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REACTIONS OF FLUORINATED ALKYNES WITH THE TUNGSTEN HYDRIDE $[(\eta^5\text{-}C_5H_5)(CO)_3WH]$

II *. PHOSPHINE AND PHOSPHITE SUBSTITUTION REACTIONS AND THE X-RAY STRUCTURES OF THE η^3-ACRYLOYL COMPLEXES $[(\eta^5\text{-}C_5H_5)(CO)L\overline{WC(O)C(CF_3)}{=}C(CF_3)H]$, L = CO, $P(OMe)_3$

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Summary

Insertion of hexafluorobut-2-yne into the W–H bond of the complex $[(\eta^5\text{-}C_5H_5)(CO)_3WH]$ yields the η^1-vinyl complex $[(\eta^5\text{-}C_5H_5)(CO)_3WC(CF_3){=}C(CF_3)H]$ (I). Migration and insertion of CO into the metal–vinyl bond gives the η^3-acryloyl complex $[(\eta^5\text{-}C_5H_5)(CO)_2\overline{WC(O)C(CF_3)}{=}C(CF_3)H]$ (II) for which the crystal structure has been determined. Phosphites and phosphines (L = $P(OMe)_3$, PPh_3, PMe_3, PMe_2Ph, PPh_2H) displace CO from II to give IIIa in which the η^3-acryloyl structure is conserved and CO is adjacent to the acryloyl carbonyl group, as shown by an X-ray analysis of $IIIa_1$, the product with $P(OMe)_3$. Heating IIIa generates the η^1-vinyl complexes $[(\eta^5\text{-}C_5H_5)(CO)_2LWC(CF_3){=}C(CF_3)H]$ (IV) whereas prolonged photolysis of IIIa yields isomeric η^3-acryloyl compounds (IIIb) in which the phosphorus donor ligands are now adjacent to the acryloyl carbonyl groups.

Introduction

The insertion of alkynes into hydrido–transition metal bonds is believed to form part of the mechanism of various reactions which are catalysed by transition metals [2]. The products of such insertion reactions, involving alkynes and metal carbonylhydrides [3,4] or -alkyls [5,6] have been characterised; a particularly rich insertion chemistry is displayed by methanethiolates, which form five- and six-membered

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* For part I see Ref. 1.

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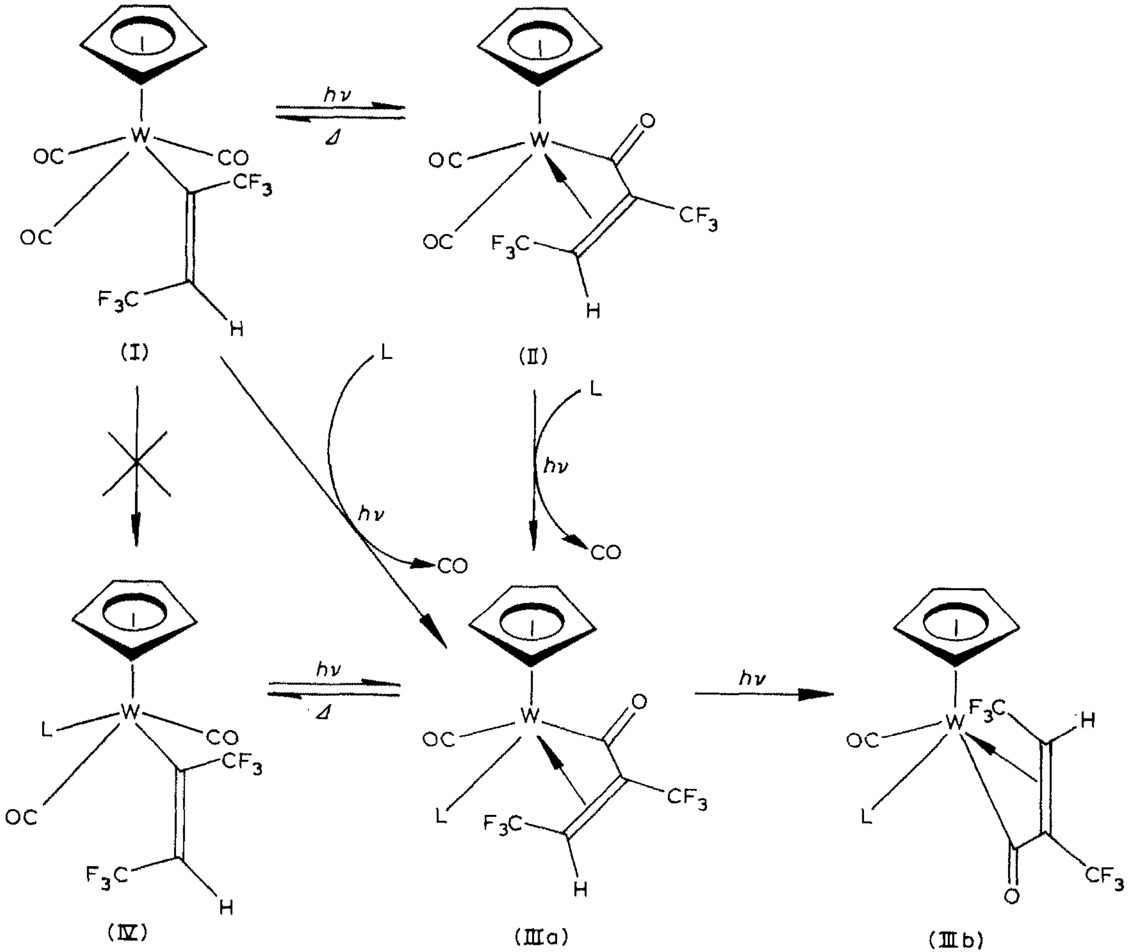


SCHEME 1

heterocycles [1,7,8]. In a previous paper [1] we described the reaction of hexafluorobut-2-yne with the tungsten hydride [(η^5-C_5H_5)(CO)$_3$WH] in the presence of dimethyl disulphide to give the vinyl derivative (I) and its isomer (II) which was tentatively identified as an acryloyl complex (see Scheme 1) (the molybdenum analogues of I and II were similarly obtained from [(η^5-C_5H_5)(CO)$_3$MoH]). More recently Brix and Beck have described insertions of aminoalkynes into the M–H bonds of metal carbonyl-hydrides to give η^1-vinyl and η^3-acryloyl complexes [9].

Results and discussion

The thermal or photolytic reaction of the hydride [(η^5-C_5H_5)(CO)$_3$WH] with hexafluorobut-2-yne, in the presence of dimethyl disulphide, gives the insertion products I and II. I is mainly obtained in the thermal reaction whereas II is produced in better yield photolytically. Photolysis of I gives II in good yield. On heating II is transformed back into I. I has previously been characterised as a vinyl derivative with a *trans* configuration about the C=C bond [1] and an X-ray analysis (see Fig. 1 and Table 1) now confirms that II is an η^3-acryloyl compound.

