# Crystal and Molecular Structures of Pentane-2,4-dionato-(α,1,2-η-triphenylmethyl)-palladium and -platinum

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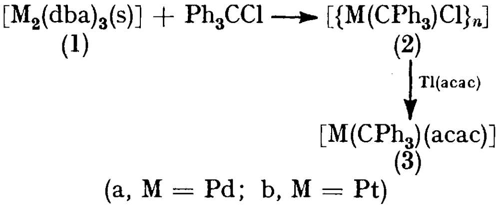
The crystal and molecular structures of [M(α,1,2-η-CPh$_3$)(acac)] [M = Pd (3a) or Pt (3b); acac = pentane-2,4-dionate) have been determined. The unit cell of each contains enantiomers of two crystallographically independent molecules which are very similar in structure. Crystals of (3a) are triclinic, space group $F\bar{1}$, with $a$ = 14.99, $b$ = 13.18, $c$ = 11.33 Å, α = 101.08, β = 90.54, γ = 115.48°, and $Z$ = 4; $R$ = 0.050 for 5 607 independent reflections. Crystals of (3b) are triclinic, space group $F\bar{1}$, with $a$ = 14.94, $b$ = 11.41, $c$ = 17.15 Å, α = 120.78, β = 122.03, γ = 90.13°, and $Z$ = 4; $R$ = 0.045 for 5 978 independent reflections. Both structures were solved using Patterson and Fourier methods. The structures of (3a) and (3b) are very similar; each has an approximately square-planar metal atom $OO'$-bonded to acac and η$^3$-benzylically bonded to the CPh$_3$ ligand with Pd–C(α) 2.104(7), Pd–C(1) 2.158(7), Pd–C(2) 2.202 Å and Pt–C(α) 2.080 (19), Pt–C(1) 2.127(20), and Pt–C(2) 2.153(23) Å.

OXIDATIVE addition of chlorotriphenylmethane to the olefin-palladium(0) and -platinum(0) complexes (1a) and (1b) gave the rather insoluble and probably dimeric chloro-complexes (2) which were converted into the readily soluble and crystallisable pentane-2,4-dionato-(acac) complexes (3). As reported in our preliminary communication the properties and n.m.r. spectra of (3a) and (3b) led us to conclude that they were η$^3$-benzylic complexes which underwent a variety of fluxional processes in solution.[1] This is now confirmed by the single-crystal structure determinations on both (3a) and (3b) described here. The preceding paper described in detail the preparation of these complexes and discussed their fluxional behaviour.[2]



$$\begin{tikzcd} \underset{(1)}{[\mathrm{M_2(dba)_3(s)}]} + \mathrm{Ph_3CCl} \arrow[r] & \underset{(2)}{[\{\mathrm{M(CPh_3)Cl}\}_n]} \arrow[d, "\mathrm{Tl(acac)}"] \\ & \underset{(3)}{[\mathrm{M(CPh_3)(acac)}]} \end{tikzcd}$$

(a, M = Pd; b, M = Pt)

## EXPERIMENTAL

[Pd(CPh$_3$)(acac)] (3a).—A crystal of dimensions *ca.* 0.012 × 0.030 × 0.019 cm was selected for the determination from a batch [2] grown from benzene–light petroleum (b.p. 40—60 °C).

*Crystal data.* C$_{24}$H$_{22}$O$_2$Pd, $M$ = 448.8, Triclinic, $a$ = 23.84(1), $b$ = 24.91(2), $c$ = 15.113(6) Å, α = 63.53(2), β = 98.12(1), γ = 100.19(1)°, $U$ = 7 888 Å$^3$, $D_m$ = 1.56 g cm$^{-3}$, $Z$ = 16, $D_c$ = 1.511 g cm$^{-3}$, space group $F\bar{1}$ from systematic absences, Mo-$K_\alpha$ radiation, λ = 0.710 69 Å. The cell constants were determined from a least-squares fit to the setting angles of 76 reflections centred manually.

