Aryltriazenido-complexes. Crystal and Molecular Structure of *trans*-Carbonyl(1,3-di-*p*-tolyltriazenido)bis(triphenylphosphine)iridium(I)

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The structure of the title compound has been determined by counter data. In this square-planar iridium complex the triazenido-ligand is unidentate and *trans* to the carbonyl group. The Ir–N(1) distance is 2.16(1) and the Ir–C(26)(carbonyl) 1.79(1) Å. The complex crystallizes in the monoclinic system, space group $C2/c$, with unit-cell dimensions a = 22.121(3), b = 19.190(3), c = 10.111(2) Å, and β = 92.77(5)°. The structure is refined to a conventional R index of 0.032.

THE 1,3-diaryltriazenido-ligand p-$CH_3C_6H_4N{-}N{=}NC_6H_4$-$CH_3$-$p$ (dtt) is unidentate in palladium(II) and platinum(II) square-planar complexes.[1-4] Variable-temperature ^1H n.m.r. experiments on these complexes have shown that the two signals for the methyl protons collapse reversibly between −40 and −60 °C giving rise to a unique signal at higher temperature indicating a fluxional process. For the title complex $[Ir(CO)(dtt)(PPh_3)_2]$ the nitrogen atoms remain equivalent even down to −90 °C (in CD_2Cl_2) suggesting either the occurrence of a dynamic process or the presence of a chelating ligand. The i.r. spectrum shows bands at 1 361, 1 302, 1 278, 1 211, and 1 157 cm^{-1} which have been proposed as diagnostic for the dtt group acting as a unidentate ligand.[5,6]

In order to understand better the bonding mode of the dtt ligand in the title complex its crystal structure has been studied by X-ray diffraction methods.

RESULTS AND DISCUSSION

Crystal Data.—Orange prismatic crystals (0.1 × 0.2 × 0.1 mm), Monoclinic, space group $C2/c$, a = 22.121(3), b = 19.190(3), c = 10.111(2) Å, β = 92.77(5)°, U = 4 287 Å^3, D_c = 1.48 g cm^{-3}, Z = 4, μ = 35.2 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å.

Intensity Data, Structure Determination, and Refinement.—A total of 3 370 independent reflections were collected by means of a Philips PW 1100 four-circle diffractometer ($3 < \theta < 24°$, $d_{min.}$ = 0.87 Å) using a graphite monochromator; of these, 2 835 having $I > 3\sigma(I)$ (σ based on counting statistics) were used in the structure determination and refinement. Corrections for Lorentz and polarization effects were applied, while absorption correction was disregarded, due to the crystal size.

Systematic absences and Patterson-function examination confined the choice of space group to Cc without any molecular symmetry or $C2/c$ with a C_2 symmetry axis.

From the Patterson function the positions of Ir and P atoms were found to conform to $C2/c$ symmetry and the electron-density map phased with the above contributions confirmed the two-fold molecular symmetry, likewise for the PPh_3 groups. In the region of the dtt ligands, however, the electron-density map showed elongated peaks indicating either: (*i*) that the true symmetry is lower, without a two-fold axis; or (*ii*) that the two-fold axis does exist in the crystal but is derived from the occurrence of two statistically equivalent orientations for dtt. In the first case the space group should be Cc in the second $C2/c$. However, in both hypotheses the dtt group behaves as a unidentate ligand bonding through a single nitrogen atom.

The two models were refined by least squares with block-diagonal approximation for the whole structure, except for the dtt ligand which was refined by full-matrix least squares. Anisotropic thermal-vibration parameters were considered for iridium and the triphenylphosphine ligand and isotropic parameters for all other non-hydrogen atoms. In both cases the two PPh_3 groups remained symmetrically related. In the last cycles of refinement the hydrogen-atom contribution was considered by calculating the atomic positions of phosphine hydrogens, assuming the usual geometry for phenyl groups.

