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The distortion of pentafluorophenyl groups in metal complexes: limitations of rigid-body refinement

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Abstract

Pentafluorophenyl groups tend to be distorted, often severely, at the *ipso*-carbon atom; the distortions are larger in metal-C_6F_5 complexes, where the relevant C–C–C angle can be as low as 109°. The use of rigid, idealized hexagons in X-ray refinement can give misleading values for the M–C bond length.

Introduction

Rigid-body refinement of crystal structures is a commonly employed technique. A well-known variant is the use of idealized hexagons, with C–C 1.395 Å and all angles 120°, for aromatic C_6 (typically phenyl) rings. The advantages of this method are: (i) a reduction of computing time, especially if many such rings are present (e.g. in PPh_3 complexes) and (ii) an increased stability of refinement if the data are not particularly good (e.g. for crystals containing disordered solvent). The obvious disadvantage is that any distortions of the rings from the ideal geometry cannot be detected, but the distortions are often tacitly assumed to be small, and the main interest in structure determinations of transition metal complexes generally lies elsewhere. Moreover, the standard deviations of light atom parameters in heavy-atom structures are often high, so that small deviations from ideality would disappear in the statistical noise.

In 1975, in a paper entitled "Rigid-body refinement: a caveat", Domenicano and Vaciago [1] pointed out that the internal C–C–C angle α at the *ipso*-carbon atom in a phenyl ring can vary considerably (they quoted a range of 114–125°) depending on the nature of the substituent. Especially low values were obtained with substituents of low electronegativity and with perfluorinated ring systems [2]. In view of these observations, the authors warned that rigid-body refinement "*cannot be recommended as a correct procedure in the final stages of a crystal structure analysis*", and pointed out that it could lead to systematic errors in the C–X bond length (too short if the true angle is above 120°, too long if it is under 120°).

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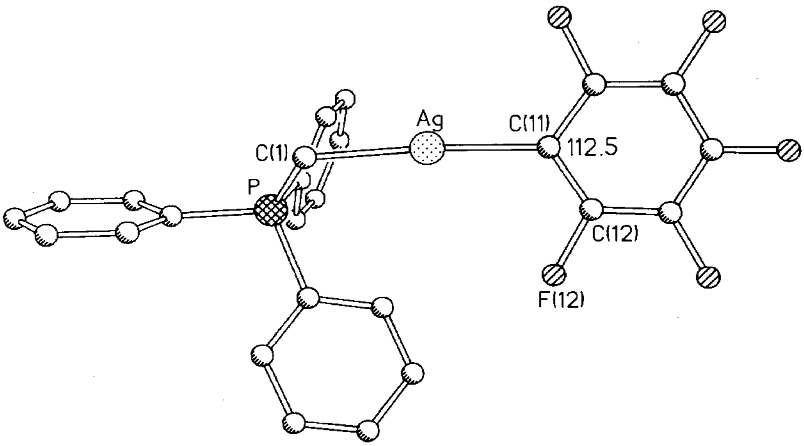

Fig. 1. A clear case of C_6F_5 distortion; the monoclinic modification of $[Ph_3PCH_2Ag(C_6F_5)]$ [18]. H atoms omitted for clarity.

The pentafluorophenyl ligand, C_6F_5, has not been commonly employed in transition metal chemistry. One fairly early, yet precise, study of such a crystal structure was that of *trans*-$[Ni(PPh_2Me)_2(C_6Cl_5)(C_6F_5)]$ [3]. It was noted that the angles at the *ipso*-carbons of both aromatic rings were well below 120° (113.5(6) and 112.0(6)°, respectively). The authors presented a Table of C–C–C angles from the limited number of structures of metal aryl complexes then known; the average angle at the *ipso*-carbon was 114.3°.

