Structure and Bonding in (Dimethyl acetylenedicarboxylate)bis(triphenylphosphine)palladium

By **John A. McGinnety**, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520, U.S.A.

The crystal and molecular structure of a disubstituted acetylene complex of palladium, $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$, has been determined from three-dimensional *X*-ray diffraction data. The complex crystallises in space group $P2_1/c$, C^5_{2h}, of the monoclinic system, with four molecules in a unit cell of dimensions a = 11·816(3), b = 15·331(4), c = 21·891(6) Å, β = 113·22(1)°. No crystallographic symmetry is imposed upon the molecules and there is one molecule in the asymmetric unit. The structural parameters were refined by least squares techniques, the *R*-factor on *F* converging to 5·2% for the 3365 reflections, collected using a four-circle diffractometer, for which $F > 0$. Co-ordination around palladium is approximately planar: the dihedral angle between the plane defined by the palladium and two phosphorus atoms and that defined by the palladium and the two acetylenic carbon atoms is 9·7(4)°. The acetylenic carbon–carbon separation in the complex is 1·28(1) Å, longer than expected for the free acetylene. Each substituent upon acetylene is planar to a reasonable approximation and is bent away from the metal by about 35° from the C≡C bond axis. The acetylenic carbon atoms are separated from the metal by 2·074(6) and 2·051(6) Å and the metal–phosphorus bond lengths are 2·321(2) and 2·330(2) Å. This slight asymmetry in the bond lengths to palladium is tentatively ascribed to the electronic effects of the differing orientations of the substituents upon acetylene.

IN their interaction with metals to form complexes, acetylenes can be classed with a number of other types of ligand in that the two central atoms of the ligand (in this case the two acetylenic carbon atoms) are essentially equidistant from the metal in the complex. With this in mind, two limiting structures can be envisioned for acetylene complexes of the general formula $M(RCCR)L_2$, where M is a d^{10} metal such as Ni^0, Pd^0, or Pt^0 and L is a two electron donor such as triphenylphosphine: the MLL plane defined by the metal atom and the donating atoms of the ligands L may be either coplanar with or perpendicular to the MCC plane defined by the metal atom and the two acetylenic carbon atoms. The structures of two such complexes, specifically $[Ni(PhCCPh)(Bu^tNC)_2]$ and $[Pt(PhCCPh)(PPh_3)_2]$, have been determined by *X*-ray diffraction experiments.[1,2] In the former compound, the angle between the two planes is 3°, which corresponds quite well to the limiting structure of planar geometry around the metal. In the latter compound, the angle between the two planes is 14°, intermediate between the two extreme geometries; angles varying up to 15° have been observed in other compounds where, instead of an acetylene, there is allene,[3] carbon disulphide,[4] dioxygen,[5] or an olefin.[6]

In order to explore further the stereochemistry of this type of complex, the crystal and molecular structure of (dimethyl acetylenedicarboxylate)bis(triphenylphosphine)palladium has been determined. The substituents upon the acetylene are planar, unsaturated, and electron withdrawing and thus the degree of interaction between acetylene and metal may depend upon the orientation of the substituents relative to the MCC plane. Such an effect has been postulated to be important in a diphenylcyclopropaneplatinum complex[7] and this relatively unexplored aspect of stereochemistry will be considered for complexes formed by acetylenes and similar ligands.

EXPERIMENTAL

Collection and Reduction of X-*ray Diffraction Data*.—The crystals were kindly supplied by Professor P. M. Maitlis. Optical examination and preliminary *X*-ray photography showed that the crystals belonged to the monoclinic system and the conditions for reflection ($h0l$ zone, $l = 2n$; $0k0$ axis, $k = 2n$) were consistent with the space group $C^5_{2h} - P2_1/c$. The cell constants, obtained by least-squares refinement using the setting angles of 12 reflections carefully centred on a Picker four-circle automatic *X*-ray diffractometer with Mo-K_{α_1} radiation (λ = 0·70930 Å), are (at 20°): a = 11·816(3),[†] b = 15·331(4), c = 21·891(6) Å; β = 113·22(1)°. For four formula weights of the acetylene complex in the unit cell, the calculated density is 1·41 g cm^{-3}; the observed density (by flotation) is 1·40 g cm^{-3}. No symmetry is crystallographically imposed upon the molecules.

Two data sets were collected, both using a Picker four-circle automatic diffractometer in $\omega - 2\theta$ scan mode with crystal monochromated Mo-K_α radiation. During the course of collection of the first data set, there was considerable decomposition of the crystal, as evidenced by decreases in the intensities of three standard reflections; the magnitude of these decreases were different for each of the three reflections and varied between 35 and 50%. This situation was clearly unsatisfactory and when the course of refinement (described below) progressed badly, a second *X*-ray intensity data set was measured; the following

---

[†] The numbers in parentheses here and elsewhere in this paper are estimated standard deviations in units of the last digit.

