

## THE MOLECULAR STRUCTURE OF PENTACARBONYL(TRIFLUOROPHOSPHINE)MOLYBDENUM

D. M. BRIDGES, G. C. HOLYWELL AND D. W. H. RANKIN

*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ (Great Britain)*

J. M. FREEMAN

*Department of Chemistry, University of Manchester Institute of Science and Technology, Sackville Street, Manchester, M60 1QD (Great Britain)*

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### SUMMARY

The molecular structure of pentacarbonyl(trifluorophosphine)molybdenum,  $\text{PF}_3\text{Mo}(\text{CO})_5$ , in the gas phase has been determined by the sector-microphotometer method of electron diffraction. The principal bond lengths and angles are:  $r(\text{C}-\text{O})$   $1.154 \pm 0.005$ ,  $r(\text{Mo}-\text{C})$   $2.063 \pm 0.006$ ,  $r(\text{Mo}-\text{P})$   $2.369 \pm 0.010$ ,  $r(\text{P}-\text{F})$   $1.557 \pm 0.004$  Å,  $\angle(\text{F}-\text{P}-\text{F})$   $99.5 \pm 0.5^\circ$ . Several methods of describing the partial wave phase shifts have been used, and their relative merits are discussed.

### INTRODUCTION

Considerable interest has recently been shown in the changes of properties of trifluorophosphine on coordination. Studies by electron diffraction of the structures of tetrakis(trifluorophosphine)nickel<sup>1,2</sup> and -platinum<sup>1</sup> have indicated that the angles between the phosphorus-fluorine bonds are very little changed in the coordinated compounds compared with trifluorophosphine<sup>3</sup>, while the bonds are shorter, much more so in the platinum complex than in the nickel one. Similar effects have been noted in trifluorophosphine-borane<sup>4</sup>. These observations have been correlated with photo-electron data for the 4-coordinated metal complexes and the free ligands<sup>5</sup>, while *ab initio* SCF-MO calculations for trifluorophosphine<sup>6</sup> and trifluorophosphine oxide<sup>7</sup> have given an understanding of the bonding in these compounds. The electron diffraction studies also showed the nickel-phosphorus bond in tetrakis(trifluorophosphine)nickel to be unusually short, whereas the platinum-phosphorus bond in tetrakis(trifluorophosphine)platinum has been found to be of typical length.

This present work on pentacarbonyl(trifluorophosphine)molybdenum is therefore of importance, as it provides the first structural information about a trifluorophosphine complex of a second transition series metal.

### EXPERIMENTAL

Pentacarbonyl(trifluorophosphine)molybdenum was prepared by the reaction

TABLE 1

WEIGHTING FUNCTIONS, ETC.

Height (mm)	Delta s	$s_{\min}$	$s_1$	$s_2$	$s_{\max}$	$p/h$	Scale factor	Wavelength
250	0.40	5.20	7.00	23.50	30.40	0.4746	$0.810 \pm 0.027$	0.056650
500	0.20	3.40	5.00	12.00	15.80	0.4947	$1.252 \pm 0.039$	0.056650
1000	0.10	1.30	2.60	6.40	7.30	0.4985	$0.542 \pm 0.027$	0.057913

of *N*-methylpyridinium molybdenum pentacarbonyl iodide and trifluorophosphine in dichloromethane, a method not used for this compound previously. The product always contained a small percentage of tetracarbonyl *cis*-bis(trifluorophosphine)-molybdenum which could not be removed by fractional condensation in a vacuum system.

Electron diffraction scattering intensities were recorded photographically (Ilford N.60 plates) using a Balzers' KD.G2 instrument<sup>8</sup>. The sample and nozzle were maintained at 333K during the exposures. The data were transferred to punched tape using an automatic Joyce-Loebl microdensitometer. Three plates, taken at nozzle-to-plate distances of 250, 500 and 1000 mm were used, giving a range of 1.3 to 30.4 Å<sup>-1</sup> in the scattering variable *s*.