In the late 1970's, Usón and co-workers established that the pentafluorophenyl ligand was particularly useful in the chemistry of the coinage and noble metals (notably Au, Ag, Pd and Pt). I have been involved in the crystal structure determinations of many such complexes and confess to having used rigid body refinement of C_6 rings in several cases. Worse still; I was unaware of the articles by Domenicano and Vaciago, and I failed to notice the deviations from ideal geometry in those structures where rigid body refinement had not been used, until an extreme case in a small molecule was blatantly apparent (Fig. 1).

It is the purpose of this paper (i) to remind structural chemists of the problem of distorted aromatic rings, (ii) to present corrected results for some of my own structures, and (iii) to establish a rule-of-thumb for the applicability of the ideal hexagon model. For reasons of space, only C_6F_5 complexes (rather than all aryl complexes) are treated, and molecular formulae are shown linearly rather than in two dimensions.

Results

The extent of the problem

Table 1 summarizes values of the angle α for all structures with an M–Ar bond (where M is a transition metal and Ar is the C_6F_5 group); the data have been extracted either from the Cambridge Crystallographic Data Centre or from my own archives. The majority of the compounds were synthesized by Prof. Usón and co-workers.

The unweighted mean α value is 114.7(2)°, which is obviously significantly less than 120°. However, the metal atom is not alone responsible for this distortion; a search of the Cambridge data bank for all C_6F_5 rings *not* bonded to metals gave a mean α of 115.9(2)°. In other words, pentafluorophenyl rings show an intrinsic distortion at the *ipso*-carbon, but the extent of distortion is greater when coordinated to a metal (consistent with the electronegativity correlation mentioned above [2]). These σ values show that the use of an idealized rigid-body model for C_6F_5 rings must introduce systematic errors.

Some re-refined structures

trans-$C_6F_5Au(\mu$-dppm)$Pd(C_6F_5)_2(\mu$-dppm)AuC_6F_5 (1) [26]. This compound crystallizes in space group $P2_1/c$ with a 17.091(4), b 19.892(4), c 10.254(2) Å, β 90.85(2)°, $Z = 2$ (the molecule possesses crystallographic inversion symmetry). The original refinement used idealized rigid hexagons for all aromatic rings; the R value was 0.059 for 4324 reflections, 205 parameters. The Pd–C and Au–C bond lengths were 2.106(8), 2.074(7) Å, respectively. The new refinement, eschewing rigid groups, gave R 0.054 for 457 parameters (not a great improvement), with α angles of 115.5(8)° to Pd, 113.3(9)° to Au and corresponding bond lengths of 2.085(8) and 2.032(9) Å. (No great significance should be attached to the small increase in e.s.d.'s, because the old refinement was blocked, whereas the new refinement was full-matrix).

$[\{(dppe)Pd(\mu$-$S_2CS)\}_2Pt(C_6F_5)_2] \cdot CH_2Cl_2$ (2) [13]. This complex crystallizes in the trigonal space group $P3_221$ with a 14.636(2), c 29.237(4) Å, $Z = 3$ (crystallographically imposed twofold symmetry). The original refinement used the ideal hexagon model; the R value was 0.059 for 5413 reflections, 181 parameters. The Pt–C bond length was 2.072(6) Å. The new refinement with all ring atoms refining freely gave R 0.058 for 241 parameters, with an α of $112.0(10)^3$ and a Pt–C bond length of 2.023(10) Å.

Full details of the new refinements of structures **1** and **2** (atom coordinates, bond lengths and angles, temperature factors, structure factors) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Fed. Rep. of Germany. Any request for this material should quote the reference number CSD 52832 and a full literature citation.

$[Au(C_6F_5)_2\{PPh_2CHPPh_2CH(CO_2Me)\}Au(C_6F_5)]$ (3) [31]. Complex **3** crystallizes in the space group $P\bar{1}$ with a 12.719(5), b 12.830(5), c 17.918(5) Å, α 70.67(3), β 76.11(3), γ 72.07(3)°, $Z = 2$ *. The published structure involved idealized hexagons; the R value was 0.072, with Au–C bond lengths 2.071(13), 2.111(12), 2.098(13) Å. The free refinement gave the same R value, with α angles 116.9(27), 115.7(23), 119.7(25)° and corresponding bond lengths 2.040(26), 2.085(22), 2.098(22) Å. In view of the large e.s.d.'s, the changes are barely significant.