[1] R. S. Dickson and J. A. Ibers, *J. Organometallic Chem.*, 1972, **36**, 191.

[2] J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometallic Chem.*, 1967, **7**, P9.

[3] M. Kadonaga, N. Yasuoka, and N. Kasai, *Chem. Comm.*, 1971, 1597.

[4] T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 296; R. Mason and A. I. M. Rae, *J. Chem. Soc.* (*A*), 1970, 1767.

[5] T. Kashiwagi, N. Yasuoka, N. Kasai, and M. Kakudo, *Chem. Comm.*, 1969, 743; P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Canad. J. Chem.*, 1971, **49**, 3772.

[6] (*a*) V. W. Dreissig and H. Dietrich, *Acta Cryst.*, 1968, **B24**, 108; (*b*) P.-T. Cheng, C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *ibid.*, 1971, **B27**, 1904; (*c*) P.-T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, 1971, **10**, 2210; (*d*) G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani, and G. Bandoli, *J. Chem. Soc.* (*A*), 1970, 1313; (*e*) J. N. Francis, A. McAdam, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 131; (*f*) A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 149; (*g*) L. J. Guggenberger, *Inorg. Chem.*, 1973, **12**, 499.

[7] J. A. McGinnety, *J. Organometallic Chem.*, 1973, **59**, 429.

description applies to the second set. The crystal was bounded by the faces $\bar{1}00$, $00\bar{1}$, $10\bar{2}$, 100, 108, $0\bar{1}0$, and $11\bar{1}$; the lengths of the normals of these faces to a convenient origin are 0·00, 0·56, 0·61, 0·39, 0·00, 0·00, and 0·85 mm respectively. The crystal was initially aligned about the *b* axis of the cell and the crystal was mis-set before data collection. A symmetric scan of 1·4° in 2θ was used with a scan rate of 2° min^{-1}. Stationary-crystal–stationary-counter background counts of 4 s were measured at each end of the scan. The intensities of the symmetry-equivalent reflections $hk\overset{\pm}{l}$, $h\bar{k}\overset{\pm}{l}$, and hkl were recorded out to a 2θ value (for Mo-K_α radiation) of 40°. The intensities of three standard reflections were measured at intervals throughout data collection and only small variations (<10%) in their intensities were observed.

TABLE 1

Positional and thermal parameters for the non-group atoms in $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$

Atom	x	y	z	B_{iso}/Å^2 or β_{11}*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0·01047(4)	0·07612(3)	0·21579(2)	0·00422(6)	0·00300(3)	0·00173(2)	0·00012(3)	0·00115(2)	−0·00002(1)
P(1)	−0·19622(16)	0·08567(10)	0·19800(8)	0·00434(18)	0·00304(9)	0·00199(5)	0·00001(10)	0·00110(8)	−0·00025(5)
P(2)	0·12150(16)	0·05609(10)	0·32940(8)	0·00458(18)	0·00263(8)	0·00193(5)	−0·00017(9)	0·00114(8)	−0·00005(5)
O(1)	0·2880(4)	0·1664(3)	0·1781(3)	0·0055(5)	0·0058(3)	0·0045(2)	0·0002(3)	0·0029(3)	0·0004(2)
O(2)	0·3265(5)	0·0234(3)	0·1852(3)	0·0078(6)	0·0055(3)	0·0046(2)	0·0019(3)	0·0029(3)	−0·0006(2)
O(3)	−0·1574(5)	0·0203(3)	0·0399(2)	0·0105(6)	0·0048(3)	0·0018(1)	−0·0013(3)	0·0012(2)	−0·0002(1)
O(4)	−0·0466(6)	0·1182(4)	0·0125(3)	0·0156(9)	0·0117(5)	0·0027(2)	−0·0059(5)	0·0018(3)	−0·0015(2)
C(1)	0·1280(7)	0·0772(4)	0·1661(4)	0·0058(9)	0·0035(4)	0·0030(2)	0·0003(4)	0·0023(4)	−0·0001(2)
C(2)	0·0166(7)	0·0741(4)	0·1235(3)	0·0074(10)	0·0034(3)	0·0024(2)	0·0003(4)	0·0023(4)	0·0004(2)
C(3)	0·2559(7)	0·0834(5)	0·1767(3)	3·6(1)					
C(4)	−0·0617(7)	0·0741(4)	0·0535(4)	3·7(1)					
C(5)	0·4146(11)	0·1845(7)	0·1884(5)	6·5(2)					
C(6)	−0·2436(10)	0·0178(6)	−0·0274(5)	5·9(2)					
H(1)	0·418(8)	0·242(5)	0·188(4)	7·0 †					
H(2)	0·466(8)	0·164(5)	0·229(4)	7·0 †					
H(3)	0·429(7)	0·162(5)	0·160(4)	7·0 †					
H(4)	−0·199(7)	0·012(4)	−0·053(3)	7·0 †					
H(5)	−0·287(8)	−0·035(5)	−0·029(4)	7·0 †					
H(6)	−0·302(8)	0·069(5)	−0·036(4)	7·0 †					

* The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hk + 2\beta_{23}kl)]$. † This parameter was not varied in the refinement.