Photolysis of 1/1 mixtures of II and phosphine or phosphite (L) in tetrahydrofuran gives the complexes [(η^5-C_5H_5)(CO)$_2$LW(CF_3)$_2C_2$H] (IIIa) (L = P(OMe)$_3$, IIIa$_1$; L = PPh$_3$, IIIa$_2$; L = PMe$_3$, IIIa$_3$; L = PMe$_2$Ph, IIIa$_4$; L = PPh$_2$H, IIIa$_5$) in yields varying from 30 to 71%.

The new complexes IIIa have been characterised by an X-ray diffraction study of the trimethylphosphite derivative IIIa$_1$ and by spectroscopy. The X-ray study (Fig. 2

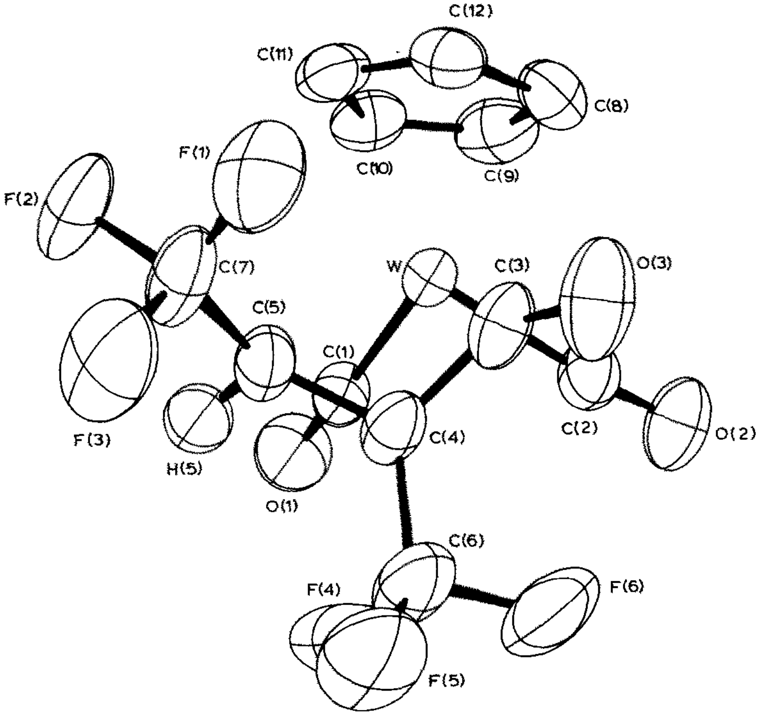


Fig. 1. An ORTEP drawing of II. Here, and in Fig. 2, thermal ellipsoids display 50% probability. The cyclopentadienyl hydrogen atoms are omitted.

TABLE 1

SELECTED DISTANCES (Å) AND ANGLES (°) IN II

Bond lengths			
W–C(1)	2.022(6)	C(1)–O(1)	1.139(8)
W–C(2)	2.015(5)	C(2)–O(2)	1.114(7)
W–C(3)	2.112(5)	C(3)–O(3)	1.195(7)
W–C(4)	2.239(5)	C(3)–C(4)	1.434(9)
W–C(5)	2.239(5)	C(4)–C(5)	1.430(7)
W–C(Cp)	2.271(8)–2.340(6)	C(4)–C(6)	1.478(9)
C–C(Cp)	1.397(11)–1.421(9)	C(5)–C(7)	1.494(8)
C–F	1.310(7)–1.343(7)	C(5)–H(5)	0.97(6)
Bond angles			
C(1)–W–C(2)	84.9(2)	W–C(3)–O(3)	143.2(5)
C(1)–W–C(4)	89.5(2)	W–C(3)–C(4)	75.6(3)
C(2)–W–C(4)	89.1(2)	O(3)–C(3)–C(4)	140.3(5)
W–C(1)–O(1)	177.5(5)	C(3)–C(4)–C(5)	111.7(5)
W–C(2)–O(2)	177.5(6)	C(3)–C(4)–C(6)	124.6(5)
C–C–C(Cp)	107.0(6)–109.0(6)	C(5)–C(4)–C(6)	123.8(6)
C–C–F	111.1(6)–115.9(5)	C(4)–C(5)–C(7)	118.4(5)
F–C–F	104.7(5)–107.1(5)	C(4)–C(5)–H(5)	118(4)
		C(7)–C(5)–H(5)	108(4)
Torsion angles			
C(1)–W–C(4)–C(5)	−71.9(3)	C(2)–W–C(4)–C(3)	78.0(3)
C(1)–W–C(4)–C(6)	46.9(6)	C(2)–W–C(4)–C(6)	−38.0(6)
O(3)–C(3)–C(4)–C(5)	132.9(8)	C(7)–C(5)–C(4)–C(3)	−63.4(6)
O(3)–C(3)–C(4)–C(6)	−47.3(11)	C(7)–C(5)–C(4)–C(6)	116.7(6)

and Table 2) establishes that the phosphorus donor ligand displaces in II the terminal carbonyl which is *trans* to the η^3-acryloyl carbonyl function, and that IIIa$_1$ is also an η^3-acryloyl derivative. The spectroscopic data for the other complexes IIIa are fully consistent with this η^3-acryloyl structure. For example, the characteristic IR absorptions of the acryloyl carbonyls are found near 1700 cm^{-1} [3,9].

On heating complexes IIIa at 50°C in tetrahydrofuran for about 20 h new vinyl complexes $[(\eta^5\text{-}C_5H_5)(CO)_2LWC(CF_3){=}C(CF_3)H]$ (IV) ($L = P(OMe)_3$, IV$_1$; $L = PPh_3$, IV$_2$; $L = PMe_3$, IV$_3$; $L = PMe_2Ph$, IV$_4$) are formed in good yields. Complexes IV have been fully characterised by spectroscopy. Only terminal metal carbonyl absorptions are found in the IR spectra, which also show weak absorption at 1610 cm^{-1} attributable to olefinic C=C bonds. In the ^{1}H NMR spectra, the olefinic resonances are found at low field and the chemical shifts (ca. 6.8 ppm/TMS) are in the range expected for alkenyl protons. The observation of only one doublet ($J(^{31}P-^1H)$ 1.5 Hz) for the cyclopentadienyl protons shows that a single isomer is formed – that in which the phosphorus ligand is *trans* to the vinylic group [10]. The *trans* configuration of the trifluoromethyl groups relative to the vinylic C=C bond (cf. I) is shown by characteristic coupling constants in the ^{1}H and ^{19}F NMR spectra [1]. Photolysis of IV regenerates the acryloyl complexes IIIa in good yields.