All calculations were carried out using the IBM 360/50 computer at the Edinburgh Regional Computing Centre. The data reduction programme is described below, and the least squares programme has been described elsewhere<sup>9</sup>. The weighting functions and correlation parameters used in the construction of the off-diagonal weight matrix for the least-squares refinements are given in Table 1, together with scale factors and the wavelengths used. The latter values were determined from the diffraction pattern of powdered thallos chloride and by direct measurement of the accelerating voltage.

#### Data reduction programme

The data reduction programme has been developed from that used in Cambridge<sup>10</sup>. Normally eight diameters of each plate are traced by the microdensitometer. Each diameter is centred, corrected for emulsion response, plate planarity and for sector shape, and the data are interpolated in even *s* intervals. The sixteen sets of data are then averaged, and the calculated coherent atomic scattering is subtracted. Subtraction of some of the extraneous scattering is achieved by fitting a cubic function to the data by a least squares procedure. Any subsequent corrections are made by drawing a smooth background through the molecular intensity curves followed by a further subtraction.

The molecular intensity curves and final weighted difference curves for the three data sets for pentacarbonyl(trifluorophosphine)molybdenum are shown in Fig. 1. Details of the three corresponding uphill curves can be obtained from the authors.

#### MOLECULAR MODEL

In all the refinements it was assumed that the P-Mo(CO)<sub>5</sub> group possessed