Comparison of the observed structure factors with the calculated ones for either Cc or $C2/c$ models shows only very slight differences between them since most atoms conform to the higher symmetry in both cases. In fact the conventional R indices are quite similar: 0.033 for Cc and 0.032 for $C2/c$. This does not allow a definite determination of the crystal symmetry on structure-factor grounds only. Furthermore, comparison of the resulting geometry for the dtt ligand does not help in discriminating between the two models since bond lengths and angles are equal within error limits. The $C2/c$ space group, however, appears more likely on crystal-packing grounds: the absence of dtt ··· dtt short contacts and the C_2 symmetry of the ' cavity ' available for the ligand make the two ligand orientations energetically equivalent and hence favoured by entropy considerations.

Observed and calculated structure factors and thermal parameters are available as Supplementary Publication No. SUP 22734 (25 pp.).† The atomic scattering factors used were those given in ref. 7 while the anomal-

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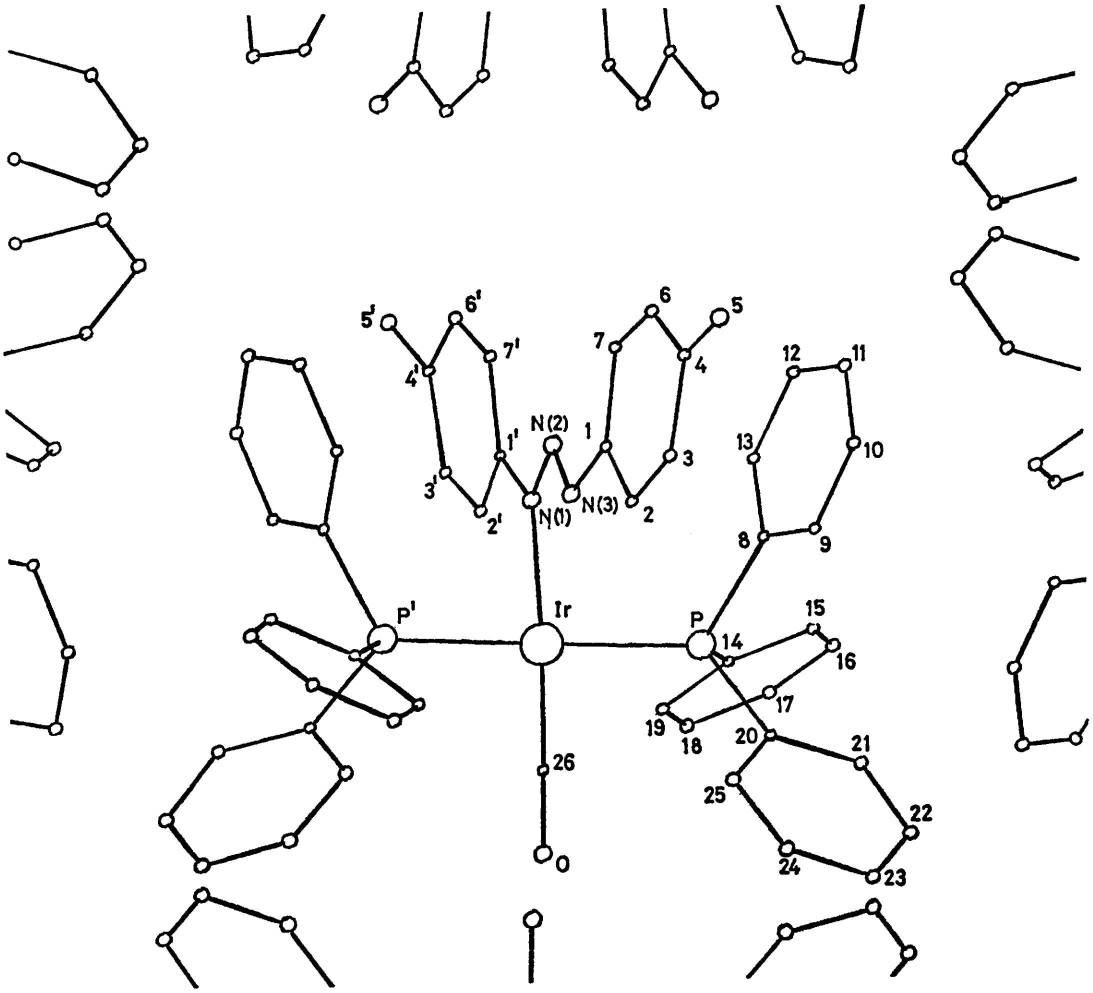
† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

ous dispersion corrections for iridium and phosphorus atoms were taken from ref. 8. The computations were carried out using programs by Immirzi.[9]

Description of the Structure.—The projection of the structure along the *z* axis, obtained with the program ORTEP (see the Figure), shows the whole molecule and the crystal packing.