Photolysis in tetrahydrofuran of the complexes IIIa gives rise to a new series of compounds IIIb. Mass spectra and spectroscopic data suggest that IIIa and IIIb are geometric isomers, with the phosphorus donor ligand *trans* to the acryloyl carbonyl

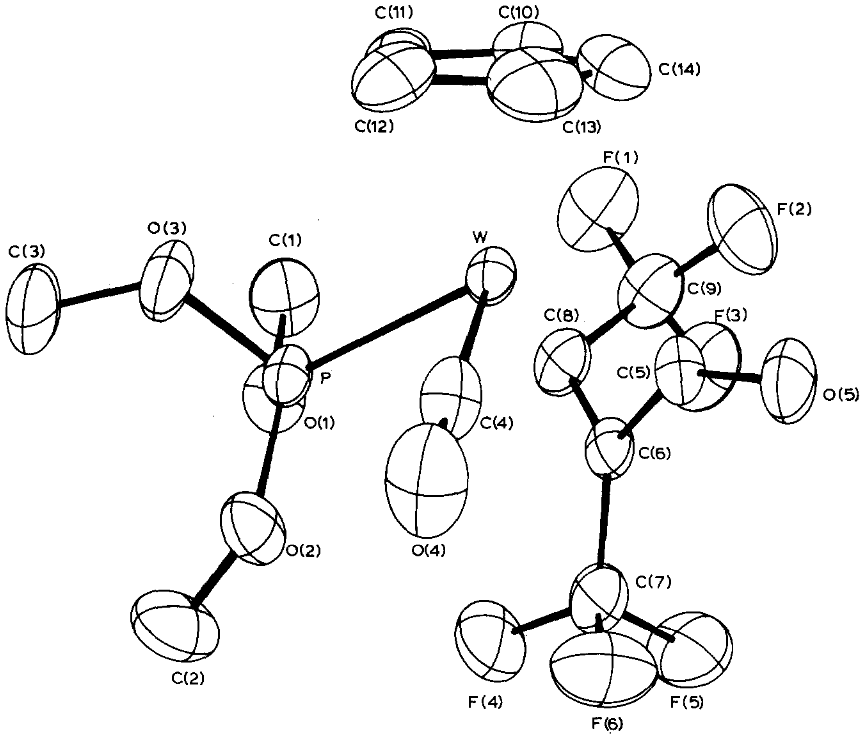


Fig. 2. A perspective view of $IIIa_1$. Hydrogen atoms are omitted.

function in IIIa but *cis* to it in IIIb. The *cis* arrangement of the phosphorus donor ligand and acryloyl carbonyl in IIIb is established by the observation of a characteristic doublet ($J(^{31}P-^{1}H)$ 1.5 Hz) for the cyclopentadienyl proton resonances [10]. However, there is no observable $J(^{31}P-^{1}H)$ coupling constant in the olefinic proton signal of IIIb, which occurs at lower field than the corresponding olefinic signal for IIIa. This may reflect the relative *trans* influences of carbonyl and phosphorus ligands on the coordination to tungsten of the C=C double bond. It is interesting that IIIb does not seem to be formed directly from II on photolysis with the phosphorus donor ligand. However, IIIb appears to be more stable than IIIa and the photolytic isomerisation of IIIa to IIIb is irreversible.

Complexes IV, IIIa, and IIIb are not formed in the direct reaction of the hydride $[(\eta^5\text{-}C_5H_5)(CO)_2LWH]$ ($L = PPh_3$ or $P(OMe)_3$) with hexafluorobut-2-yne either in the presence or in the absence of dimethyl disulphide. No reaction was detected up to 50°C and the main feature of the photolytic reaction is the loss of the phosphorus donor ligand; the only products of that reaction are $[\{(\eta^5\text{-}C_5H_5)W(CO)_2\}_2(\mu\text{-}CF_3C_2CF_3)]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2\overline{WC(O)C(CF_3)\!=\!C}(CF_3)H]$ (II) identified spectroscopically [1]. Attempts to obtain IV directly by heating the vinyl complex I with phosphite were unsuccessful. However, with phosphine the reaction gave rise to a mixture of IIIa and IV in low yields. Photolysis of I with phosphines gave only the acryloyl complexes IIIa in good yields.

The structural similarity between II and $IIIa_1$ is apparent from Figs. 1 and 2. In

TABLE 2

SELECTED DISTANCES (Å) AND ANGLES (°) IN $IIIa_1$

Bond lengths			
W–P	2.453(2)	C(4)–O(4)	1.162(8)
W–C(4)	1.977(6)	C(5)–O(5)	1.210(7)
W–C(5)	2.091(5)	C(5)–C(6)	1.450(7)
W–C(6)	2.251(5)	C(6)–C(8)	1.431(8)
W–C(8)	2.244(5)	C(6)–C(7)	1.467(8)
W–C(Cp)	2.274(7)–2.356(7)	C(8)–C(9)	1.490(8)
C–C(Cp)	1.392(10)–1.410(10)	P–O	1.571(4)–1.595(5)
C–F	1.327(8)–1.357(7)	O–CH_3	1.421(8)–1.445(9)
Bond angles			
P–W–C(4)	83.2(2)	W–C(4)–O(4)	178.1(5)
P–W–C(6)	93.0(2)	W–C(5)–O(5)	144.7(4)
C(4)–W–C(6)	89.0(2)	W–C(5)–C(6)	76.6(3)
W–P–O	107.9(2)–123.1(2)	O(5)–C(5)–C(6)	137.3(5)
O–P–O	99.7(3)–106.5(3)	C(5)–C(6)–C(8)	111.2(5)
P–O–C	120.9(4)–127.0(5)	C(5)–C(6)–C(7)	124.3(5)
C–C–C(Cp)	106.5(7)–109.4(6)	C(7)–C(6)–C(8)	124.5(5)
C–C–F	111.6(5)–115.8(5)	C(6)–C(8)–C(9)	118.5(5)
F–C–F	104.1(5)–106.7(6)		
Torsion angles			
P–W–C(6)–C(8)	73.0(3)	C(4)–W–C(6)–C(5)	–78.0(3)
P–W–C(6)–C(7)	–47.0(5)	C(4)–W–C(6)–C(7)	36.1(6)
O(5)–C(5)–C(6)–C(8)	–136.6(9)	C(7)–C(6)–C(8)–C(9)	–113.8(7)
O(5)–C(5)–C(6)–C(7)	40.9(7)		

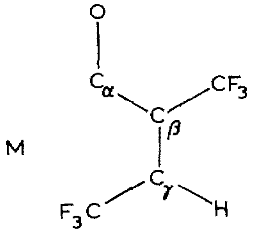
both complexes the tungsten coordination can be described as square-pyramidal, with apical C_5H_5 and two *cis* basal sites occupied by the η^3-acryloyl ligand. Alternatively, the tungsten atoms can be regarded as pseudooctahedral, with C_5H_5 occupying three *facial* sites and CO, L (CO in II, $P(OMe)_3$ in $IIIa_1$) and η^3-acryloyl taking up the remaining three. The angles subtended at the metal atoms by CO, L, and the central carbon atom C_β of the η^3-acryloyl group (see Va) are perhaps more in keeping with the second description, particularly the OC–W–L angles (84.9(2) in II, 83.2(2)° in $IIIa_1$, cf. *cis* angles of 75° typical of square-pyramidal complexes [11]).