Three-dimensional $X$-ray data ($6.5 < 2\theta < 50°$) were collected with the crystal mounted along the $c$ axis using Mo-$K_\alpha$ radiation (graphite monochromator) and a Stoe STADI-2 diffractometer by the moving-crystal–stationary-counter method. Scans of variable width were measured with a background count at each extremity of the scan. 5 607 Independent reflections were collected with $I_{\mathrm{obs.}} \geqslant 3\sigma(I_{\mathrm{obs.}})$ and the structure was solved using Patterson and Fourier methods. Lorentz and polarisation corrections were applied, but no allowance was made for extinction or absorption since μ = 9.4 cm$^{-1}$. After processing, the Miller indices of the data were re-indexed to correspond to a primitive unit cell with $a$ = 14.99, $b$ = 13.18, $c$ = 11.33 Å, α = 101.08, β = 90.54, and γ = 115.48° obtained from Delaunay reduction of the original cell. The structure has refined using block-diagonal least squares to a final $R$ of 0.050, with anisotropic thermal parameters for the palladium atoms and isotropic thermal parameters for the remaining non-hydrogen atoms.

[Pt(CPh$_3$)(acac)] (3b).—A crystal of dimensions *ca.* 0.018 × 0.029 × 0.029 cm$^{-1}$ was selected for the determination from a batch grown from benzene–light petroleum (b.p. 40—60 °C).

*Crystal data.* C$_{24}$H$_{22}$O$_2$Pt, $M$ = 537.5, Triclinic, $a$ = 18.79(2), $b$ = 24.17(3), $c$ = 18.84(4), α = 92.54(2), β = 105.33(3), γ = 105.27(3), $U$ = 7 900.4 Å$^3$, $D_m$ = 1.80 g cm$^{-3}$, $Z$ = 16, $D_c$ = 1.807 g cm$^{-3}$, space group $F\bar{1}$ from systematic absences, Mo-$K_\alpha$ radiation, λ = 0.710 69 Å. The cell constants were determined from a least-squares fit to the setting angles of 61 reflections centred manually.

Three-dimensional $X$-ray data ($6.5 < 2\theta < 50°$) were collected with the crystal mounted along the $c$ axis using Mo-$K_\alpha$ radiation (graphite monochromator) and a Stoe STADI-2 diffractometer by the moving-crystal–stationary-counter method. Scans of variable width were measured with a background count at each extremity of the scan. 5 978 Independent reflections were collected with $I_{\mathrm{obs.}} \geqslant 3\sigma(I_{\mathrm{obs.}})$ and the structure was solved using Patterson and Fourier methods. Lorentz and polarisation corrections were applied, but no allowance was made for extinction or absorption (μ = 74.9 cm$^{-1}$); after processing, the Miller indices of the data were re-indexed to correspond to a primitive unit cell with $a$ = 14.942, $b$ = 11.410, $c$ = 17.146 Å, α = 120.78, β = 122.03, and γ = 90.13° obtained from Delaunay reduction of the original cell. The structure has refined using block-diagonal least squares to a final $R$ of 0.045, with anisotropic thermal parameters for the platinum atoms and isotropic thermal parameters for the remaining non-hydrogen atoms.

Atomic scattering factors were taken from ref. 3. Programs used were part of the Sheffield $X$-ray system and calculations were performed on the Sheffield University ICL 1906S and 1907 computers. Atomic co-ordinates are given for (3a) in Table 1 and for (3b) in Table 2; selected interatomic distances and angles as well as angles between some of the least-squares planes in the molecules are collected in Table 3. Tables of thermal parameters and observed and calculated structure factors as well as the equations of the least-squares planes are listed as Supplementary Publication No. SUP 22390 (143 pp.).†

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† For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

## RESULTS AND DISCUSSION

In both cases the crystals contain enantiomers of two different molecules per unit cell; the structures of four independent molecules were therefore determined. The bond lengths and bond angles, collected and compared in Table 3, show that all four molecules have the same structure and differ only to a minor degree. The Figure illustrates the general features of all these molecules, and shows that the approximately square-planar metal atom is bound to O(1) and O(2) of the acac ligand and is also allylically co-ordinated to the benzylic carbon atoms C(α), C(1), and C(2). The M(acac) unit is essentially planar [the angles between the planes M–O(1)–O(2) and O(1)–C(19)–C(21)–C(22)–O(2) average 1.8°] and the angles between the co-ordination plane of the metal and the allylic plane C(α)–C(1)–C(2) average 116.6° for the palladium complex (3a) and 118.1° for the platinum complex (3b). The former is a little larger than the typical value for $\eta^3$-allylic palladium complexes (*ca.* 112°).[4]