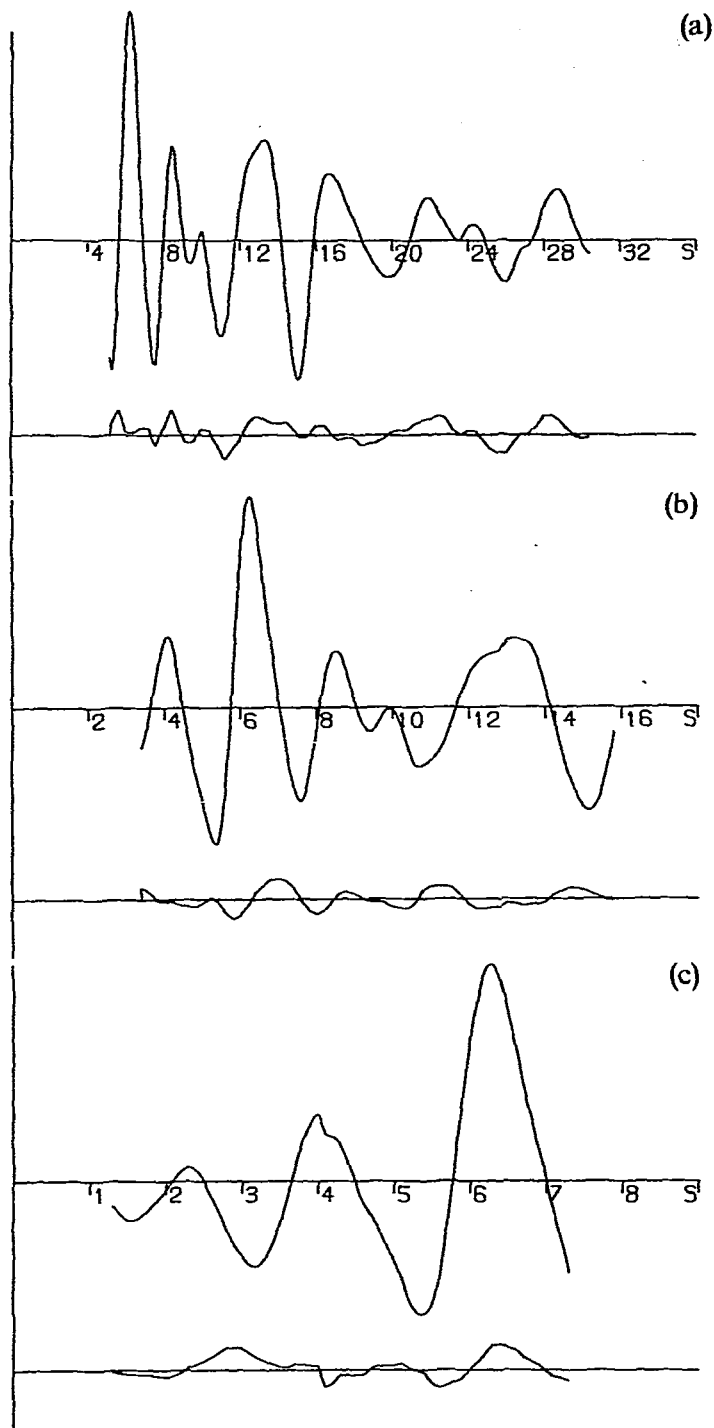


Fig. 1. Observed and weighted difference molecular intensity data for  $\text{PF}_3\text{Mo}(\text{CO})_5$ . a: 250 mm intensity data; b: 500 mm intensity data; c: 1000 mm intensity data.

local  $C_{4v}$  symmetry, and that the  $F_3P-Mo$  group had local  $C_{3v}$  symmetry. Further, as there is a twelve-fold barrier to rotation about the phosphorus-molybdenum bond, free rotation of the  $-PF_3$  group was assumed. With these assumptions the geometry of the molecule may be described in terms of the four bonded distances, the  $F-P-F$  angle, and the bending of the equatorial carbonyl groups, both at molybdenum and at carbon, away from or towards the trifluorophosphine ligand.

#### REFINEMENT

The radial distribution curve for pentacarbonyl(trifluorophosphine)molybdenum (Fig. 2) falls naturally into two regions. Below 2.5 Å lie peaks associated with all the bonded distances in the molecule, with only one non-bonded distance ( $F\cdots F$ ). The four main peaks are well separated, and the distances of 1.15, 1.55, 2.05 and 2.35 Å may be assigned to C-O, P-F, Mo-C and Mo-P separations respectively. The region above 2.5 Å consists of a large number of overlapping peaks, due to the remaining non-bonded atom pairs, dominated by the large Mo $\cdots$ O and Mo $\cdots$ F peaks at about 3.2 and 3.4 Å. Thus the five main parameters describing the molecular geometry are determined by the most prominent features of the radial distribution curve. The main problems in the course of the refinements were concerned with attempts to vary the parameters used to define the phase shifts for atom pairs including molybdenum, and with maximising the number of amplitudes of vibration that could be refined at one time. In addition, allowance had to be made for the proportion of tetracarbonylbis(trifluorophosphine)molybdenum in the samples used. This was done at a fairly late stage in the refinement by varying the percentage of impurity assumed, and comparing the  $R$  indices for each data set. The optimum percentages found were 28, 19 and 9 for the 250, 500 and 1000 mm data sets respectively. In the later refinements these fixed percentages were included, the bis(trifluorophosphine) complex being assumed to have the same bond lengths, and angles at phosphorus, as

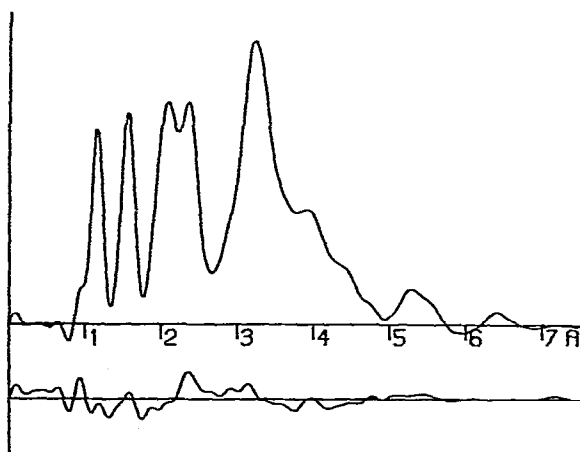


Fig. 2. Experimental and difference radial distribution curves,  $P(r)/r$  for  $PF_3Mo(CO)_5$ . Before Fourier inversion, the data were multiplied by  $s \cdot \exp(-0.002 s^2)/(z_{Mo} - f_{Mo})(z_F - f_F)$ .

the mono-complex, with the carbonyl groups bent slightly away from the trifluorophosphine ligands, as in the mono-complex.