TABLE 2

Group * parameters † in $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$

Group	x_c	y_c	z_c	δ		η
1A	−0·2398(3)	0·2007(2)	0·3101(2)	0·255(4)	2·549(2)	1·506(4)
1B	−0·3554(3)	0·1842(2)	0·0607(1)	−0·950(3)	2·940(3)	−2·342(3)
1C	−0·3432(3)	−0·0944(2)	0·1823(1)	−2·162(3)	2·341(3)	0·102(3)
2A	0·1551(3)	0·2102(2)	0·4353(1)	1·001(3)	2·695(2)	0·845(3)
2B	−0·0023(3)	−0·1051(2)	0·3751(1)	2·598(7)	2·040(2)	1·591(6)
2C	0·4035(3)	−0·0004(2)	0·3654(1)	−0·183(3)	2·779(3)	−0·200(3)

* The groups are all phenyl rings and each set of six parameters apply to both the six carbon atoms and the five hydrogen atoms of that ring. † The parameters have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 773.

The data were corrected for background and the changes in the standard reflections. The linear absorption coefficient is 5·60 cm^{-1} and corrections were applied,[8] the transmission coefficients ranging between 0·75 and 0·85. The equivalent forms were averaged and the *R*-factor of averaging ($R_{av} = 100\sum_n|I_m - I_i|/nI_m$, where I_m and I_i are the mean and individual intensities and *n* is the number of forms collected for that reflection) was 4·3% for those 2546 reflections classed as observed and measured more than once. The independent reflections were corrected for Lorentz-polarisation effects. Individual standard deviations, $\sigma(F^2)$, of the corrected intensities were calculated both from counting statistics and from the range of equivalent forms; the larger of these two estimates was assigned to the reflection. A total of 8687 reflections were measured and processed. There were a total of 3413 independent reflections, of which 2624 could be classed as observed (using the criterion that, to be classed as observed, the net intensity of at least one form be greater than three times the estimated standard deviation, calculated from counting statistics, of the total background counts).

There was no obvious reason why the first crystal underwent such extensive decomposition whilst the second crystal did not. The room temperatures were very similar during the two experiments and no simple explanation seems possible. The second data set was collected at a faster rate, but the crystal proved so stable that it was possible to examine symmetry-equivalent reflections of crystal and the total exposure to *X*-radiation was actually greater in the second case.

Solution and Refinement of the Structure.—Initial values of the atomic co-ordinates of the palladium atom were obtained from a three-dimensional Patterson function.[8] Successive applications of least-squares and difference Fourier calculations yielded the co-ordinates of all non-hydrogen atoms, the carbon atoms of the phenyl rings being refined as groups with one thermal parameter.

Anisotropic thermal parameters were used to describe the palladium and two phosphorus atoms and isotropic thermal

---

[8] Calculations were performed on an IBM 370/155 computer and the programs used included modified versions of Zalkin's FORDAP, Busing, Martin, and Levy's ORFLS (with the Doedens and Ibers subroutines for group refinements), and ORFFE, Johnson's ORTEP, and Coppens and Hamilton's DATTAP.

parameters were used for all other atoms. The scattering factors were calculated using analytical approximations for neutral atoms[9] and the effects of anomalous dispersion[10] were included in F_c. The function minimised in refinement was $\Sigma\omega||F_o| - |F_c||^2$, where $\omega = 4F_o^2/\sigma^2(F_o^2)$. Using the first data set, the R-factor (on F) converged to 10·3% and the thermal parameters varied in magnitude to an unreasonable degree. This first data set was suspect because there was extensive crystal decomposition during the collection and this unsatisfactory refinement showed that it must be rejected. Using the second data set, refinement was continued and, after a further three cycles, the R-factor was 6·5% for the 2624 independent reflections classed as observed. Varying an extinction parameter[11] and individual thermal parameters for carbon atoms in the phenyl groups and including contributions from the phenyl hydrogen atoms (as groups of idealised symmetry with a C–H bond length of 0·95 Å) led to an R-factor of 4·7%. A difference Fourier revealed amongst the 25 largest peaks, six that could be realistically considered to be the methyl hydrogen atoms. The orientation of idealised tetrahedral methyl atom arrays (with C–H bond lengths of 0·95 Å[12]) were varied to obtain best fits with the observed positions for the two groups and contributions from these idealised positions were included. The R-factor for the calculation was 4·4% and in the following least-squares cycle (in which these hydrogen atom positions were not varied), there were some appreciable parameter changes, particularly amongst the atoms of the CO_2Me groups; the largest shift was some four times the estimated standard deviation (e.s.d.) in that parameter calculated from the inverse matrix, demonstrating once again that the scattering from all electron density must be included before the e.s.d.'s are valid. A further cycle of refinement in which the positional parameters of the methyl hydrogen atoms were permitted to vary led to a final R-factor of 4·3% for the 2624 'observed' reflections. The weighted R-factor, $R_\omega = [\Sigma\omega(F_o - F_c)^2/\Sigma\omega F_o^2]^{\frac{1}{2}}$, was 6·2%. Since there is no valid reason to exclude any reflections with positive net count from the least-squares refinement, a further two cycles of refinement were performed using the 3365 measured reflections with $F^2 > 0$. The final values of the R-factor and weighted R-factor were 5·2 and 6·3% respectively and the error in an observation of unit weight was 2·1. In the last two cycles of refinement, the parameters changed by up to 70% of their final estimated standard deviations; the final estimated standard deviations were about 80% of the values obtained using only the 'observed' reflections, showing that the precision of the experiment was improved by avoiding the arbitrary exclusion of part of the data set. A final difference Fourier showed no peaks higher than 0·4 e$Å^{-3}$.

