	0.356 4(5)
C(32)	0.441 6(8)	0.766(1)	0.676(1)	0.392 2(4)	0.070 0(4)	0.251 0(5)
C(33)	0.454 0(9)	0.818(1)	0.828(1)	0.363 1(5)	−0.024 4(5)	0.201 9(6)
C(34)	0.365(1)	0.834(1)	0.872(1)	0.251 7(6)	−0.019 2(5)	0.259 3(8)
C(35)	0.265 6(8)	0.804(1)	0.763(1)	0.172 2(5)	0.080 0(5)	0.365 0(7)
C(36)	0.252 0(7)	0.753 2(9)	0.610 1(9)	0.200 8(4)	0.174 4(4)	0.413 8(5)

complexes of the sacac ligand are longer. Metal–sulfur distances in the present two sacac complexes are the same. However, they appear short (by 0.05–0.1 Å) compared to other M–S bonds *trans* to P reported in the literature (Table 3).

A consideration of M–P bond distances in these complexes provides some interesting comparative data. In the acac complexes, where P is *trans* to O, the M–P bonds appear relatively short [Pd–P 2.209(2), Pt–P 2.182(2)], the Pt–P bond being noticeably shorter than the Pd–P, by 0.027(2) Å. The M–P distances in the two sacac complexes, where P is *trans* to S, are significantly longer [Pd–P 2.274(1), Pt–P 2.247(1)], falling within the normal range expected for M–P bonds *trans* to sulfur, clearly demonstrating the greater *trans* influence of S. The Pd–P distance in the sacac complex is 0.065(2) Å longer than in its acac counterpart and a similar difference exists for the Pt–P bond distances [0.065(2) Å] in the two platinum complexes. The Pt–P bond is again shorter than the Pd–P, by 0.027(1) Å.

Table 2 Molecular core geometries (distances in Å, angles in °) for $[MR(\beta\text{-dit})(PPh_3)]$

	M = Pd, R = Me		M = Pt, R = Et	
	X = O	X = S	X = O	X = S
M-C(0)	2.003(9)	2.033(7)	2.013(9)	2.058(6)
M-X(1)	2.083(4)	2.296(1)	2.064(5)	2.296(1)
M-O(2)	2.078(6)	2.095(4)	2.087(6)	2.105(4)
M-P	2.209(2)	2.274(1)	2.182(2)	2.247(1)
C(0)-C(0′)			1.56(2)	1.533(8)
X(1)-C(1)	1.29(1)	1.701(6)	1.27(1)	1.704(6)
C(1)-C(1′)	1.519(9)	1.508(8)	1.46(1)	1.518(7)
C(1)-C	1.36(1)	1.337(9)	1.39(1)	1.357(9)
C-C(2)	1.39(1)	1.417(7)	1.39(1)	1.410(7)
O(2)-C(2)	1.257(9)	1.249(6)	1.28(1)	1.252(6)
C(2)-C(2′)	1.52(1)	1.50(1)	1.48(1)	1.505(9)
P-C(11)	1.822(6)	1.826(4)	1.812(9)	1.829(4)
P-C(21)	1.819(6)	1.811(4)	1.824(8)	1.827(4)
P-C(31)	1.811(8)	1.822(5)	1.824(7)	1.833(5)
C(0)-M-X(1)	87.4(3)	86.4(2)	86.1(3)	86.8(1)
C(0)-M-O(2)	175.2(2)	176.7(2)	175.2(2)	178.4(1)
C(0)-M-P	88.3(2)	88.8(2)	92.7(2)	89.6(1)
X(1)-M-O(2)	88.8(2)	91.35(9)	89.2(2)	91.59(9)
X(1)-M-P	175.1(2)	175.02(6)	178.2(2)	176.32(6)
O(2)-M-P	95.6(1)	93.48(9)	92.1(1)	91.98(9)
M-C(0)-C(0′)			112.1(6)	114.7(4)
M-X(1)-C(1)	124.4(5)	110.7(2)	126.4(5)	110.9(2)
X(1)-C(1)-C(1′)	113.2(7)	112.6(5)	115.7(8)	113.2(4)
X(1)-C(1)-C	127.6(6)	128.8(4)	125.6(7)	128.7(4)
C(1′)-C(1)-C	119.2(7)	118.5(5)	118.7(9)	118.0(5)
C(1)-C-C(2)	126.6(7)	129.4(5)	128.5(9)	129.2(5)
M-O(2)-C(2)	126.0(5)	133.0(3)	125.9(5)	133.0(3)
C-C(2)-O(2)	126.5(9)	126.0(6)	124.4(8)	126.3(5)
C-C(2)-C(2′)	119.6(7)	118.0(5)	120.7(9)	118.2(5)
O(2)-C(2)-C(2′)	113.9(7)	115.9(4)	114.9(7)	115.5(4)
M-P-C(11)	114.0(2)	114.7(1)	114.8(2)	114.7(1)
M-P-C(21)	115.8(2)	115.1(1)	115.4(3)	115.1(1)
M-P-C(31)	112.9(2)	113.7(2)	111.0(3)	114.6(2)
C(11)-P-C(21)	105.1(3)	105.6(2)	106.0(4)	104.4(2)
C(11)-P-C(31)	104.3(3)	103.1(2)	104.0(4)	102.8(2)
C(21)-P-C(31)	103.5(3)	103.1(2)	104.5(3)	103.6(2)