However the metal coordination in II and $IIIa_1$ is described, the tungsten atoms in both complexes are chiral, prompting comparisons with asymmetric complexes of the types $[(\eta^5\text{-}C_5H_5)M(CO)_2\ (L\text{–}L')]$ [12] and $[(\eta^5\text{-}C_5H_5)M(CO)L(\eta^3\text{-allyl})]$ [13]. Additionally, the γ-carbon atom of the acryloyl ligand becomes chiral on coordination to tungsten. The existence of diastereoisomers may explain why multiple terminal and acryloyl carbonyl absorptions appear in the solution IR spectra of IIIa. However, the ^1H and ^{19}F NMR spectra between -90 and 40°C in various solvents ($CDCl_3$, $(CD_3)_2CO$, C_6D_6) show only one signal per substituent, indicating fast equilibration on the NMR timescale between the various isomeric forms. The solution spectra of IIIb (but not those of II) show similar effects. An alternative explanation for the complex carbonyl solution spectra of IIIa and IIIb is fast *endo-exo* conformational exchange of the η^3-acryloyl ligand, analogous to that known to occur in η^3-allyl complexes [13]. Variable temperature NMR studies suggest that $[(\eta^5\text{-}C_5H_5)(CO)_2Mn(Ph_2C{=}C{=}O)]$ behaves in a similar way to IIIa and IIIb [14].

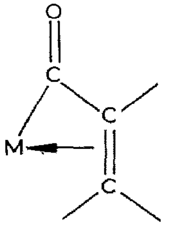
The W–C(carbonyl) bond length in $IIIa_1$ is shorter (by 0.04 Å) than those in II indicating enhanced W → CO back-donation in the species with fewer carbonyl ligands. The W–P distance of 2.453(2) Å in $IIIa_1$ is typical for $W\text{–}P(OR)_3$ bonds [15].

The most interesting feature of the structural results for II and $IIIa_1$ relates to the η^3-acryloyl ligands. Although complexes containing η^3-acryloyl ligands were first reported more than twenty years ago [16] few have been characterised crystallographically. Of these only the $[(OC)_3FeC(O)C(CO_2Me){=}C(CO_2Me)H]^-$ anion would appear to be closely comparable to II and $IIIa_1$ [3].

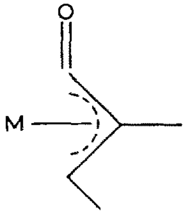
Up to this point in the argument, we have tacitly assumed that the extreme valence bond structure (Vb), with an η^1-acyl- and η^2-alkene-metal linkage, is adequate to describe η^3-acryloyl-metal bonding. Within a valence bond formalism the alternative would appear to be the η^3-allyl grouping (Vc). There has already been some disagreement [3,9] as to whether Vb or Vc is more appropriate for the description of the η^3-acryloyl-metal bonding. In our view neither is satisfactory but the bonding in II and $IIIa_1$ can conveniently be discussed in terms of deviations from Vb and Vc.



(Va)



(Vb)



(Vc)

In both II and IIIa the three C–C bonds radiating from C_β are coplanar, and the C_α–C_β and C_β–C_γ bonds are equal in length, lying between 1.430(7) and 1.450(7) Å. These features, also found in $[(OC)_3FeC(O)C(CO_2Me){=}C(CO_2Me)H]^-$ [3], are more in keeping with Vc. However, the C_α–C_β–C_γ angles in II, $IIIa_1$, and the iron complex, respectively 111.7(5), 111.2(5), and 110.4(4)°, are appreciably less obtuse than corresponding angles in η^3-allyl complexes which are typically 115–125° [17]. However, this may arise from the presence of electron-withdrawing substituents on C_β in the acryloyl complexes rather than from a fundamental difference in the electronic nature of η^3-acryloyl and η^3-allyl ligands.

The least satisfactory aspect of models Vb and Vc relates to the torsion angles about the C_α–C_β and C_β–C_γ bonds. The F_3C–C_β–C_α–O torsion angles of −47.3(11) and 40.9(7)° imply rather weak p_π–p_π overlap across the C_α–C_β bonds. The F_3C–C_β–C_γ–CF_3 torsion angles (116.7(6) and −113.8(7)°) approach the 90° value which would preclude π-overlap across C_β–C_γ. An MO treatment is needed to discuss structure and bonding in η^3-acryloyl complexes adequately.

In both complexes the tungsten atom is equidistant from C_β and C_γ. The W–C_β and W–C_γ bond lengths are 2.239(5)–2.251(5) Å, whereas the W–C_α distances (2.112(5) and 2.091(5) Å) are appreciably shorter. Indeed the W–C_α bond lengths seem usually short for W–C_{sp^2} single bonds, which are normally 2.19 Å or more

[11,18,19]. The pattern of long-long-short M–C distances in the η^3-acryloyl complexes contrasts with the typical η^3-allyl long-short-long pattern [17]. The similarity between corresponding W–C(acryloyl) distances in II and $IIIa_1$ extends to the C_α–O bond lengths which imply bond orders close to two. Evidently the substitution of $P(OMe)_3$ for CO *trans* to C_α has little effect on the geometry of the W–η^3-acryloyl interaction. This similarity also includes the orientations of the acryloyl ligands in II and $IIIa_1$: corresponding torsion angles across the W–C_β bonds agree to within 2° in the two complexes. It thus appears that the orientational preference of the η^3-acryloyl ligand in the symmetrical complex II is the same as that in the unsymmetrical complex $IIIa_1$, as we have recently found for molybdenum-alkyne compounds [20].

In conclusion, the present study establishes that incorporation of terminal carbonyl groups in η^3-acryloyl ligands is an easily reversible process. The differences between the reactions we have described and those which aminoacetylene derivatives undergo [9] probably arise from the differing electronic nature of the alkyne substituents. For the amino derivatives the corresponding vinylic complexes are isolated with difficulty and the acryloyl derivatives are stable only at low temperature. The acryloyl compounds give carbene complexes or decarbonylate on heating [9].

Experimental

The complexes I and II were prepared via published procedures [1]. All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were distilled by standard methods and deoxygenated before use. Chromatographic separations and purifications were effected using Florisil. Phosphines, phosphites and hexafluorobut-2-yne were commercial products. A Hanau TQ 150 mercury vapour lamp placed approximately 10 cm from a Pyrex vessel was used for irradiation.

Physical measurements

NMR spectra were recorded at room temperature on a JEOL FX 100 spectrometer (^1H and ^{13}C in ppm with reference to $SiMe_4$, ^{19}F in ppm with reference to CCl_3F and ^{31}P in ppm with reference to external H_3PO_4 in D_2O) (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). IR spectra were recorded on a PYE-UNICAM SP 2000 spectrophotometer, and mass spectra on MS 12 (Glasgow) and Mass-1500 RIBERMAG (Brest) mass spectrometers. Analyses were performed by the Centre de Microanalyse du CNRS, Lyon.