The final values of the positional and thermal parameters for the non-group atoms and their standard deviations calculated from the inverse matrix are given in Table 1. The phenyl ring atoms were refined as groups and the parameters are given in Table 2. Each carbon atom of these rings was described by an isotropic thermal parameter, individually refined, and Table 3 lists these thermal parameters and the fractional co-ordinates of the carbon atoms derived from the group parameters. Each hydrogen atom in a phenyl group was assigned an isotropic thermal parameter 0·2 $Å^2$ larger than that of the carbon atom to which it is bound. The root-mean-square amplitudes of vibration for those atoms refined with anisotropic thermal parameters are given in Table 4. Observed and calculated structure factors are listed in Supplementary Publication SUP 20961 (5 pp.).*

TABLE 3

Thermal parameters and derived fractional co-ordinates of phenyl group carbon atoms in $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$

Ring	Atom	$B_{iso}/Å^2$	x	y	z
1A	C(1)	3·3(1)	−0·2298	0·1505	0·2599
	C(2)	4·2(1)	−0·2580	0·2384	0·2495
	C(3)	4·2(1)	−0·2116	0·1128	0·3205
	C(4)	5·5(2)	−0·2680	0·2886	0·2997
	C(5)	5·5(2)	−0·2216	0·1630	0·3708
	C(6)	5·9(2)	−0·2498	0·2509	0·3604
1B	C(1)	3·0(1)	−0·2888	0·1404	0·1193
	C(2)	4·0(1)	−0·2341	0·2069	0·0978
	C(3)	4·3(2)	−0·4102	0·1177	0·0822
	C(4)	4·8(2)	−0·3006	0·2506	0·0392
	C(5)	6·1(2)	−0·4768	0·1615	0·0236
	C(6)	5·7(2)	−0·4220	0·2279	0·0020
1C	C(1)	2·6(1)	−0·2801	−0·0161	0·1913
	C(2)	3·2(1)	−0·2478	−0·0857	0·1610
	C(3)	3·3(1)	−0·3755	−0·0249	0·2125
	C(4)	4·0(1)	−0·3109	−0·1639	0·1521
	C(5)	4·2(1)	−0·4385	−0·1032	0·2036
	C(6)	4·5(2)	−0·4063	−0·1727	0·1733
2A	C(1)	2·7(1)	0·1441	0·1440	0·3903
	C(2)	3·9(1)	0·0657	0·2151	0·3713
	C(3)	4·0(1)	0·2335	0·1390	0·4543
	C(4)	4·5(2)	0·0767	0·2814	0·4163
	C(5)	4·7(2)	0·2445	0·2052	0·4993
	C(6)	4·4(2)	0·1661	0·2764	0·4803
2B	C(1)	2·7(1)	0·0544	−0·0352	0·3586
	C(2)	3·3(1)	0·0002	−0·1005	0·3125
	C(3)	4·2(1)	0·0519	−0·0399	0·4212
	C(4)	4·6(2)	−0·0564	−0·1703	0·3291
	C(5)	4·8(2)	−0·0048	−0·1098	0·4378
	C(6)	5·0(2)	−0·0589	−0·1750	0·3917
2C	C(1)	2·8(1)	0·2822	0·0219	0·3513
	C(2)	4·4(2)	0·3616	0·0827	0·3429
	C(3)	5·4(2)	0·3241	−0·0612	0·3738
	C(4)	5·3(2)	0·4829	0·0603	0·3570
	C(5)	7·5(2)	0·4454	−0·0835	0·3879
	C(6)	6·2(2)	0·5248	−0·0228	0·3795