TABLE 1

Atomic fractional co-ordinates (× 10$^4$, × 10$^5$ for Pd) for [Pd($\eta^3$-CPh$_3$)(acac)] (3a) †

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd(A) | 43 005(4) | 70 330(4) | 19 150(4) |
| CA(00) | 4 285(4) | 8 393(5) | 12 11(5) |
| CA(01) | 5 129(4) | 8 197(5) | 797(5) |
| CA(02) | 6 143(5) | 9 005(5) | 1 171(6) |
| CA(03) | 6 894(6) | 8 679(7) | 938(7) |
| CA(04) | 6 669(6) | 7 520(7) | 329(7) |
| CA(05) | 5 711(6) | 6 738(7) | −46(7) |
| CA(06) | 4 905(5) | 7 045(6) | 154(6) |
| CA(07) | 4 471(5) | 9 486(5) | 2 079(6) |
| CA(08) | 4 061(5) | 10 188(6) | 1 780(6) |
| CA(09) | 4 235(6) | 11 229(7) | 2 567(7) |
| CA(10) | 4 820(6) | 11 577(7) | 3 673(8) |
| CA(11) | 5 232(6) | 10 883(7) | 3 975(8) |
| CA(12) | 5 055(6) | 9 839(7) | 3 189(8) |
| CA(13) | 3 343(4) | 7 917(5) | 382(5) |
| CA(14) | 2 441(5) | 7 609(6) | 890(6) |
| CA(15) | 1 566(6) | 7 334(7) | 174(7) |
| CA(16) | 1 600(6) | 7 340(7) | −1 060(7) |
| CA(17) | 2 487(5) | 7 608(6) | −1 507(6) |
| CA(18) | 3 370(5) | 7 904(5) | −857(6) |
| OA(1) | 4 453(4) | 5 618(4) | 2 284(4) |
| OA(2) | 3 467(3) | 7 065(4) | 3 346(4) |
| CA(19) | 4 064(5) | 5 134(6) | 3 147(6) |
| CA(20) | 4 276(7) | 4 129(8) | 3 280(8) |
| CA(21) | 3 468(5) | 5 422(6) | 3 944(7) |
| CA(22) | 3 197(5) | 6 314(6) | 3 997(6) |
| CA(23) | 2 534(6) | 6 445(7) | 4 950(7) |
| Pd(B) | 9 273(4) | 25 110(4) | 26 892(4) |
| CB(00) | 549(5) | 1 672(5) | 4 139(5) |
| CB(01) | 579(5) | 851(5) | 3 093(6) |
| CB(02) | 1 497(5) | 1 209(6) | 2 544(6) |
| CB(03) | 1 516(6) | 531(7) | 1 392(7) |
| CB(04) | 691(6) | −414(7) | 833(7) |
| CB(05) | −212(6) | −784(7) | 1 389(7) |
| CB(06) | −274(5) | −160(6) | 2 482(6) |
| CB(07) | −440(5) | 1 481(5) | 4 595(5) |
| CB(08) | −1 261(5) | 1 252(6) | 3 816(6) |
| CB(09) | −2 200(6) | 975(7) | 4 244(7) |
| CB(10) | −2 301(6) | 956(7) | 5 471(7) |
| CB(11) | −1 477(5) | 1 225(6) | 6 256(7) |
| CB(12) | −547(5) | 1 492(5) | 5 828(6) |
| CB(13) | 1 436(5) | 2 310(5) | 5 079(6) |
| CB(14) | 1 638(5) | 3 423(6) | 5 711(6) |
| CB(15) | 2 434(6) | 4 018(7) | 6 612(7) |
| CB(16) | 3 036(7) | 3 517(7) | 6 894(8) |
| CB(17) | 2 839(6) | 2 418(7) | 6 255(8) |
| CB(18) | 2 030(5) | 1 800(6) | 5 360(7) |
| OB(1) | 1 452(4) | 3 171(4) | 1 163(4) |
| OB(2) | 464(3) | 3 779(4) | 3 264(4) |
| CB(19) | 1 429(5) | 4 076(6) | 962(7) |
| CB(20) | 1 909(7) | 4 437(8) | −167(9) |
| CB(21) | 1 017(5) | 4 734(6) | 1 640(7) |
| CB(22) | 565(5) | 4 558(6) | 2 694(6) |
| CB(23) | 93(7) | 5 345(7) | 3 238(8) |

† See footnote to Table 3.