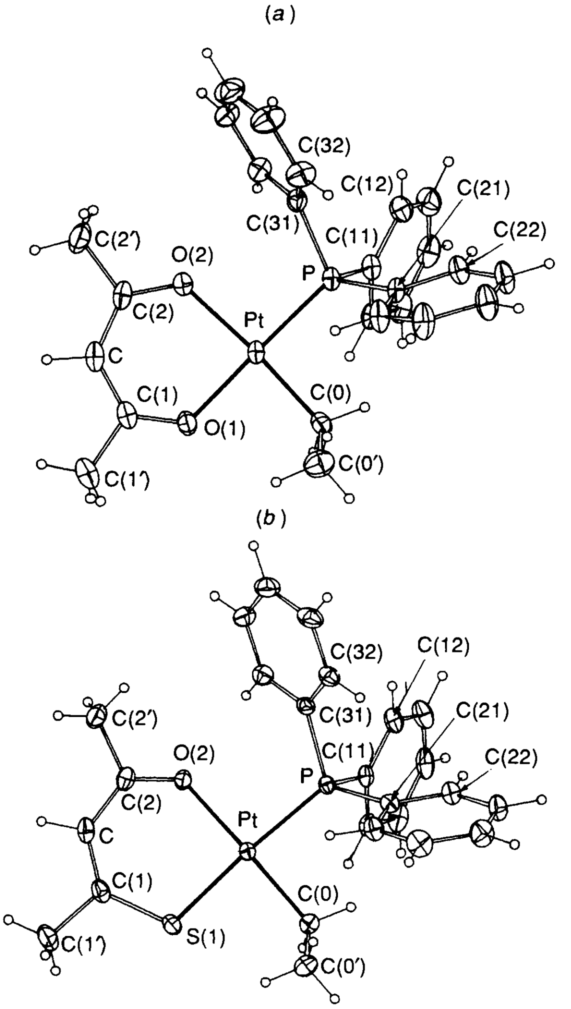


Fig. 1 Molecular projections of (*a*) $[PtEt(acac)(PPh_3)]$ and (*b*) $[PtEt(sacac)(PPh_3)]$ normal to the co-ordination plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å. The palladium analogues are isomorphous with $[PtEt(sacac)(PPh_3)]$ and hence are not shown

Another bond of particular importance with respect to these studies is the M-C. The Pd-Me distances at 2.003(9) and 2.033(7) Å appear short and are among the shortest Pd-C(sp^3) σ bonds reported. However, comparisons with literature values are difficult as very few complexes containing Pd-Me bonds *trans* to oxygen have been structurally characterised. Similarly, few platinum complexes with Pt-C bonds *trans* to oxygen have been studied. Of the two palladium complexes, the Pd-Me bond in the sacac complex is longer by 0.030(8) Å. A comparison of the Pt-C bond lengths in the two platinum complexes also reveals that the bond in the sacac complex is longer [by 0.045(8) Å] than in the acac complex. These results suggest that the sacac ligand may cause a slight weakening of the M-C bond.

Probably of greater importance is the consistent trend in M-C bond distances within these complexes as in each pair the bond is longer for the platinum than for the related palladium compound. The standard deviations and the uncertainty in the influence of changing from Me to Et limit the significance of these observations somewhat. However, the difference of 0.01 Å found for M-C in $[MR(acac)(PPh_3)]$ (Table 2), *trans* to common O(2), is in keeping with that between previous estimates of 2.07, 2.08 Å for Pd-C and Pt-C(sp^3) distances,[25] suggesting that the difference imposed by interchange of methyl and ethyl is minimal. In more general terms, there appear to be no substantial grounds for believing M-Me/M-Et differences in a common unhindered environment to be appreciably greater than 0.01 Å; specifically, for Pd^{II} and Pt^{II}-Me/Et. Consequently a comparison of M-C distances particularly for the sacac complexes of Pd and Pt is valid and the consistent trend in distances is of interest. Furthermore the relative covalent radii of platinum and palladium can be assumed to be about the same (*ca.* 1.3 Å)[25,26] and consequently will not have a significant bearing on M-C bond distances.

From the preceding discussion it is evident that while these four complexes are structurally very closely related, important differences in the structural parameters of the inner co-ordination sphere exist. To a limited extent M-C and in particular the M-P bond distances show distinct trends. Using the notation of Ibers and co-workers,[14] the difference in M-C distances may be expressed as Δ(M-C) values: Δ[M-C(acac)] = *d*(Pt-C) − *d*(Pd-C) = 0.010(9) and Δ[M-C(sacac)] = *d*(Pt-C) − *d*(Pd-C) = 0.025(7) Å. Values for Δ(M-P) are much more significant: Δ[M-P(acac)] = *d*(Pt-P) − *d*(Pd-P) = −0.027(2) and Δ[M-P(sacac)] = *d*(Pt-P) − *d*(Pd-P) = −0.027(1) Å.