TABLE 4

Root-mean-square amplitudes of vibration/Å along principal axes for $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$

Pd	0·156(1)	0·188(1)	0·191(1)
P(1)	0·160(3)	0·184(3)	0·210(2)
P(2)	0·163(3)	0·178(3)	0·201(3)
O(1)	0·159(9)	0·260(7)	0·308(6)
O(2)	0·174(9)	0·269(7)	0·317(6)
O(3)	0·190(7)	0·228(6)	0·274(6)
O(4)	0·200(8)	0·256(9)	0·437(8)
C(1)	0·165(13)	0·207(10)	0·249(10)
C(2)	0·181(11)	0·197(11)	0·233(12)

DISCUSSION

Description of the Structure.—The crystal structure consists of the packing of the monomeric molecular units $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$; there are no exceptionally short intermolecular contacts. An overall view of the

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index Issue. Items less than 10 pp. are sent as full-size copies.

[9] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[11] W. H. Zachariasen, *Acta Cryst.*, 1968, **A24**, 212.

[12] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

molecule is given in Figure 1; the phenyl ring hydrogen atoms have been omitted. Each triphenylphosphine ligand has adopted the customary propellor-like conformation of phenyl rings. Figure 2 shows the co-ordination sphere around palladium and gives a more detailed view of the co-ordinated acetylene moiety; the view-point for Figure 2 is normal to the Pd,C(1),C(2) plane and directly above the palladium atom. An important feature of the structure is the C(1)–C(2) bond length of 1·279(11) Å; this is intermediate between lengths typical of unco-ordinated acetylenes and those of unco-ordinated olefins and can be compared with the values of 1·28(2), 1·32(9), and 1·32(4) Å observed in other acetylene complexes.[1,2,13]

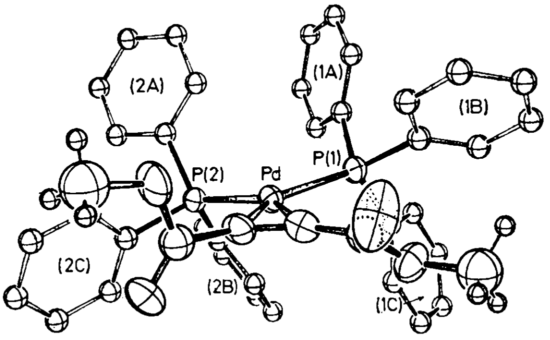

FIGURE 1 General view of a molecule of $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$. The atoms are represented by 50% probability ellipsoids, except the phenyl ring carbon atoms and the methyl group hydrogen atoms which are described here by artificially low thermal parameters for the purpose of clarity. The atoms and bond obscured by O(4) are indicated by broken lines; this is not done for other obscurations. The phenyl ring nomenclature is specified in this Figure

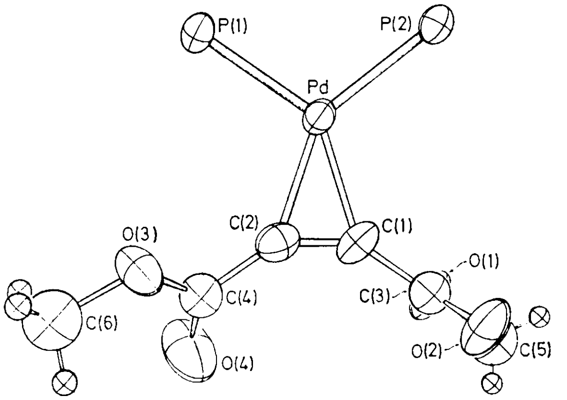

FIGURE 2 A molecule of $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$ from a view-point normal to the Pd,C(1),C(2) plane. The atoms of the phenyl rings are omitted. The other atoms are represented by 50% probability ellipsoids, except the methyl group hydrogen atoms which are described here by artificially low thermal parameters. The atom nomenclature (except for the methyl group hydrogen atoms) is specified in this Figure

The dihedral angle between the planes Pd,P(1),P(2) and Pd,C(1),C(2) is 9·7(4)°; an alternative description of this distortion from coplanarity is given by the displacements of C(1),C(2) from the Pd,P(1),P(2) plane, which are 0·031(6) and 0·228(6) Å respectively (see Figure 1). C(3) and C(4) are both displaced from the Pd,C(1),C(2) plane by 0·05(2) Å. The substituents upon the acetylene are each bent away from the metal atom, the carboxylic carbon atoms being *ca.* 35° away from collinearity with the acetylenic carbon atoms. There is an interesting difference between the orientations of the planes through the CO_2Me substituents, relative to the Pd,C(1),C(2) plane. The plane of the substituent on C(1) is nearly normal to the Pd,C(1),C(2) plane, whereas the plane of the substituent on C(2) is not; the two dihedral angles are 89·5(3) and 41·6(3)° respectively. This difference is clearly shown in Figure 2. The substituent groups are planar to a good approximation: carbon atoms C(1) and C(5) are displaced by 0·05(3) and 0·05(2) Å from the O(1),C(3),O(2) plane and carbon atoms C(2) and C(6) are displaced by 0·05(3) and 0·01(2) Å from the O(3),C(4),O(4) plane.