TABLE 2

Atomic fractional co-ordinates (× 10$^4$, × 10$^5$ for Pt) for [Pt($\eta^3$-CPh$_3$)(acac)] (3b) †

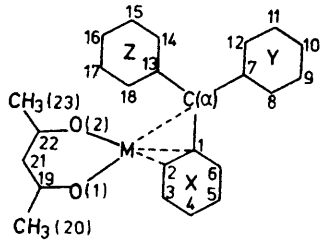
| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt(C) | 27 534(5) | 1 108(6) | 20 252(5) |
| CC(00) | 4 125(12) | 2 132(15) | 3 352(12) |
| CC(01) | 3 088(13) | 2 359(17) | 3 180(13) |
| CC(02) | 2 159(15) | 1 806(19) | 1 985(14) |
| CC(03) | 1 027(16) | 1 720(20) | 1 715(16) |
| CC(04) | 863(19) | 2 124(25) | 2 495(19) |
| CC(05) | 1 797(18) | 2 709(23) | 3 687(17) |
| CC(06) | 2 884(14) | 2 797(17) | 3 986(13) |
| CC(07) | 5 061(12) | 2 387(16) | 4 477(12) |
| CC(08) | 6 142(14) | 3 434(18) | 5 209(14) |
| CC(09) | 7 015(15) | 3 691(20) | 6 245(15) |
| CC(10) | 6 808(19) | 2 938(24) | 6 580(18) |
| CC(11) | 4 833(14) | 1 655(18) | 4 845(14) |
| CC(12) | 5 673(16) | 1 941(20) | 5 915(16) |
| CC(13) | 4 611(14) | 2 562(18) | 2 917(14) |
| CC(14) | 5 196(14) | 1 747(18) | 2 601(14) |
| CC(15) | 5 834(20) | 2 231(25) | 2 325(19) |
| CC(16) | 5 808(21) | 3 471(27) | 2 375(21) |
| CC(17) | 5 146(17) | 4 227(22) | 2 647(17) |
| CC(18) | 4 572(16) | 3 786(21) | 2 951(16) |
| OC(1) | 1 211(10) | −1 658(13) | 607(10) |
| OC(2) | 3 572(10) | −1 295(12) | 2 038(9) |
| CC(19) | 1 077(15) | −3 008(19) | 121(14) |
| CC(20) | −130(18) | −4 107(23) | −883(18) |
| CC(21) | 1 942(16) | −3 515(21) | 438(16) |
| CC(22) | 3 109(14) | −2 720(18) | 1 281(14) |
| CC(23) | 3 909(16) | −3 513(21) | 1 447(16) |
| Pt(D) | 83 947(5) | 51 637(6) | 24 540(5) |
| CD(00) | 8 837(12) | 7 402(16) | 3 243(12) |
| CD(01) | 9 699(13) | 7 202(16) | 4 075(13) |
| CD(02) | 10 224(14) | 6 263(18) | 3 701(14) |
| CD(03) | 10 924(17) | 5 781(22) | 4 376(17) |
| CD(04) | 11 061(16) | 6 152(21) | 5 309(16) |
| CD(05) | 10 528(16) | 7 127(20) | 5 731(16) |
| CD(06) | 9 833(14) | 7 632(18) | 5 128(14) |
| CD(07) | 8 049(13) | 8 139(16) | 3 509(13) |
| CD(08) | 7 487(15) | 7 575(19) | 3 720(15) |
| CD(09) | 6 816(17) | 8 351(21) | 4 048(17) |
| CD(10) | 6 752(16) | 9 603(21) | 4 085(16) |
| CD(11) | 7 344(16) | 10 086(20) | 3 793(15) |
| CD(12) | 7 972(14) | 9 380(18) | 3 536(14) |
| CD(13) | 9 085(13) | 7 776(17) | 2 658(13) |
| CD(14) | 8 206(15) | 7 284(20) | 1 527(15) |
| CD(15) | 8 419(16) | 7 604(21) | 941(16) |
| CD(16) | 9 487(20) | 8 429(25) | 1 495(19) |
| CD(17) | 10 371(19) | 8 855(24) | 2 569(19) |
| CD(18) | 10 213(16) | 8 537(21) | 3 151(16) |
| OD(1) | 8 277(11) | 3 022(14) | 1 820(11) |
| OD(2) | 6 678(10) | 4 394(13) | 1 150(10) |
| CD(19) | 7 335(16) | 1 884(21) | 940(16) |
| CD(20) | 7 542(21) | 388(27) | 565(21) |
| CD(21) | 6 271(16) | 1 893(20) | 283(16) |
| CD(22) | 6 010(14) | 3 059(18) | 402(14) |
| CD(23) | 4 773(21) | 2 848(27) | −375(21) |