For molecules containing no heavy atoms, the calculated intensity expression used in the least squares programme includes the term  $\cos(\eta_i - \eta_j)$ , where  $\eta_i$  and  $\eta_j$  are phase angles for the  $i$ - $j$  atom pair. Normally the tabulated values of  $\eta$  given by Cox and Bonham<sup>11</sup> are used, a cubic function being fitted by a least-squares process to the values interpolated at the correct voltage. Thus the phase shift term is of the form

$$\eta_i - \eta_j = a_i - a_j + (b_i - b_j) \cdot s + (c_i - c_j) \cdot s^2 + (d_i - d_j) \cdot s^3$$

For pentacarbonyl(trifluorophosphine)molybdenum, this treatment was inadequate, and it was impossible to refine amplitudes of vibration for atom pairs including molybdenum. Alternative values for the constants  $a$ ,  $b$  and  $c$  for each element were calculated using the analytical expressions of Bonham and Ukaji<sup>12</sup>, but this change made very little difference to the refinements. The expressions for the three constants are of the form

$$a_i = a_1 \cdot e^{a_2 \cdot z_i} + a_3 \cdot e^{a_4 \cdot z_i}$$

where  $a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$  are constants independent of the atomic number ( $z_i$ ) of the element. In one refinement, the effective value of the atomic number of molybdenum was allowed to vary insofar as it affected the phase shifts, this procedure giving a small but significant decrease in the  $R$  index. The best value for the effective atomic number was 38.5.

- An alternative way of varying the phase shifts involved multiplication of the values of  $(b_i - b_j)$  for different atom pairs by refineable numbers, initially 1. This procedure reduced the  $R$  factor at that stage of the refinements from 0.27 to 0.25 and, more importantly, enabled the amplitudes of vibration to refine reasonably satisfactorily. The values finally adopted were 1.12 for Mo-C and Mo...F, 1.22 for Mo...O and 0.96 for Mo-P.

One other approach to the problem was even more successful. The expression for the phase shifts for the  $i$ - $j$  atom pair stated above may be written in the form

$$\begin{aligned} \Delta\eta &= \Delta a + \Delta b \cdot s + \Delta c \cdot s^2 + \Delta d \cdot s^3 \\ &= \Delta a' + \Delta b' \cdot (s - s_c) + \Delta c' \cdot (s - s_c)^2 + \Delta d \cdot (s - s_c)^3 \end{aligned}$$

Initial values of  $s_c$  for the atom pairs were calculated so that  $\Delta\eta = \pi/2$  when  $s = s_c$ .  $s_c$  is then the "cut-off" or "beat-out" point. Once the new constants  $\Delta a'$ ,  $\Delta b'$ ,  $\Delta c'$  and  $\Delta d$  had been evaluated, the values of  $s_c$  were allowed to refine. Initial values of  $s_c$  for Mo-C, Mo...O, Mo...F and Mo-P, calculated using the tabulated phases of reference 11, were 19.8, 19.7, 19.7 and 24.1  $\text{\AA}^{-1}$ . The first three were therefore assumed to remain equal. Final refined values were 21.7 and 26.0. At the stage in the refinements when this method was first used, the  $R$  factor was 0.170, and improved to 0.165.

It should be pointed out that with data extending only as far as 30  $\text{\AA}^{-1}$ , any estimates of the beat-out points must be used with caution. However, agreement with values found in studies of molybdenum hexafluoride<sup>13</sup> and molybdenum hexacarbonyl<sup>14</sup> is reasonably good.

In the final series of refinements shrinkage corrections were applied. The corrections, listed in Table 2, were estimated on the basis of calculated values for molybdenum hexacarbonyl<sup>15</sup> and trifluorophosphine<sup>3</sup>. The final  $R$  factor ( $R_G$ <sup>9</sup>) was 0.14.