How valid is the hexagon model? Some generalizations

Structures **1** and **2** show that, with good-quality X-ray data, the hexagon model should not be used for C_6F_5 rings; the angles α deviate so far from the ideal 120° that serious systematic errors in the M–C bond lengths must result. For other types

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* The ring angle α should not be confused with the cell constant α!

Table 1

Angles α at the *ipso*-carbon atom in pentafluorophenyl complexes of transition metals (Ar = C_6F_5, PP = bidentate ligand)

Compound	Ref.	Angle α (°)	Comments
$[NiBr(PPh_2Me)_2Ar]$	4	113.7(4)	*trans*
$[Ni(C_5H_5)(PPh_3)Ar]$	5	114.2(13)	
$[Ni(PPh_2Me)_2Ar_2]$	6	114.0(3)	*trans*
$[Ni(C_6H_3Me_3)Ar_2]$	7	114.6(3), 114.2(3)	
$[Ni(PPh_2Me)_2(C_6Cl_5)Ar]$	3	112.0(6)	gives Refs. to other M-Ar species
$[Ni(C_6H_5Me)Ar_2]$	8	114.3(5)	(see also Acta Cryst., B31 (1975) 221)
$[Co(C_6H_5Me)Ar_2]$	8	115.4(4)	
$[Ir(CO)(PPh_3)_2Ar$	9	113(1)	*trans*
$[HgAr_2]$	10	115.9, 116.9	no e.s.d.'s given
$[Pd(PEt_3)_2(Et_3PCS_2)Ar]ClO_4$	11	115.4(13)	
$[Pd(Cy_3PCS_2)Ar_2]$	12	115.9(3), 115.1(5)	*cis*
$[Pt(Cy_3PCS_2)(CO)Ar_2]$	12	115.7(6), 115.6(7)	
$[PtAr_2\{SCS_2Pd(PP)\}_2]$	13	112.0(10)	originally with rigid body (see text)
$[Pt_2Ag_2Cl_4Ar_4][NBu_4]_2$	14	114.8, 116.5	no e.s.d.'s given
$[Pt(C_{41}H_{30}OP_2)Ar_2]$	15	113.4, 113.7	no e.s.d.'s given; substituted cyclopentadienyl ligand
$[PtCl(PEt_3)_2Ar]$	16	115(2)	
$[Pt(C_4H_8S)Ar_3(AgPPh_3)]$	17	111.9, 112.6, 112.6	no e.s.d's given; metal–metal bonding
$[Pt_2(Et_2O)AgAr_6]NBu_4$	17	109.0, 114.9, 112.2, 110.8, 119.1, 115. 6	all Ar bonded to Pt; metal–metal bonding; no e.s.d.'s given
$[Ag(CH_2PPh_3)Ar]$	18	113.1(5), 112.5(5)	two modifications
$[Au^I(PPh_3)Ar]$	19	114(2)	
$[Au^IAr_2][Au(diars)_2]$	20	113.2(9), 114.7(8)	
$[Au^{III}(diars)Ar_3]$	21	117.2(11) *trans* to As 117.3(10), 114.9(10)	