† See footnote to Table 3.

A detailed comparison of the palladium and the platinum complexes is not possible due to the large estimated standard deviations (e.s.d.s) of the latter structure. However, it does appear that in general the Pt–C distances are shorter than the corresponding Pd–C

TABLE 3

Interatomic distances and bond angles for complexes (3a) and (3b) (estimated standard deviations in parentheses)



(a) Bond lengths (Å)

| | (3a) | | (3b) | |
|---|---|---|---|---|
| | Pd(A) † | Pd(B) † | Pt(C) † | Pt(D) † |
| M–C(α) | 2.105(6) | 2.102(7) | 2.088(18) | 2.073(19) |
| M–C(1) | 2.154(6) | 2.163(7) | 2.120(20) | 2.133(20) |
| M–C(2) | 2.200(7) | 2.204(7) | 2.148(23) | 2.158(22) |
| M–C(3) | 3.165(8) | 3.206(8) | 3.143(24) | 3.169(26) |
| M–C(6) | 3.132(7) | 3.149(7) | 3.081(21) | 3.143(22) |
| M–C(7) | 3.101(6) | 3.086(7) | 3.117(19) | 3.127(20) |
| M–C(13) | 2.934(7) | 2.897(7) | 2.993(21) | 2.934(21) |
| M–O(1) | 2.091(5) | 2.093(5) | 2.076(15) | 2.064(17) |
| M–O(2) | 2.061(5) | 2.071(5) | 2.021(15) | 2.061(15) |
| C(α)–C(1) | 1.461(9) | 1.459(9) | 1.466(27) | 1.460(28) |
| C(α)–C(7) | 1.492(9) | 1.507(9) | 1.526(26) | 1.576(28) |
| C(α)–C(13) | 1.502(9) | 1.509(10) | 1.507(28) | 1.469(28) |
| C(1)–C(2) | 1.442(10) | 1.439(10) | 1.477(31) | 1.416(30) |
| C(2)–C(3) | 1.436(11) | 1.441(11) | 1.486(33) | 1.452(34) |
| C(3)–C(4) | 1.362(12) | 1.356(12) | 1.334(38) | 1.318(36) |
| C(4)–C(5) | 1.440(12) | 1.425(12) | 1.463(40) | 1.477(35) |
| C(5)–C(6) | 1.377(11) | 1.377(11) | 1.405(34) | 1.398(33) |
| C(6)–C(1) | 1.430(10) | 1.433(10) | 1.412(29) | 1.501(30) |
| C–C bonds in ring Y (average) | 1.400(10) | 1.400(11) | 1.401(33) | 1.402(33) |
| C–C bonds in ring Z (average) | 1.399(12) | 1.397(12) | 1.407(38) | 1.382(37) |
| O(1)–C(19) | 1.278(9) | 1.271(10) | 1.272(27) | 1.296(30) |
| C(19)–C(21) | 1.389(11) | 1.391(11) | 1.372(34) | 1.382(35) |
| C(21)–C(22) | 1.392(11) | 1.388(11) | 1.389(33) | 1.331(33) |
| C(22)–C(2) | 1.276(9) | 1.271(9) | 1.299(26) | 1.264(27) |
| C(19)–C(20) | 1.523(13) | 1.528(13) | 1.508(36) | 1.585(41) |
| C(22)–C(23) | 1.510(11) | 1.533(12) | 1.496(33) | 1.519(39) |