View down the *c* axis of the molecule (only one of the two alternative orientations of dtt is indicated for clarity)

Principal interatomic distances and angles are given in Table 1. The co-ordination around the Ir is nearly square planar, with the two PPh_3 groups *trans* to each other.

The carbonyl group shows distances comparable to carbonyls in other iridium compounds. The present iridium–carbon distance of 1.79(1) Å is comparable with the values of 1.800(8) Å reported for $[Ir(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ [10] and falls in the range excepted for this type of bond. The iridium–phosphorus distance 2.316(1) is comparable with the values of 2.316(5) and 2.329(5) Å found in $[Ir(C_8H_{12}Me)(PPhMe_2)_2]$ [11] and related compounds. The iridium–nitrogen bond length 2.16(1) Å is in agreement with the metal–nitrogen bonds in square-planar compounds containing platinum bonded to the dtt ligand {2.09(2) Å in *trans*-$[PtH(dtt)(PPh_3)_2]$[3] and 2.11(2) Å in *cis*-$[PtCl(dtt)(PPh_3)_2]$[4]} and with the values of 2.089(6) and 2.088(5) Å reported for *cis*-$[Pt(PhN_3Ph)_2(PPh_3)_2]\cdot C_6H_6$.[12]

The dtt ligand has a *trans* conformation with respect to both N(2)–N(3) and N(1)–N(2) bonds, as a consequence the C(1)–N(1)–N(2)–N(3)–C(1) group is fairly planar. The mean plane of dtt forms an angle of 82° with the mean co-ordination plane.

The asymmetry of the dtt ligand and the *C*2/*c* crystal symmetry imply that there are two statistically equivalent orientations for the dtt ligand (in both cases dtt is unidentate), that may correspond either with a *space* disorder or a *time* disorder, *i.e.* in the latter case, a fluxional process in the crystal.

In fact diffraction cannot distinguish between *static* disorder and *dynamic* disorder. Nevertheless, the symmetric orientation of the two phosphines and the arrangement of dtt in the crystal should make the fluxional processes available not only in solution but also in the crystal. In fact, the intermolecular contacts which control the size of the unit cell are all among the phenyl group and there are no short dtt ··· dtt or dtt ··· phenyl contacts (none are less than 3.9 Å). This possibility is also suggested by the short Ir ··· N(3) contact [2.58(1) Å], compared with the analogous contacts in *trans*-[PtH(dtt)(PPh$_3$)$_2$] [2.91(2) Å] and in *cis*-[PtCl(dtt)(PPh$_3$)$_2$] [3.01(2) Å] which would make the dynamic process easier. These observations and the magnetic equivalence of the methyl protons observed in solution (CD$_2$Cl$_2$) even down to −90 °C strongly support the existence of a fluxional process in the solid state at room temperature.