$[\mathrm{Au^{III}(PP)Ar_2]ClO_4}$	22	114.4(9)	
$[\mathrm{Au^{I}Ar_2Ag(C_4H_8S)}]$	23	113.1(11), 115.6(11)	Au–Ag bonds present
$[\mathrm{Au^{I}Ar_2Ag(C_6H_6)}]$	23	115.0(10), 112.6(10)	Au–Ag bonds present
$[\mathrm{Au^{III}Ar_2(Ph_2PCHPPh_2)Au^{I}Ar}]$	24	115.2(6) to Au$^{\mathrm{III}}$, 117.2(7) to Au$^{\mathrm{I}}$	
$[\mathrm{Au^{III}Ar_2(C_{22}H_{21}N_4)}]$	25	115.8(5), 115.9(5)	carbene-type ligand
$[\mathrm{Au^{I}Ar(PP)PdAr_2(PP)AuR}]$	26	115.5(8) to Pd, 113.3(9) to Au	originally as rigid body
$[\mathrm{(Au^{II}ArCl)_2(PP)}]$	27	115.8(5)	
$[\mathrm{Au^{I}Ar(PPh_2CHPPh_2Me)}]$	28	113.3(4)	
$[\mathrm{Au^{I}Ar(PPh_2CHPPh_2Me)Au^{I}Ar}]$	28	114.6(14) *trans* to P, 112.5(1) *trans* to C	
$[\mathrm{(Au^{I}Ar)_2(CHPh_2PAuPPh_2CH)_2}]$	29	113.2(14)	
$[\mathrm{Au^{III}(S_2CPEt_3)Ar_3}]$	30	115.2(4) *trans* to S, 115.4(5), 116.2(5)	
$[\mathrm{Au^{III}Ar_2\{PPh_2CHPPh_2CH(CO_2Me)\}Au^{I}Ar}]$	31	116.9(27) to Au$^{\mathrm{I}}$, 115.7(23) *trans* to C, 119.7(25) *trans* to P	originally as rigid body
$[\mathrm{Au^{I}Ar(SPPh_2CHPPh_2Me)Au^{I}Ar}]$	32	112.4(29) *trans* to S 111.5(29) *trans* to C	
$[\mathrm{Au^{III}Ar_2(CH_2PPh_2Me)(SPPh_2O)}]$	33	114.4(30) *trans* to C 121.2(29) *trans* to S	
$[\mathrm{Au^{III}Ar_3(AuCHPPh_2CH)_2}]$	34	115.0(11) *trans* to Au$^{\mathrm{I}}$ 116.4(12), 115.0(12)	
$[\mathrm{Au^{III}Ar_2(SPPh_2CHPPh_2)}]$	35	114.8(8) *trans* to P, 116.7(6) *trans* to S	
$[\mathrm{Au^{III}Ar_2\{S_2CN(CH_2Ph)\}_2}]$	36	115.4(6), 114.8(6)	

of ring (e.g. PhP moieties) there is also little point in using the idealized model if sufficient data are available, but the errors are less serious; the eight such rings in compounds **1** and **2** show a mean α of 118.4°.

The increase in bond length e.s.d.'s on changing from the idealized to the free refinement model is to some extent an artefact of the (purely coincidental) difference in the refinement mathematics adopted (blocked or full-matrix), but some increase would be expected anyway; a large rigid group, involving many electrons, can be located with apparently greater precision than the single *ipso*-C atom. However, if the model is not valid, then the increased precision is entirely spurious.

The improvement in R value is minimal, as would be expected for changes in light atom positions in heavy atom structures.

Compound **3** behaves quite differently. The X-ray data were poor both in quantity and quality, because the crystals diffracted weakly; C_6F_5 groups are often associated with high thermal motion. The idealized refinement was stable, but the free refinement converged slowly; the e.s.d.'s of the light atom positions were high. The use of rigid groups here is justified because little significant extra information is provided by the free refinement. As a rule of thumb, it could be suggested that the use of rigid-body refinement for C_6F_5 groups is acceptable for poorish data with light atom angle e.s.d.'s ca. 2.5° or more, because the distortions are not likely to be very large compared with the e.s.d.'s. Clearly, possible systematic errors in metal–carbon bond lengths should be taken into account in any discussion of such structures. See also Refs. 22, 24, 30, 37, 38 for further examples.

For moderate data and structures involving PhP and C_6F_5 groups, a useful compromise is to fix the phenyl groups but not the C_6F_5 rings.

Conclusion

It is seldom necessary or desirable to use idealized hexagons in the final stages of X-ray refinement of C_6F_5 rings unless the refinement would otherwise be unstable or the data to parameter ratio too low. The strategy of refinement should always be based on the quality of the data rather than the speed of computing.

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