(b) Bond angles (°)

| | (3a) | | (3b) | |
|---|---|---|---|---|
| | Pd(A) | Pd(B) | Pt(C) | Pt(D) |
| O(1)–M–O(2) | 91.5(2) | 91.2(2) | 90.1(6) | 89.5(6) |
| O(1)–M–C(2) | 98.1(2) | 100.1(2) | 97.4(7) | 99.1(8) |
| C(α)–M–C(2) | 69.8(3) | 69.5(3) | 71.1(8) | 70.3(8) |
| O(2)–M–C(α) | 100.4(2) | 99.0(2) | 100.9(7) | 100.7(7) |
| C(1)–C(α)–C(7) | 119.3(6) | 118.8(6) | 118.5(1.6) | 117.5(1.6) |
| C(1)–C(α)–C(13) | 120.0(6) | 119.5(6) | 120.0(1.7) | 120.0(1.7) |
| C(7)–C(α)–C(13) | 113.0(5) | 115.4(6) | 111.6(1.6) | 113.4(1.6) |
| C(α)–C(1)–C(2) | 116.3(6) | 115.8(6) | 113.5(1.8) | 115.7(1.8) |
| C(2)–C(1)–C(6) | 119.2(6) | 119.1(6) | 120.8(1.9) | 119.9(1.8) |
| C(α)–C(1)–C(6) | 123.6(6) | 124.2(6) | 124.7(1.8) | 122.8(1.8) |

(c) Angles (°) between planes

| | Pd(A) | Pd(B) | Pd(C) | Pd(D) |
|---|---|---|---|---|
| O(1)–C(19)–C(21)–C(22)–O(22) and M–O(1)–O(2) | 2.3 | 1.4 | 1.9 | 2.6 |
| C(α)–C(1)–C(2) and O(1)–C(19)–C(21)–C(22)–O(2) | 119.2 | 117.6 | 117.8 | 118.7 |
| C(α)–C(1)–C(2) and M–O(1)–O(2) | 116.9 | 116.3 | 117.1 | 119.2 |
| C(α)–C(1)–C(2) and ring Y | 71.8 | 56.4 | 73.6 | 59.2 |
| C(α)–C(1)–C(2) and ring Z | 61.7 | 64.1 | 62.2 | 67.5 |

TABLE 3 (*Continued*)

(d) Distances (Å) from plane C(α)–C(1)–C(2)

| | Pd(A) | Pd(B) | Pd(C) | Pd(D) |
|---|---|---|---|---|
| M | 1.65 | 1.66 | 1.63 | 1.61 |
| C(3) | 0.29 | 0.24 | 0.29 | 0.26 |
| C(4) | 0.52 | 0.46 | 0.53 | 0.53 |
| C(5) | 0.48 | 0.43 | 0.49 | 0.55 |
| C(6) | 0.23 | 0.23 | 0.26 | 0.32 |
| C(7) | 0.26 | 0.30 | 0.26 | 0.32 |
| C(13) | −0.91 | −0.88 | −0.98 | −0.96 |

† A and B refer to the two independent molecules of (3a), and C and D to the two independent molecules of (3b), found in the unit cells of the two crystals.

bond lengths.* This may be due to a stronger binding of the Pt to the organic ligand.

In every case the metal is only bonded to C(α), C(1), and C(2) and all the other M–C distances are greater than 2.9 Å. The palladium is significantly closer to C(α) than to C(1) (0.06 Å, 8σ) or to C(2) (0.098 Å, 14σ); a similar trend is also discernible for the platinum complex (3b). The $\eta^3$-benzylic bonding to C(α), C(1), and C(2) implies that an electron localisation as shown in (i) is to be expected. This is indeed so; C(2)–C(3), C(4)–C(5), and C(1)–C(6) are significantly longer (0.055—0.080 Å, 5—7σ) than C(3)–C(4) and C(5)–C(6). However, C(α)–C(1) (1.460 Å) and C(1)–C(2) (1.441 Å) are slightly longer than the normal values for π-allylic C–C bonds [1.357—1.395(15) Å].[4] By comparison, C(α)–C(7) and C(α)–C(13) are 0.043 Å (4σ) longer than C(α)–C(1) and are in the range expected for C–C single bonds between two $sp^2$ carbons.[6]