TABLE 1

Atomic fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ir	0(0)	1 794(0)	2 500(0)
P	1 022(1)	1 811(1)	2 094(2)
O	30(5)	247(4)	2 201(9)
N(1)	−81(4)	2 860(5)	1 839(11)
N(2)	49(5)	3 273(5)	2 846(8)
N(3)	170(6)	2 909(5)	3 886(12)
C(1)	388(5)	3 267(7)	5 022(15)
C(2)	561(7)	2 863(9)	6 071(20)
C(3)	801(7)	3 206(9)	7 235(16)
C(4)	881(7)	3 954(9)	7 496(20)
C(5)	1 102(17)	4 235(20)	8 591(35)
C(6)	668(7)	4 274(9)	6 247(18)
C(7)	438(7)	4 003(9)	5 079(20)
C(1′)	−287(5)	3 184(8)	635(15)
C(2′)	−406(7)	2 775(9)	−397(16)
C(3′)	−636(6)	3 058(8)	−1 594(18)
C(4′)	−753(6)	3 802(7)	−1 834(15)
C(5′)	−1 018(14)	4 158(16)	−3 280(36)
C(6′)	−590(8)	4 197(10)	−648(22)
C(7′)	−365(6)	3 916(8)	556(17)
C(8)	1 409(3)	2 621(3)	2 563(6)
C(9)	1 732(3)	2 683(3)	3 776(6)
C(10)	1 975(3)	3 323(4)	4 155(7)
C(11)	1 907(3)	3 895(4)	3 343(8)
C(12)	1 579(3)	3 838(3)	2 139(8)
C(13)	1 332(3)	3 198(4)	1 748(6)
C(14)	1 196(3)	1 689(3)	360(6)
C(15)	1 735(3)	1 944(14)	−110(6)
C(16)	1 862(3)	1 819(4)	−1 490(7)
C(17)	1 460(3)	1 464(4)	−2 278(7)
C(18)	936(3)	1 210(4)	−1 816(8)
C(19)	783(3)	1 331(4)	−465(6)
C(20)	1 473(3)	1 146(3)	2 964(6)
C(21)	2 056(3)	957(4)	2 566(7)
C(22)	2 381(3)	446(4)	3 267(8)
C(23)	2 148(4)	114(3)	4 352(8)
C(24)	1 592(4)	313(4)	4 778(7)
C(25)	1 238(3)	819(4)	4 106(7)
C(26)	23(7)	866(4)	2 285(13)

All C–C distances (see Table 2) differ from the expected values to within 0.06 Å for the phosphine (mean C–C = 1.396 Å) and 0.08 Å for the triazenido-rings (mean C–C = 1.412 Å), except for the C(4)–C(5) and C(4′)–C(5′) distances. We do not think that such anomalous values for these distances have any physical significance and they are attributed to the very high correlation between the two methyl groups; such effects are enhanced by the exceedingly high thermal vibration for the methyl groups.

TABLE 2

Principal interatomic distances (Å) and angles (°) with standard deviations in parentheses

Ir–P	2.316(1)	C(1)–C(2)	1.35(2)
Ir–C(26)	1.79(1)	C(1)–C(7)	1.42(2)
Ir–N(1)	2.16(1)	C(2)–C(3)	1.43(3)
Ir–N(2)	2.86(1)	C(3)–C(4)	1.47(2)
Ir–N(3)	2.58(1)	C(4)–C(5)	1.31(4)
P–C(8)	1.83(1)	C(4)–C(6)	1.46(3)
P–C(14)	1.83(1)	C(6)–C(7)	1.37(3)
P–C(20)	1.82(1)	C(1′)–C(2′)	1.32(2)
N(1)–N(2)	1.31(1)	C(1′)–C(7′)	1.42(2)
N(2)–N(3)	1.28(2)	C(2′)–C(3′)	1.40(2)
N(1)–C(1′)	1.42(2)	C(3′)–C(4′)	1.47(2)
N(3)–C(1)	1.40(2)	C(4′)–C(5′)	1.69(4)
C(26)–O	1.19(1)	C(4′)–C(6′)	1.45(3)
		C(6′)–C(7′)	1.40(3)
Ir–P–C(8)	114.5(5)	Ir–N(1)–C(1′)	134.3(5)
Ir–P–C(14)	115.0(5)	Ir–N(1)–N(2)	108.7(5)
Ir–P–C(20)	115.0(5)	C(1′)–N(1)–N(2)	116.7(5)
C(26)–Ir–P′	93.9(5)	N(1)–N(2)–N(3)	109.7(5)
C(26)–Ir–P	87.6(5)	N(2)–N(3)–C(1)	117.1(6)
P–Ir–N(1)	89.8(5)	Ir–C(26)–O	176.9(5)
P′–Ir–N(1)	88.6(5)		

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