Preparation of complexes $[(\eta^5\text{-}C_5H_5)(CO)L\overline{WC(O)C(CF_3)\text{=}}C(CF_3)H]$ *(IIIa)*

Method 1

In a typical preparation a solution of complex II (2 mmol in 30 cm^3 THF) was added to an excess of phosphite or phosphine (~ 4 mmol in 20 cm^3 THF). The reaction mixture was stirred and irradiated for 18 h and then concentrated to dryness. After extraction with dichloromethane the solution was chromatographed using 20/1 CH_2Cl_2/THF as eluent to give complexes IIIa which were recrystallised from hexane/CH_2Cl_2.

$IIIa_1$ ($L = P(OMe_3)$). Yellow solid, yield 51%. Found: C, 29.2; H, 2.4; F, 18.5; P, 5.2; W, 29.4. $C_{14}H_{15}F_6O_5PW$ calcd.: C, 28.4; H, 2.5; F, 19.2; P, 5.2; W, 31.0%. IR

(CH_2Cl_2): ν(CO) 2000vs, 1992sh; ν(C(O)) 1745s, 1725s, 1695sh. ^1H NMR (CD_2Cl_2): 5.15 (s, C_5H_5); 3.65 (d, $P(OMe)_3$, $^3J(P{-}H)$ 11.1 Hz); 3.30 (m, H, $J(F{-}H_{gem})$ 8 Hz, $^3J(P{-}M{-}H)$ 14 Hz). ^{31}P NMR (CD_2Cl_2): 134.3 ($J(W{-}P)$ 393 Hz). ^{19}F NMR (CD_2Cl_2): 59.1(s); 55.4 (d, $J(F{-}H_{gem})$ 8 Hz). ^{13}C NMR (CD_2Cl_2): 248.7 (s-br,CO); 223.0 (d,CO,$^2J(P(M)C)$ 16.5 Hz); 131.4 (q,CF_3,$^1J(C{-}F)$ 273 Hz); 127.7 (q,CF_3, $^1J(C{-}F)$ 275 Hz); 89.3 (s,C_5H_5): 54.0 (m,$P(OMe)_3$, $^1J(C{-}H)$ 147.7 Hz, $^2J(C{-}P)$ 6.6 Hz); 28.9 (m,CH,$^2J(C{-}F)$ 36.3 Hz, $^3J(C{-}P)$ 10 Hz, $^1J(C{-}H)$ 148.4 Hz). Mass spectrum m/e: $[M]^+ = 592$.

$IIIa_2$ ($L = PPh_3$). Orange solid, yield 31%. Found: C, 47.6; H, 2.8; F, 15.6; P, 4.2; W, 24.7. $C_{29}H_{21}F_6O_2PW$ calcd.: C, 47.7; H, 2.9; F, 15.6; P, 4.2; W, 25.2%. IR (CH_2Cl_2): ν(CO) 1980vs, 1970sh; ν(C(O)) 1740sh, 1725s, 1690m. ^1H NMR (CD_2Cl_2): 7.44 (m, Ph); 4.85 (s,C_5H_5); 2.78 (dq,H,$J(F{-}H_{gem})$ 7.9 Hz, $^3J(P(M)H)$ 12.5 Hz). ^{31}P NMR: 20.4 ($J(W{-}P)$ 227 Hz). ^{19}F NMR $(CDCl_3)$ 58.67(s); 56.84 (d,$J(F{-}H_{gem})$ 8.0 Hz).

$IIIa_3$ ($L = PMe_3$). Yellow solid, yield 32%. Found: C, 31.1; H, 2.8; F, 20.1; P, 5.2; W, 32.3. $C_{14}H_{15}F_6O_2PW$ calcd.: C, 30.9; H, 2.8; F, 20.9; P, 5.7; W, 33.7%. IR (CH_2Cl_2): ν(CO) 1975vs, 1965sh; ν(C(O)) 1725s, 1685s. ^1H NMR (CD_2Cl_2): 5.08 (s,C_5H_5); 2.95 (dq,H,$J(F{-}H_{gem})$ 7.5 Hz, $^3J(P(M)H)$ 14 Hz); 1.51 (d,PMe_3, $^2J(P{-}H)$ 7.5 Hz). ^{31}P NMR $(CDCl_3)$: −34.18(s). ^{19}F NMR $(CDCl_3)$: 58.35(s); 57.30(d,$J(F{-}H_{gem})$ 7.5 Hz). Mass spectrum m/e: $[M]^+ = 544$.

$IIIa_4$ ($L = PMe_2Ph$). Orange solid, yield 48%. Found: C, 37.9; H, 2.8; F, 18.1. $C_{19}H_{17}F_6O_2PW$ calcd.: C, 37.7; H, 2.8; F, 18.8%. IR (CH_2Cl_2): ν(CO) 1975vs, 1968sh; ν(C(O)) 1730s, 1720sh, 1690m. ^1H NMR $(CDCl_3)$: 7.48 (m,Ph); 4.91 (s,C_5H_5); 2.90 (dq,H,$J(F{-}H_{gem})$ 7.5 Hz, $^3J(P{-}(M){-}H)$ 13.7 Hz); 1.87 (d,Me, $^2J(P{-}H)$ 7.5 Hz); 1.70 (d,Me,$^2J(P{-}H)$ 7.5 Hz). ^{31}P NMR $(CDCl_3)$: −21.91(s). ^{19}F $(CDCl_3)$: 58.68(s); 56.17 (d,$J(F{-}H_{gem})$ 7.5 Hz).

$IIIa_5$ ($L = PPh_2H$). Yellow-orange solid, yield 71%. Found: C, 40.8; H, 2.6; F, 16.2; P, 4.3. $C_{23}H_{17}F_6O_2PW$ calcd.: C, 42.2; H, 2.6; F, 17.4; P, 4.7%. IR (CH_2Cl_2): ν(CO) 1985vs; ν(C(O)) 1732s, 1720sh, 1690m. ^1H NMR $(CDCl_3)$: 7.48 (m,C_5H_5); 6.95 (d,PPh_2H, $^1J(P{-}H)$ 370 Hz); 5.02 (s,C_5H_5); 2.98 (dq,H, $J(F{-}H_{gem})$ 7.5 Hz, $^3J(P{-}(M){-}H)$ 14.3 Hz). ^{31}P NMR $(CDCl_3)$: −4.6 ($J(W{-}P)$ 373 Hz). ^{19}F NMR: 58.9(s); 56.7 (d, $J(F{-}H_{gem})$ 7.5 Hz).

Method 2

Complexes IIIa could also be obtained by photolysis of a 1/1 mixture of derivative I and the appropriate ligand. The yields are as good as in method 1 (for instance: 60% when $L = P(OMe)_3$).