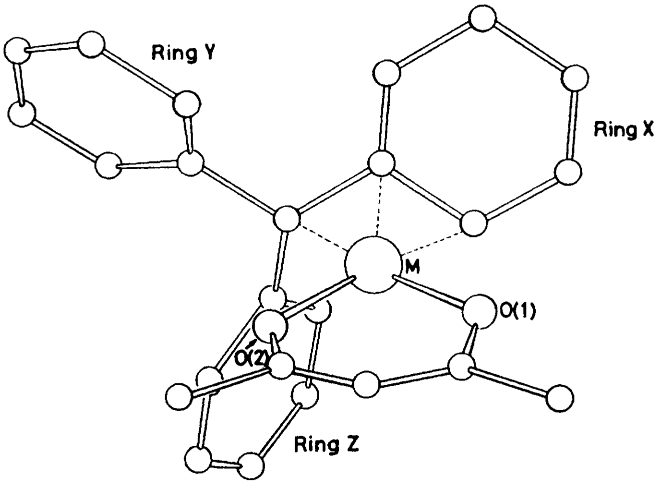
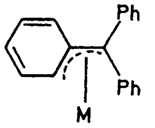


Figure. View of the structure of complexes (3) projected on to the $\eta^3$-benzyl plane (hydrogen atoms are omitted



( i )

The co-ordination about the metal is a very distorted square plane with the $\eta^3$-benzylic moiety acting as a

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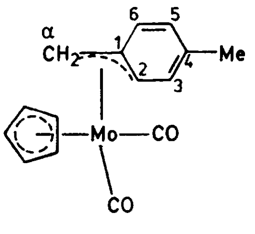
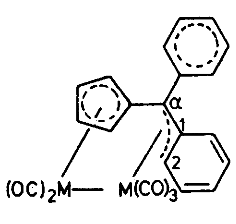
* The covalent radii of $Pd^{II}$ and $Pt^{II}$ are normally regarded as virtually identical; for example, Pd-Cl is 2.316(2) Å in $K_2[PdCl_4]$ and Pt-Cl is 2.318(2) Å in $K_2[PtCl_4]$.[5]

rather small bidentate ligand [average angle C(α)–M–C(2) 69.7 (Pd) and 70.7° (Pt)]. This is compensated by opening out both the O–M–C angles to *ca.* 100°.

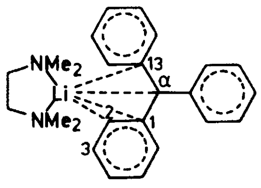
Further distortions are observed in the angles about C(α) and C(1) in the palladium complex (3a). The angle C(7)–C(α)–C(13) is smaller (average 114.2°) than the other two [C(1)–C(α)–C(7) and C(1)–C(α)–C(13), average 117.6°] which are not significantly different from each other. More interestingly, the effect of co-ordination to Pd on the angle at C(1) is to decrease C(α)–C(1)–C(2) to an average of 116.1° for Pd. This is compensated by an increase in the other external angle C(α)–C(1)–C(6). The decrease in the benzylic C–C–C angle from 120° is rather unexpected; however, although C–C–C angles of 119.8° for $[\{Pd(\eta\text{-}C_3H_5)Cl\}_2]$ [7] and 118.5° for $[\{Pd(\eta^3\text{-}1,1,3,3\text{-}Me_4C_3H)Cl\}_2]$ [8] have been noted, a smaller angle [112.4(1.6)°] was found for the 2-substituted complex $[\{Pd(2\text{-}MeC_3H_4)Cl\}_2]$.[9] The e.s.d.s of the angles at carbon of the platinum complex are so large as to make any direct comparison doubtful; however, the pattern is strikingly similar to that shown by the palladium complex.