TABLE 2  
 MOLECULAR PARAMETERS

## (A) Independent distances

	Distance (Å)	Amplitude (Å)	Anharmonic constant
$r_1$ (C-O)	$1.154 \pm 0.005$	0.035 (fixed)	2.0
$r_2$ (Mo-C)	$2.063 \pm 0.006$	$0.069 \pm 0.010$	2.0
$r_3$ (Mo-P)	$2.369 \pm 0.010$	0.079 (tied to $u_2$ )	2.0
$r_4$ (P-F)	$1.557 \pm 0.004$	$0.059 \pm 0.006$	2.0

## (B) Dependent distances

	Distance (Å)	Amplitude (Å)	Shrinkage correction
$d_5$ (Mo...O <sub>ax</sub> )	$3.211 \pm 0.014$	$0.073 \pm 0.012$	0.0059
$d_6$ (Mo...O <sub>eq</sub> )	$3.209 \pm 0.014$	0.073 (tied to $u_5$ )	0.0059
$d_7$ (C <sub>eq</sub> ...O <sub>eq</sub> )	$5.249 \pm 0.023$	$0.088 \pm 0.018$	0.0227
$d_8$ (O <sub>eq</sub> ...O <sub>eq</sub> )	$6.382 \pm 0.028$	0.089 (tied to $u_7$ )	0.0342
$d_9$ (C <sub>eq</sub> ...C <sub>eq</sub> )	$4.111 \pm 0.018$	0.088 (tied to $u_7$ )	0.0133
$d_{10}$ (C <sub>eq</sub> ...C <sub>eq</sub> )	$2.868 \pm 0.037$	$0.134 \pm 0.025$	0.0025
$d_{11}$ (C <sub>eq</sub> ...C <sub>ax</sub> )	$2.913 \pm 0.015$	0.134 (tied to $u_{10}$ )	0.0025
$d_{12}$ (O <sub>eq</sub> ...O <sub>eq</sub> )	$4.388 \pm 0.048$	$0.339 \pm 0.031$	0.0140
$d_{13}$ (O <sub>eq</sub> ...O <sub>ax</sub> )	$4.522 \pm 0.021$	0.339 (tied to $u_{12}$ )	0.0140
$d_{14}$ (C <sub>eq</sub> ...O <sub>eq</sub> )	$3.758 \pm 0.050$	$0.200 \pm 0.019$	0.0082
$d_{15}$ (C <sub>ax</sub> ...O <sub>eq</sub> )	$3.700 \pm 0.025$	0.200 (tied to $u_{14}$ )	0.0082
$d_{16}$ (C <sub>eq</sub> ...O <sub>ax</sub> )	$3.808 \pm 0.016$	0.200 (tied to $u_{14}$ )	0.0082
$d_{17}$ (P...C <sub>ax</sub> )	$4.418 \pm 0.019$	$0.100 \pm 0.016$	0.0143
$d_{18}$ (P...C <sub>eq</sub> )	$3.188 \pm 0.034$	0.220 (fixed)	0.0028
$d_{19}$ (P...O <sub>ax</sub> )	$5.562 \pm 0.025$	0.102 (tied to $u_{17}$ )	0.0238
$d_{20}$ (P...O <sub>eq</sub> )	$4.103 \pm 0.025$	0.250 (fixed)	0.0090
$d_{21}$ (Mo...F)	$3.389 \pm 0.015$	$0.133 \pm 0.021$	0.0059
$d_{22}$ (F...C <sub>ax</sub> )	$5.324 \pm 0.021$	$0.187 \pm 0.028$	0.0227
$d_{23}$ (F...O <sub>ax</sub> )	$6.435 \pm 0.027$	$0.225 \pm 0.036$	0.0342
$d_{24}$ (F...F)	$2.376 \pm 0.011$	$0.066 \pm 0.009$	0.0007
(F...C <sub>eq</sub> )	Between 3.26 and 4.65		0.008
(F...O <sub>eq</sub> )	Between 3.80 and 5.61		0.014

## (C) Angles (°)

<1	(F-P-F)	$99.5 \pm 0.5$
<2	(C <sub>ax</sub> -Mo-C <sub>eq</sub> )	$88 \pm 2$
<3	(Mo-C <sub>eq</sub> -O <sub>eq</sub> )	$175 \pm 2$

## RESULTS AND DISCUSSION

The distances [ $r_g(1)^{16}$ ] and angles obtained from the least squares analysis, and the final least-squares correlation matrix are presented in Tables 2 and 3.