Preparation of complexes $[(\eta^5\text{-}C_5H_5)(CO)_2LWC(CF_3){=}C(CF_3)H]$ (IV)

Method 1

The acryloyl complexes IIIa were warmed in tetrahydrofuran at 50°C for about 20 h. The reaction mixture was chromatographed and eluted with hexane/CH_2Cl_2 2/1. Complexes IV were obtained in 42–50% yield.

IV_1 ($L = P(OMe)_3$). Yellow solid. IR (CH_2Cl_2): ν(CO) 1980s, 1895vs; ν(C=C) 1608w.

IV_2 ($L = PPh_3$). Yellow solid. IR (CH_2Cl_2): ν(CO) 1970s, 1875vs; ν(C=C) 1610w. ^1H NMR $(CDCl_3)$: 7.42 (m,C_6H_5); 6.95 (m,H); 4.96 (d,C_5H_5,$J(P{-}H)$ 1.5

Hz). ^{31}P NMR ($CDCl_3$): -5.38(s). ^{19}F NMR ($CDCl_3$): 60.13(s); 57.32 (d, $J(F-H_{gem})$ 9.8 Hz).

IV_3 ($L = PMe_3$). Yellow solid. Found: C, 32.4; P, 5.8; W, 33.1. $C_{14}H_{15}F_6O_2PW$ calcd.: C, 30.9; P, 5.7; W, 33.8%. IR ($CDCl_3$): ν(CO) 1960s, 1870vs; ν(C=C) 1610w. ^{1}H NMR ($CDCl_3$); 6.87 (qq, H, $J(F-H_{gem})$ 9.4 Hz, $J(F-H_{cis})$ 1.9 Hz, ^3J(P-(M)-H) 2.2 Hz); 5.10 (d,C_5H_5, J(P-H) 2.5 Hz); 1.72(d,CH_3,^2J(P-H) 9.4 Hz). ^{19}F NMR ($CDCl_3$): 53.0 (q, J(F-F) 2.0 Hz); 50.0 (d, $J(F-H_{gem})$ 9.4 Hz). Mass spectrum m/e: $[M]^+ = 544$.

IV_4 ($L = PMe_2Ph$). Yellow solid. Found: C, 38.1; H, 2.9; F, 18.1; P, 5.1; W, 29.4. $C_{19}H_{17}F_6O_2PW$ calcd.: C, 37.7; H, 2.8; F, 18.8; P, 5.1; W, 30.3%. IR (CH_2Cl_2): ν(CO) 1960s, 1865vs; ν(C=C) 1610w. ^{1}H NMR ($CDCl_3$): 7.5 (m,C_6H_5); 6.85 (m,H,$J(F-H_{gem})$ 9.4 Hz); 4.93 (d,C_5H_5,J(P-H) 2.5 Hz); 2.04 (d,CH_3,^2J(P-H) 9.4 Hz). ^{31}P NMR ($CDCl_3$): -5.8(s). ^{19}F NMR ($(CD_3)_2CO$): 61.7 (m, J(F-F) 1.8 Hz); 59.1(d, J(F-H) 9.4 Hz).

Method 2

On heating I (1.2 mmol) in tetrahydrofuran at 50°C with an equimolecular amount of phosphine for 40 h, complex IV is formed in a low yield (8–30%) for $L = PMe_2Ph$ and PPh_3.

Preparation of complexes $[(\eta^5\text{-}C_5H_5)(CO)LWC(O)C(CF_3)=C(CF_3)H]$ (IIIb)

A solution of complex IIIa (0.6 mmol in 30 cm^3 THF) was stirred and irradiated for about 30 h. The solvent was evaporated and the product dissolved in the minimum of dichloromethane for chromatography. The products were eluted with dichloromethane or a mixture of dichloromethane and tetrahydrofuran (20/1). Only $IIIb_5$ has been obtained pure, the other complexes IIIb could not be separated from small amounts of starting materials IIIa.

$IIIb_1$ ($L = P(OMe)_3$). Yellow solid, yield 65%. IR (CH_2Cl_2): ν(CO) 1995vs; ν(C(O)) 1735s, 1725sh, 1690w. ^{1}H NMR ($(CD_3)_2CO$): 5.33 (d,C_5H_5,J(P-H) 1.3 Hz); 3.76 (d,CH_3,^3J(P-H) 11.4 Hz); 3.19 (q,H,$J(F-H_{gem})$ 7.8 Hz). ^{31}P NMR ($CDCl_3$): 131.0(s). ^{19}F ($(CD_3)_2CO$): 62.47(s); 57.30 (d, $J(F-H_{gem})$ 8.3 Hz).

$IIIb_2$ ($L = PPh_3$). This compound could not be identified.

$IIIb_3$ ($L = PMe_3$). Orange solid, yield 25%. IR (CH_2Cl_2): ν(CO) 1975vs; ν(C(O)) 1730s, 1720sh, 1705sh, 1688m. ^{1}H NMR ($CDCl_3$): 5.05 (d,C_5H_5, J(P-H) 1.5 Hz); 3.41 (q,H, ^3J(P-M-H) 7.5 Hz); 1.58 (d,CH_3,^2J(P-H) 9 Hz). ^{31}P NMR ($CDCl_3$): -33.3(s). ^{19}F NMR ($CDCl_3$): 59.81(s); 57.50 (d, $J(F-H_{gem})$ 9 Hz).

$IIIb_4$ ($L = PMe_2Ph$). Red-orange solid, yield 35%. IR (CH_2Cl_2): ν(CO) 1970vs; ν(C(O)) 1730s, 1708sh, 1690m. ^{1}H NMR ($CDCl_3$): 7.50 (m,C_6H_5); 4.66 (d,C_5H_5,J(P-H) 1.5 Hz); 3.40 (q,H,$J(F-H_{gem})$ 8.25 Hz); 1.88 (d,CH_3,^2J(P-H) 9 Hz; 1.80(d,CH_3,^2J(P-H) 9 Hz). ^{31}P NMR: -19.68 (^1J(W-P) 297 Hz). ^{19}F NMR ($CDCl_3$): 59.72(s); 57.48 (d, $J(F-H_{gem})$ 8.3 Hz).

$IIIb_5$ ($L = PPh_2H$). Orange-yellow solid, yield 40%. Mass spectrum m/e: $[M]^+$ 654 (parent: 654); $[M-CO]^+$ 626; $[M-2CO]^+$ 598. IR (CH_2Cl_2): ν(CO) 1990vs, 1985sh; ν(C(O)) 1730s, 1725sh, 1710m, 1690m,br. ^{1}H NMR ($CDCl_3$): 7.48 (m,C_6H_5); 7.07 (d,HPPh$_2$,^1J(P-H) 381 Hz); 4.94 (d,C_5H_5,J(P-H) 2.2 Hz); 3.45 (q,H,$J(CF_3-H_{gem})$ 7.9 Hz). ^{31}P NMR ($CDCl_3$): -2.97 (J(W-P) 292 Hz). ^{19}F NMR ($CDCl_3$): 59.23(s); 57.72(d, $J(CF_3-H_{gem})$ 7.9 Hz). ^{13}C NMR ($CDCl_3$): 245.0 (d,C(O), J(P-C) 8.8 Hz); 221.6 (d,CO,J(P-C) 8.8 Hz); 131.0 (m,Ph); 88.5 (s,C_5H_5); 23.4 (q,CHCF_3,^2J(F-C) 38 Hz).