Within the limitations discussed above the differences in metal-ligand bond lengths demonstrate several important features. Metal-phosphorus bond distances are greater for Pd than for Pt, whereas in contrast metal-carbon bond distances show the reverse trend, *i.e.* the Pt-C distances are greater than the Pd-C. These trends are consistent with those previously reported[14] for isomorphous complexes of Pd and Pt and add

Table 3 Metal–ligand bond distances in some complexes of Pd^{II} and Pt^{II}

Complex *	Bond type	Bond distance		Ref.
		Pd	Pt	
[MR(acac)(PPh_3)]	M–C	2.003(9)	2.013(9)	This work
	M–P	2.209(2)	2.182(2)	
	M–O (*trans* C)	2.083(4)	2.064(5)	
	M–O (*trans* P)	2.078(6)	2.087(6)	
[MR(sacac)(PPh_3)]	M–C	2.033(7)	2.058(6)	This work
	M–P	2.274(1)	2.247(1)	
	M–O (*trans* C)	2.095(1)	2.105(4)	
	M–S (*trans* P)	2.296(1)	2.296(1)	
[Pt(mnap)$_2$(SEt_2)]	Pt–C (sp^2, *trans* O)		1.976(6)	17
	Pt–C (sp^2, *trans* S)		1.962(7)	
	Pt–O (*trans* C)		2.229(5)	
	Pt–S (*trans* C)		2.367(2)	
[M(S_2CNEt_2)(PR_3)Cl]	M–S (*trans* P)	2.352(2)	2.349(7)	18
	M–P (*trans* S)	2.284(1)	2.253(7)	
[PdPr^n($S_2CNC_4H_8$)(PEt_3)]	Pd–S (*trans* P)	2.384(2)		12
	Pd–S (*trans* C)	2.406(1)		
	Pd–P	2.238(1)		
	Pd–C	2.048(5)		
[PdPr^i($S_2CNC_4H_8$)(PEt_3)]	Pd–S (*trans* P)	2.395(1)		12
	Pd–S (*trans* C)	2.439(1)		
	Pd–P	2.241(1)		
	Pd–C	2.074(4)		
[Pt{C(PPh_2S)$_3$}Cl(PEt_3)$_2$]	Pt–S (*trans* P)		2.351(4)	19
	Pt–P		2.254(4)	
[Pt_2Cl_2(μ-SEt_2)(PEt_3)$_2$]	Pt–S (*trans* P)		2.37	20
	Pt–P		2.26	
[Pd_2(dppp)$_2$(μ-OH)$_2$]	Pd–O	2.081(4)		21
	Pd–P (*trans* O)	2.230(1)		
[Pd_2(hfacac)$_2$(μ-MeO)$_2$]	Pd–O (μ-MeO)	1.996		22
[Pt_2(μ-C_2H_5)$_2$(acac)$_2$]	Pt–O (*trans* δ-C)		2.07(2)	23
	Pt–C (σ)		2.00(4)	
[Pd(OCO_2)Me(PEt_3)$_2$]	Pd–C (*trans* O)		2.05(2)	24
	Pd–O (*trans* C)		2.13(2)	

* mnap = 8-Methoxynaphthyl; dppp = $Ph_2P(CH_2)_3PPh_2$; hfacac = hexafluoroacetylacetonate

Table 4 Planarity of the metal-atom environment. Weighted least-squares planes have been calculated through the four co-ordinated atoms for the four complexes

	Pd/acac	Pd/sacac	Pt/acac	Pt/sacac
χ^2(plane)	179	252	21	10
δX(1)/Å	0.040(7)	0.006(2)	0.017(7)	0.001(2)
δO(2)/Å	−0.034(7)	−0.025(4)	−0.017(8)	−0.005(4)
δP/Å	0.005(2)	0.004(1)	0.002(2)	0.001(1)
δC/Å	−0.099(10)	−0.097(7)	−0.032(10)	−0.017(6)
δM/Å	−0.016(2)	−0.020(1)	−0.014(2)	−0.016(1)

further weight to the premise that hard ligands such as alkyls form longer bonds with Pt than with Pd, whereas soft ligands such as phosphines form shorter bonds with Pt, thus providing support for the proposals of Ibers *et al.*[14] regarding the relative 'hard' and 'soft' nature of Pd and Pt.

Correlation of structural parameters with ligand influences and complex reactivity is more difficult. However, for the platinum complexes the longer Pt–C bond in the sacac complex compared with its acac analogue is consistent with the difference in carbonylation activity observed for the two classes of complex. Carbonylation readily occurs in the [PtEt(sacac)(PPh_3)] complex but does not occur in the acac complex.[10]

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