The P(1)–Pd–P(2) angle is 107·43(6)° and the C(1)–Pd–C(2) angle is 36·1(3)°; neither of these is unusual. It is convenient to make comparisons between the two halves of the molecule defined by a plane perpendicular to the Pd,C(1),C(2) plane and which passes through Pd and the midpoint of the C(1),C(2) vector. Table 5 lists selected bond lengths observed in this molecule and gives the difference between the lengths in the two halves of the molecule, along with the estimated standard deviation of the difference. Selected bond angles (and the differences between pairs of bond angles) are given in Table 6. It can be seen that few of the differences in either bond lengths or angles are statistically significant. The Pd–P bond lengths observed in this compound can be considered in terms of all Pd–P bond lengths that have been determined by *X*-ray diffraction.[14] Eight

TABLE 5

Comparison of bond lengths/Å in $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$

Bond length 1		Bond length 2		Difference (length 1 – length 2)
Pd–P(1)	2·321(2)	Pd–P(2)	2·330(2)	–0·009(3)
Pd–C(1)	2·074(6)	Pd–C(2)	2·051(6)	0·023(9)
C(1)–C(3)	1·440(11)	C(2)–C(4)	1·444(11)	–0·004(16)
C(3)–O(1)	1·325(8)	C(4)–O(3)	1·335(9)	–0·010(12)
C(3)–O(2)	1·206(8)	C(4)–O(4)	1·193(7)	0·012(11)
O(2)–C(5)	1·449(12)	O(4)–C(6)	1·424(11)	0·035(17)

TABLE 6

Comparison of bond angles (°) in $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$

Bond angle 1		Bond angle 2		Difference (angle 1 – angle 2)
P(2)–Pd–C(1)	110·4(2)	P(1)–Pd–C(2)	106·2(2)	4·2(3)
Pd–C(1)–C(2)	71·0(4)	Pd–C(2)–C(1)	72·9(4)	–2·0(8)
Pd–C(1)–C(3)	142·6(6)	Pd–C(2)–C(4)	142·1(6)	0·5(9)
C(2)–C(1)–C(3)	146·4(7)	C(1)–C(2)–C(4)	144·9(7)	1·4(12)
O(1)–C(3)–O(2)	123·8(7)	O(3)–C(4)–O(4)	123·2(7)	0·5(10)
C(3)–O(1)–C(5)	117·7(6)	C(4)–O(3)–C(6)	116·4(6)	0·4(7)
C(1)–C(3)–O(1)	109·9(6)	C(2)–C(4)–O(3)	111·6(6)	–1·7(8)
C(1)–C(3)–O(2)	126·3(7)	C(2)–C(4)–O(4)	125·1(7)	1·2(10)

---

[13] B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276.

[14] The correct statistical methods for comparisons of this kind have been collected together and applied to the bonds formed between all Group VIII metals and phosphorus, sulphur, and chlorine; J. A. McGinnety, to be submitted for publication.

compounds have been reported[15] with a total of 16 crystallographically independent Pd–P bond lengths. The mean bond length is 2·291 Å and the standard deviation in the sample is 0·033 Å. Thus the lengths observed in $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$ are somewhat longer than the mean, but not exceptionally so. The lengths of the bonds from phosphorus to the phenyl ring C(1) atoms are in the usual range and their average is 1·84 Å. The values obtained for the C–H bond lengths range from 0·78(7) to 1·02(8) Å and their average is 0·91 Å; naturally these values do not represent an estimate of the C–H internuclear separation.

The directions of the principal axes of vibration for those atoms that were refined with anisotropic thermal parameters are indicated in Figure 2. The palladium and two phosphorus atoms are not vibrating with great anisotropy and the correction to the Pd–P bond lengths calculated using the riding model was negligibly small (*ca.* 0·001 Å). The oxygen atoms appear to have their maximum vibration in directions normal to the bonds they form to carbon, which is chemically reasonable. The anisotropy in vibrations of C(1) and C(2) is not readily interpretable and may be artificial (for this reason it was not considered necessary to refine the other carbon atoms with anisotropic thermal parameters); corrections to the Pd–C(1) and Pd–C(2) calculated using the riding model were similar (*ca.* 0·04 Å) for the two bonds and do not alter the conclusion that the Pd–C(1) length is longer than the Pd–C(2) length and that the difference between these lengths is on the borderline of being statistically significant.