(4)



(5) M = Fe
(6) M = Ru



(7)

View of the structure of complexes (3) projected on to the η-benzyl plane (hydrogen atoms are omitted)

No other structural studies have been carried out on triphenylmethyl complexes of other transition metals but it is instructive to briefly compare our structures with those that have been reported for three $\eta^3$-benzylic complexes (4),[10] (5),[11] and (6) [12] and also with that of the lithium salt of the triphenylmethyl anion (7).[13] Since $Mo^{II}$ is expected to be larger than $Pd^{II}$ the lengths of the Mo–C bonds in (4) [10] should be larger than the corresponding Pd–C bonds. This is indeed so but, whereas the Mo–C(α) bond corresponding to Pd–C(α) is 0.166 Å longer, the Mo–C(1) and Mo–C(2) bonds are 0.205 and 0.278 Å longer than Pd–C(1) and Pd–C(2) respectively. Clearly, therefore, the bonding is much more localised at the exocyclic carbon in the molybdenum complex (4) than it is in the complexes (3a) or (3b) which are therefore more symmetrically $\eta^3$-bonded. The other features we see in complexes (3a) and (3b) are also present in (4), for example the alternation of C–C bond lengths in the benzene ring.

The iron and ruthenium complexes (5) and (6) are both binuclear and the ligand will therefore be subject to greater constraints than in our complexes (3) or in the molybdenum complex (4). However, it is interesting to note that the Pd–C bonds in (3a) are more similar in length to the corresponding Fe–C bonds in the *iron* complex (5) [Fe–C(α) 2.11, Fe–C(1) 2.16, and Fe–C(2) 2.22 Å] than the Ru–C bonds in (6) (2.24, 2.32, and 2.34 Å respectively).[11] Since the covalent radius of ruthenium may be expected to be only slightly larger than that of palladium and to be substantially larger than that of iron, these data suggest that the metal–benzylic bonding is substantially stronger in (3a) and (3b) than in (5) or (6).

The structure of (7) shows the presence of a contact ion pair, but although the lithium is closest to C(α) [2.227(8) Å] it is also close to C(1) [2.488(10) Å] and to C(13) [2.511(13) Å] and is rather further from C(2) [2.541(9) Å], using the numbering of complex (3).[12] Brooks and Stucky [12] comment that ' It is not possible to explain [this] geometry . . . by two centre σ- and/or ionic interactions alone ' and they postulate that some type of delocalised bonding also occurs between the metal and carbons α, 1, 13, and 2 of the $CPh_3$ ligand. This bonding is different to the allylic bonding found in the complexes (3)—(6) as is shown by the absence in (7) of the marked alternation of C–C bond lengths in one phenyl group which is such a feature of the other structures.

Brooks and Stucky also note, as evidence for the $sp^2$ character of C(α), that this carbon is only 0.12 Å out of the plane defined by C(1)–C(7)–C(13) [using the numbering for (3)]. In our complexes this distance is much larger [0.22, 0.24 Å for (3a) and 0.27, 0.27 Å for (3b)]. The distortion away from $sp^2$ geometry at C(α) in (3a) and (3b) is also shown by the rather larger angles of twist found for the phenyls (X, Y, and Z) with respect to the plane C(1)–C(7)–C(13) [average: 23, 39, and 51° for (3a) and 24, 39, and 52° for (3b)] by comparison to those found for (7) (19.7, 44.8, and 30.6°). This shows there to be rather more localisation of the π-electron density in (3) than in (7) and less $sp^2$ character at C(α).

It may also be noted that the first triphenylmethyl transition-metal complexes were reported by Wilke and Schott [13] who obtained $[Ni(CPh_3)_2]$, by reaction of ' $C_2Ph_6$ ' [14] with $[Ni^0(\text{cyclo-octa-1,5-diene})_2]$, and $[Ni(CPh_3)Cl]$ from $Ph_3CCl$ and $[Ni^0(\text{cyclododeca-1,5,9-triene})]$. No structural studies were carried out but these complexes were regarded as containing σ-$CPh_3$ ligands. This was later questioned by King [15] who suggested an $\eta^3$-bonding to the $CPh_3$ ligand of the type we have found in (3). Although the complexes are not totally comparable, the structures we find for the palladium and platinum complexes (3a) and (3b) appear to make it certain that the bonding is similar in the nickel complexes.

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