X-Ray analyses of $[(\eta^5\text{-}C_5H_5)(CO)L\overline{WC(O)C(CF_3)}{=}C(CF_3)H]$ *($L = CO$ (II), $L = P(OMe)_3$ ($IIIa_1$))*

Crystals of II and $IIIa_1$ suitable for X-ray diffraction were obtained by recrystallisation from methylene chloride/hexane solution. All measurements (Table 3) were made with Mo-radiation on an Enraf-Nonius CAD4F diffractometer fitted with a graphite monochromator. The orientations of the crystals and the unit cell constants were determined from the setting angles of 25 reflections with $15° \leq \vartheta(\text{Mo-}K_\alpha) \leq 18°$. The intensities of all independent reflections were measured using $\vartheta/2\vartheta$ scans of 1.00° (II) or 0.87° ($IIIa_1$) in ϑ. The crystal orientations and the intensities of two standard reflections were monitored every 2 h during each experiment; no significant change was observed. The integrated intensities were corrected for Lp effects. For II a Gaussian absorption correction was applied; the transmission factors on F^2 were 0.11–0.28. For $IIIa_1$ the shape of the specimen precluded correction.

The structures were solved by the heavy atom method and refined by fullmatrix (II) or block-diagonal ($IIIa_1$) least-squares techniques. For nonhydrogen atoms anisotropic thermal parameters were refined. Isotropic hydrogen atoms were introduced in the final refinement cycles. The refinements converged with $R = 0.033$, $R_w = 0.038$ for II and $R = 0.030$, $R_w = 0.036$ for $IIIa_1$. Apart from regions close to the W atoms no significant maxima were found in the final difference syntheses.

Tables 4 and 5 contain the final atomic parameters. Scattering factors and anomalous dispersion corrections were taken from ref. 21. The calculations were performed on a GOULD SEL 32/27 computer using the GX program system [22]. The observed and calculated structure factors are available from the authors.

(Continued on p. 244)

TABLE 3

CRYSTALLOGRAPHIC DATA FOR THE COMPLEXES II AND $IIIa_1$ (Mo-K_α radiation: λ 0.71069 Å)

	II	$IIIa_1$
Formula	$C_{12}H_6F_6O_3W$	$C_{14}H_{15}F_6PO_5W$
M	496.0	592.1
Space group [a]	$P2_1/n$	$P2_1/n$
a (Å)	8.107(2)	8.975(2)
b (Å)	12.000(2)	13.714(2)
c (Å)	13.994(3)	14.943(3)
β(°)	98.71(2)	99.87(2)
V(Å^3)	1345.7	1812.0
Z	4	4
D_c (g cm^{-3})	2.448	2.170
F(000)	919.8	1127.7
μ(Mo-K_α) (cm^{-1})	82.8	66.8
θ_{max}(Mo-K_α) (°)	30	30
$I > 3\sigma(I)$	3225	3498
Refined parameters	223	304
R	0.033	0.030
R_w	0.038	0.036

[a] Each crystal belongs to the monoclinic system.

TABLE 4

POSITIONAL AND THERMAL PARAMETERS FOR II

	x	y	z	U_{11}/U_{iso} [a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	−0.04487(2)	0.23534(1)	0.16336(1)	0.0362(1)	0.0287(1)	0.0330(1)	−0.0005(1)	0.0021(1)	0.0008(1)
F(1)	0.1906(5)	0.3852(4)	0.3468(3)	0.0711(25)	0.0723(26)	0.0910(29)	−0.0261(21)	−0.0129(21)	−0.0063(19)
F(2)	−0.0196(6)	0.4937(3)	0.3291(3)	0.1194(35)	0.0342(16)	0.0890(28)	−0.0033(15)	0.0041(25)	0.0096(21)
F(3)	0.0307(7)	0.3907(4)	0.4534(3)	0.1737(49)	0.0757(25)	0.0433(19)	−0.0190(17)	0.0024(25)	−0.0032(30)
F(4)	−0.2826(7)	0.1162(4)	0.3475(3)	0.1131(36)	0.0943(33)	0.0977(33)	0.0163(29)	0.0361(29)	−0.0320(28)
F(5)	−0.0798(8)	0.1040(4)	0.4611(3)	0.1927(53)	0.0885(30)	0.0466(21)	0.0207(19)	0.0241(28)	0.0081(35)
F(6)	−0.0844(9)	0.0022(3)	0.3371(4)	0.2177(59)	0.0374(18)	0.0976(32)	0.0070(18)	0.0670(34)	−0.0111(28)
O(1)	−0.4382(6)	0.2401(4)	0.1445(5)	0.0416(23)	0.0764(31)	0.0997(43)	−0.0001(24)	0.0066(25)	0.0013(18)
O(2)	−0.0821(7)	−0.0172(3)	0.1087(4)	0.1097(39)	0.0410(22)	0.1003(37)	−0.0259(23)	0.0203(31)	−0.0013(24)
O(3)	0.2563(6)	0.1258(4)	0.2999(4)	0.0790(32)	0.0714(30)	0.0863(33)	−0.0025(25)	−0.0162(26)	0.0386(26)
C(1)	−0.2965(7)	0.2360(4)	0.1522(4)	0.0476(27)	0.0379(23)	0.0530(27)	−0.0025(18)	0.0060(22)	0.0010(18)
C(2)	−0.0725(7)	0.0727(4)	0.1286(4)	0.0673(33)	0.0412(26)	0.0499(27)	−0.0091(20)	0.0087(25)	−0.0016(22)
C(3)	0.1232(7)	0.1695(4)	0.2797(4)	0.0598(30)	0.0387(23)	0.0518(27)	−0.0021(19)	−0.0091(23)	−0.0094(21)
C(4)	−0.0270(8)	0.1892(4)	0.3197(4)	0.0748(34)	0.0349(23)	0.0359(21)	0.0029(17)	0.0054(22)	0.0045(23)
C(5)	−0.0794(7)	0.3029(4)	0.3082(3)	0.0594(29)	0.0374(22)	0.0397(22)	−0.0029(18)	0.0083(21)	0.0057(21)
C(6)	−0.1177(11)	0.1034(5)	0.3667(4)	0.1127(57)	0.0478(31)	0.0491(31)	0.0095(23)	0.0205(35)	0.0035(33)
C(7)	−0.0321(9)	0.3911(5)	0.3580(4)	0.0913(45)	0.0371(26)	0.0430(26)	−0.0085(19)	−0.0046(28)	0.0071(25)
C(8)	0.1446(9)	0.2451(6)	0.0595(6)	0.0589(37)	0.0653(36)	0.0651(39)	−0.0072(27)	0.0276(42)	−0.0037(28)
C(9)	−0.0116(11)	0.2654(5)	0.0051(4)	0.0832(48)	0.0658(38)	0.0374(26)	−0.0002(22)	0.0120(29)	−0.0203(31)
C(10)	−0.0770(8)	0.3650(5)	0.0374(4)	0.0609(34)	0.0593(33)	0.0559(32)	0.0206(25)	0.0013(27)	−0.0042(26)
C(11)	0.0437(8)	0.4077(4)	0.1116(4)	0.0724(37)	0.0417(26)	0.0589(31)	0.0078(22)	0.0180(28)	−0.0139(25)
C(12)	0.1798(7)	0.3342(5)	0.1263(4)	0.0448(27)	0.0634(33)	0.0611(33)	−0.0008(25)	0.0108(24)	0.0142(24)
H(5)	−0.192(7)	0.320(5)	0.317(4)	0.050(15)					
H(8)	0.197(8)	0.191(6)	0.054(5)	0.075(21)					
H(9)	−0.083(9)	0.217(5)	−0.051(5)	0.074(20)					
H(10)	−0.189(7)	0.388(5)	0.016(4)	0.057(17)					
H(11)	0.008(7)	0.474(5)	0.146(4)	0.061(17)					
H(12)	0.285(10)	0.352(8)	0.162(6)	0.116(30)					