Bonding in $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$ *and Similar Compounds.*—Metal–acetylene complexes of general formula $M(C_2R_2)L_2$ have received much attention and there is a plethora of review articles[16] that have summarised the primary literature and discussed the bonding in these and similar compounds. The most stable complexes are formed by acetylenes with substituents that withdraw electrons using π-symmetry orbitals; this can be rationalised by assuming that there is an important contribution to the bonding made by electrons formally associated with the metal before interaction with the acetylene. One model that can be used to describe the bonding in these complexes is a simple adaptation of the classic Dewar–Chatt–Duncanson (DCD) model.[17] Figure 3 shows the three occupied three-centre molecular orbitals constructed under the local C_{2v} symmetry from the appropriate atomic orbitals of the metal and the two carbon atoms. In terms of the DCD model the orbital shown in Figure 3(a) corresponds to donation from the occupied acetylene π-orbital to a vacant σ-symmetry orbital on the metal, that in Figure 3(b) to the C–C σ-bond and that in Figure 3(c) to back-donation from an occupied metal *d*-orbital to that acetylene π^*-orbital in the MCC plane. In addition there is a π-bond between the two carbon atoms in a plane perpendicular to the MCC plane; on geometrical grounds alone, this cannot overlap to any great extent with the metal *d*-orbitals, although one description[18] does include this interaction.

The changes in acetylene geometry which occur upon co-ordination to a metal may be due to either or both the following factors: a redistribution of the bonding electrons through the intermediacy of the metal[19] or a net transfer of electrons from the metal to the acetylene. Correlations between the observed structural changes and other physical properties should be sought in order to determine the relative importance of the above two factors, thereby improving our knowledge of the bonding in such complexes. The *X*-ray photoelectron spectra[20,21] indicate a moderate positive charge upon platinum in $[Pt(C_2Ph_2)(PPh_3)_2]$, and, from a consideration of somewhat similar compounds, the charge may be greater when the metal is palladium. Upon changing the metal, vibrational spectra of complexes of this type show distinct changes in the position of the absorption corresponding to $\nu(C{\equiv}C)$ in the free acetylene:[22] the frequency of this mode is lowest for the platinum compounds, being *ca.* 35 and 65 cm^{-1} higher for the nickel and palladium compounds respectively. These two sets of observations would indicate that the polarities of either or both the orbitals shown in Figures 3(a) and (b) are increased towards acetylene in the palladium complexes relative to the platinum complexes. However, there are no significant differences between

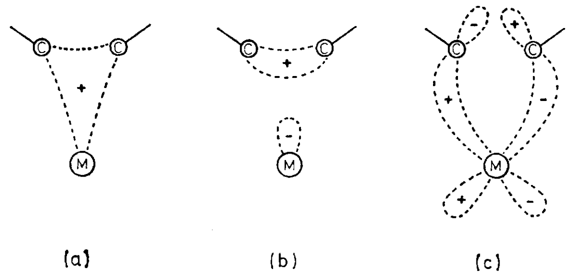

FIGURE 3 The three occupied three-centre molecular orbitals which can be used to describe the bonding in metal–acetylene and metal–olefin complexes. The positions of the metal and carbon atoms are drawn to scale for $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$ and the solid lines emanating from the carbon atoms indicate the direction of the bonds to the substituents

---

[15] N. A. Bailey and R. Mason, *J. Chem. Soc.* (*A*), 1968, 2594; R. Mason and P. O. Whimp, *ibid.*, 1969, 2709; G. Beran and G. J. Palenik, *Chem. Comm.*, 1970, 1354; R. H. Fenn and G. R. Segrott, *J. Chem. Soc.* (*A*), 1970, 3197; D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2250; G. R. Clark and G. J. Palenik, *ibid.*, p. 2754; L. L. Martin and R. A. Jacobson, *ibid.*, 1971, **10**, 1795.

[16] For example see the following articles and references therein, J. H. Nelson and H. B. Jonassen, *Co-ordination Chem. Rev.*, 1971, **6**, 27; R. D. W. Kemmitt, MTP Reviews, Inorganic Chemistry, Series 1, **6**, 227 (Butterworths, 1972).

[17] M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, **18C**, 79; J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

[18] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1969, **91**, 7005.

[19] R. Mason, *Nature*, 1968, **217**, 543; R. M. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, **47**, 20

[20] C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 1971, **93**, 1904.

[21] D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Comm.*, 1971, 602.

[22] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879.

the lengths of the acetylenic carbon–carbon bonds in compounds of this general formula whose structures have been reported to date.[1,2] This may be due to the paucity of reported structures.