Interest in these results centres mainly on the parameters involving the trifluorophosphine ligand. The results of some earlier investigations of trifluorophosphine complexes are summarised in Table 4. Of particular interest is the phosphorus-

TABLE 4

BOND LENGTHS AND ANGLES IN TRIFLUOROPHOSPHINE COMPLEXES

Compound	Method <sup>a</sup>	$r(\text{P-F})$ (Å)	$\angle(\text{F-P-F})$ (°)	Ref.
PF <sub>3</sub>	ED	1.569 ± 0.001	97.7 ± 0.2	3
(PF <sub>3</sub> ) <sub>4</sub> Ni	ED	1.561 ± 0.005	98.4 ± 0.8	1
		1.561 ± 0.003	99.3 ± 0.3	2
PF <sub>3</sub> Mo(CO) <sub>5</sub>	ED	1.557 ± 0.004	99.5 ± 0.5	<sup>b</sup>
(PF <sub>3</sub> ) <sub>4</sub> Pt	ED	1.546 ± 0.006	98.9 ± 0.7	1
PF <sub>3</sub> ·BH <sub>3</sub>	MW <sup>c</sup>	1.538 ± 0.008	99.8 ± 1.0	4
PF <sub>3</sub> ·B(BF <sub>2</sub> ) <sub>3</sub>	X	1.51 ± 0.015	101.7 ± 1.0	17

<sup>a</sup> ED = Electron diffraction, MW = microwave, X = X-ray diffraction. <sup>b</sup> This work. <sup>c</sup> Mixed  $r_s/r_o$  structure.

fluorine bond length in the molybdenum compound, as it lies between the lengths found for complexes with first and third series transition metals. Correlation between shortening of the phosphorus-fluorine bonds and widening of the F-P-F angles in the complexes is also noticeable, although more data are required to confirm the trend.

The nickel-phosphorus bond lengths found in tetrakis(trifluorophosphine)-nickel<sup>1,2</sup> (2.10 or 2.11 Å) are at least 0.12 Å shorter than those usually found in tetrahedral nickel-phosphine complexes<sup>18,19</sup>, whereas the platinum-phosphorus bond in tetrakis(trifluorophosphine)platinum<sup>1</sup> (2.23 Å) is only slightly shorter than those in many square-planar platinum-phosphine complexes<sup>20,21</sup>, that is about the length that would be expected for a tetrahedral complex. It is therefore interesting to note that the molybdenum-phosphorus distance found in the present study (2.37 Å) is some 0.08 to 0.13 Å shorter than values reported for other molybdenum-phosphine complexes<sup>22,23</sup>. It may be inferred that replacement of alkyl or aryl groups on phosphines by fluorine greatly increases the  $\pi$ -acceptor properties of the ligand. It should also be noted that the difference between molybdenum-carbon and molybdenum-phosphorus bond lengths (0.306 Å) is very close to the difference between carbon-carbon and carbon-phosphorus bond lengths in ethane<sup>24</sup> and trimethylphosphine<sup>25</sup> (0.307 Å). This demonstrates well the similarity of carbon monoxide and trifluorophosphine as ligands.