[a] Here and in Table 5 the isotropic and anisotropic temperature factor expressions respectively are $\exp(-8\pi^2 U_{iso}\sin^2\theta/\lambda^2)$ and $\exp(-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}h_ih_ja_i^{\star}a_j^{\star})$.

TABLE 5

POSITIONAL AND THERMAL PARAMETERS FOR IIIa$_1$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.08452(2)	0.25709(1)	0.31133(1)	0.03229(8)	0.02261(7)	0.03270(8)	0.00026(8)	0.01099(7)	0.00273(8)
P	0.04990(15)	0.29135(9)	0.43759(9)	0.0329(7)	0.0306(6)	0.0386(7)	0.031(5)	0.0129(5)	−0.0003(5)
F(1)	−0.1917(5)	0.0554(3)	0.2143(3)	0.059(3)	0.066(3)	0.101(3)	−0.009(2)	−0.0019(2)	−0.020(2)
F(2)	0.0331(5)	0.0464(3)	0.1829(2)	0.095(3)	0.061(2)	0.058(2)	−0.015(2)	0.020(2)	−0.029(2)
F(3)	−0.0394(5)	−0.0554(3)	0.2749(3)	0.080(3)	0.030(2)	0.107(3)	−0.012(2)	0.011(3)	−0.012(2)
F(4)	0.1476(5)	0.0865(3)	0.5210(2)	0.105(4)	0.074(3)	0.048(2)	0.017(3)	0.035(2)	0.015(2)
F(5)	0.2606(6)	−0.0211(3)	0.4563(3)	0.151(5)	0.042(2)	0.064(2)	0.037(3)	0.001(3)	0.010(2)
F(6)	0.3627(5)	0.1180(4)	0.4889(3)	0.067(3)	0.103(3)	0.060(2)	−0.011(3)	−0.001(3)	0.014(2)
O(1)	−0.1850(4)	0.2253(3)	0.4601(3)	0.037(2)	0.054(2)	0.049(2)	−0.006(2)	0.015(2)	0.003(2)
O(2)	0.0551(4)	0.2915(3)	0.5332(3)	0.042(2)	0.061(2)	0.040(2)	−0.000(2)	0.012(2)	−0.007(2)
O(3)	−0.1199(5)	0.3974(3)	0.4232(3)	0.065(3)	0.040(2)	0.068(3)	0.018(2)	0.033(2)	0.003(2)
O(4)	0.3597(5)	0.3528(3)	0.4390(3)	0.047(3)	0.062(3)	0.087(3)	−0.014(2)	0.007(3)	−0.026(2)
O(5)	0.3632(5)	0.1329(3)	0.2734(3)	0.051(3)	0.050(2)	0.063(3)	0.010(2)	0.032(2)	0.002(2)
C(1)	−0.3186(7)	0.2107(6)	0.3944(5)	0.016(3)	0.077(4)	0.077(5)	−0.008(3)	0.004(3)	−0.012(4)
C(2)	0.0105(9)	0.2762(7)	0.6188(4)	0.061(4)	0.132(7)	0.037(3)	0.014(5)	0.016(3)	0.005(4)
C(3)	−0.2040(9)	0.4440(5)	0.4856(5)	0.087(5)	0.061(4)	0.073(5)	0.033(4)	0.033(4)	−0.009(4)
C(4)	0.2570(6)	0.3167(4)	0.3931(4)	0.043(3)	0.033(2)	0.058(3)	−0.001(2)	0.020(3)	−0.005(2)
C(5)	0.2466(6)	0.1502(3)	0.3007(3)	0.038(3)	0.030(2)	0.039(3)	−0.000(2)	0.015(2)	−0.004(2)
C(6)	0.1628(6)	0.1096(3)	0.3668(3)	0.039(3)	0.023(2)	0.036(2)	0.002(2)	0.010(2)	0.001(2)
C(7)	0.2323(7)	0.0744(4)	0.4570(4)	0.057(4)	0.035(3)	0.047(3)	0.008(3)	0.009(3)	0.003(2)
C(8)	0.0044(6)	0.1048(3)	0.3311(4)	0.040(3)	0.025(2)	0.049(3)	−0.002(2)	0.006(2)	−0.003(2)
C(9)	−0.0472(7)	0.0403(4)	0.2516(4)	0.051(4)	0.038(3)	0.068(4)	−0.007(3)	0.004(3)	−0.008(3)
C(10)	−0.0686(8)	0.2719(5)	0.1672(4)	0.061(4)	0.058(3)	0.039(3)	0.011(3)	0.004(3)	0.013(3)
C(11)	−0.0982(7)	0.3507(5)	0.2203(4)	0.060(4)	0.051(3)	0.049(3)	0.018(3)	0.011(3)	0.017(3)
C(12)	0.0351(9)	0.4041(4)	0.2409(4)	0.093(5)	0.033(3)	0.059(4)	0.006(3)	0.013(4)	0.020(3)
C(13)	0.1499(8)	0.3574(5)	0.2032(4)	0.074(5)	0.063(4)	0.057(4)	−0.008(3)	0.023(4)	0.030(3)
C(14)	0.0840(8)	0.2745(5)	0.1579(4)	0.066(4)	0.073(4)	0.035(2)	0.014(4)	0.019(3)	0.016(3)

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