The possible effect of non-bond interactions upon geometry has caused some uncertainty[20] about the validity of conclusions drawn for $[Pt(C_2Ph_2)(PPh_3)_2]$, since the full set of structural parameters have not been reported. In ionic compounds, crystal forces can result in significant distortions in both bond lengths and angles, but quantitative calculations upon several compounds have shown that the major anisotropy in the applied field is from the electrostatic forces.[23] In the absence of special circumstances (such as hydrogen bonds), it is a reasonable assumption that crystal forces do not grossly perturb the molecular structure of covalent compounds and this is certainly the case for $[Pd\{C_2(CO_2Me)_2\}(PPh_3)_2]$.

If the electron withdrawing substituents upon acetylene are planar (such as CO_2Me or Ph), then the orientation of the substituent plane with respect to the MCC plane is important. If the substituent is coplanar with the MCC plane, then electron density will be withdrawn from that π-orbital between the two acetylenic carbon atoms which is normal to the MCC plane, resulting in an increase in the separation of the acetylenic carbon atoms. If the substituent and MCC planes are mutually perpendicular then the substituent will withdraw electron density from the orbital shown in Figure 3(c), resulting in a lengthening of the M–C separation and possibly also an increase in the C–C separation due to a synergic increase in the polarity towards the metal of the orbitals shown in Figure 3(a) and (b). As Figure 2 shows, the CO_2Me substituent upon C(1) is perpendicular to the Pd,C(1),C(2) plane, whereas that upon C(2) is not. Thus the Pd–C(1) separation should be greater than the Pd–C(2) separation, which it is. It is common, and reasonable, experience that a bond *trans* to a relatively long bond will be relatively short, for example see $[Pt\{Cl_2CC(CN)_2\}(PPh_3)_2]$,[6f] and so the Pd–P(1) bond length should be shorter than the Pd–P(2) bond length in the presently reported compound, which it is. Examination of Table 5 reveals that the observed differences between these two pairs of bond lengths are only up to three times the estimated standard deviation in these differences and so the statistical significance of the differences is not high. Consequently there must be reservations about this aspect of the stereochemistry of the molecule, but at least the observations are consistent with each other and with this simple model. The converse situation is observed in asymmetrically substituted olefin complexes,[6f,g] where the shortest metal–carbon separation is to that carbon with the most electron withdrawing substituents, but obviously the substituents have differing effects in both a σ and a π sense.

Whether there is an energetically favoured orientation of a planar electron withdrawing substituent upon acetylene with respect to the MCC plane is not clear, since there are two mutually perpendicular π-systems with which it can interact. The structure reported in this paper has one substituent in the perpendicular orientation but the other is intermediate. In $[Ni(C_2Ph_2)(BuNC)_2]$[1] neither substituent is in the perpendicular orientation. However, in the case of similarly substituted olefins, the plane of the substituent should be perpendicular to the MCC plane (provided this is sterically possible) in the most favoured configuration. Naturally the barrier to rotation of the substituent will not be high, but such rotation could result in appreciable changes in certain bond lengths and angles. Such a situation has been postulated[7] to be the cause of the differences between the two crystallographically independent molecules of a diphenylcyclopropane complex of platinum.

The differences between the comparable angles P(2)–Pd–C(1) and P(1)–Pd–C(2) is the most statistically significant in this molecule. The former of these angles, that to C(1), is the largest and in terms of the discussion given above the substituent upon C(1) is the most electron withdrawing with respect to the Pd,C(1),C(2) plane. Analogous situations prevail in three asymmetrically substituted olefin–metal complexes.[6f,g,24]

An apparent anomaly has been observed in a number of metal–olefin complexes. Whilst tetrafluoroethylene and tetrachloroethylene form complexes with metals that are much weaker than those formed by tetracyanoethylene, the distortion from the free olefin geometry (specifically the bending back of the substituents from coplanarity) is much greater for C_2F_4 and C_2Cl_4 than for $C_2(CN)_4$.[6d–f] The reason for this is readily understood by consideration of the orbitals shown in Figure 3, which apply equally well to metal–olefin complexes. The halogen substituents are electron withdrawing in σ-fashion and electron-donating in π-fashion:[25] the π-donation will increase the electron density in the orbital shown in Figure 3(c), which is asymmetric with respect to the plane of the olefin substituents, the larger part lying to the metal side. Increased electron density on the metal side of each carbon atom would repel the substituents back from the metal, without necessarily increasing the strength of the interaction between the metal and the olefin. The converse applies when the olefin is substituted by cyano-groups, which are electron withdrawing in a π-fashion. These simple three-centre molecular orbital schemes, used as a first approximation, are thus very useful in predicting, or at least rationalising, the changes in geometry of this type of ligand upon co-ordination to a metal.

[3/2232 *Received*, 30*th October*, 1973]

---

[23] J. A. McGinnety, *J. Amer. Chem. Soc.*, 1972, **94**, 8406.

[24] A. R. Luxmoore and M. R. Truter, *Acta Cryst.*, 1962, **15**, 1117.

[25] M. E. Schwartz and L. C. Allen, *J. Amer. Chem. Soc.*, 1970, **92**, 1466.