The refined parameters involving the molybdenum pentacarbonyl group agree well with calculated amplitudes of vibration for molybdenum hexacarbonyl<sup>15</sup>, and even better with experimental distances and vibrational amplitudes<sup>14</sup>. In a molecule as complicated as that in the present study, it is normally possible to refine only a fairly small number of amplitudes independently. It is therefore usual to constrain groups of amplitudes to remain at fixed ratios to one another, the groups being selected either on the basis of similar interatomic separations, or on the grounds that the vibrations for several distances may be physically related. The first method often makes refinement easier, but the constraints may be somewhat arbitrary. The latter method, used in the present work, is more meaningful, provided that care is taken to check for strong correlations between refining amplitudes. One such group included the amplitudes of vibration associated with the *trans*-(C<sub>eq</sub>...C<sub>eq</sub>), -(C<sub>eq</sub>...O<sub>eq</sub>) and -(O<sub>eq</sub>...O<sub>eq</sub>) distances, which were fixed at the spectroscopically determined ratios to one another<sup>15</sup>.

TABLE 3  
LEAST SQUARES CORRELATION MATRIX MULTIPLIED BY 1000

	R1	R2	R3	R4	<1	<2	<3	U2	U4	U5	U7	U10	U14	U17	U21	U23	U24	K1	K2	K3
R1	1000	-175	-89	162	34	6	-81	116	-3	254	55	49	-41	44	247	80	71	187	274	114
R2	-175	1000	343	-148	-409	-40	-47	-171	-82	-173	-76	-200	-22	-84	-124	-163	-207	-390	-424	-144
R3	-89	343	1000	-440	-112	312	-348	126	72	-487	30	-444	-227	171	-325	-109	117	43	51	64
R4	162	-148	-440	1000	418	141	-191	-86	1	-10	-55	97	-156	21	-41	1	0	63	66	22
<1	34	-409	-112	418	1000	618	-666	-212	-60	-307	-130	278	-478	152	-348	-126	38	-6	-81	-61
<2	6	-40	312	141	618	1000	-962	-218	-164	-349	-156	258	-671	181	-619	-222	-11	-241	-329	-122
<3	-81	-47	-348	-191	-666	-962	1000	227	151	421	130	-181	730	-214	688	280	19	232	312	114
U2	116	-171	126	-86	-212	-218	227	1000	187	194	168	-281	122	88	206	189	251	508	556	265
U4	-3	-82	72	1	-60	-164	151	187	1000	135	105	-145	56	69	133	126	245	488	360	125
U5	254	-173	-487	-10	-307	-349	421	194	135	1000	91	485	317	-84	546	240	57	294	297	101
U7	55	-76	30	-55	-130	-156	130	168	105	91	1000	-121	142	426	65	-250	98	208	223	105
U10	49	-200	-444	97	278	258	-181	-281	-145	485	-121	1000	-97	-63	67	-21	-198	-210	-286	-158
U14	-41	-22	-227	-156	-478	-671	730	122	56	317	142	-97	1000	-218	780	190	-13	90	110	16
U17	44	-84	171	21	152	181	-214	88	69	-84	426	-63	-218	1000	-202	-218	101	143	148	80
U21	247	-124	-325	-41	-348	-619	688	206	133	546	65	67	780	-202	1000	336	65	273	324	118
U23	80	-163	-109	1	-126	-222	280	189	126	240	-250	-21	190	-218	336	1000	119	248	308	122
U24	71	-207	117	0	38	-11	19	251	245	57	98	-198	-13	101	65	119	1000	458	374	162
K1	187	-390	43	63	-6	-241	232	508	488	294	208	-210	90	143	273	248	458	1000	684	285
K2	274	-424	51	66	-81	-329	312	556	360	297	223	-286	110	148	324	308	374	684	1000	328
K3	114	-144	64	22	-61	-122	114	265	125	101	105	-158	16	80	118	122	162	285	328	1000



The second and third angles in Table 2 indicate that the equatorial carbonyl groups are bent away from the trifluorophosphine ligand, despite the fact that no F...C and F...O interactions are less than 3.26 or 3.80 Å respectively. Equatorial carbonyl groups are usually bent (at the metal) away from the stronger  $\pi$ -acceptor axial ligand, and so trifluorophosphine would appear to be marginally better as an acceptor than a carbonyl group. However, both angles involving the carbonyl groups are strongly dependent on the precise forms of the shrinkage corrections applied, and it should be remembered that the corrections used are only approximations.

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