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X-RAY MOLECULAR STRUCTURE OF THE 1:1 ADDUCT OF $[FeH(CO)_4]^-$ AND DIMETHYL ACETYLENEDICARBOXYLATE. η^3-[trans-2,3-BIS(METHOXYCARBONYL)-ACRYLOYL]TRICARBONYLFERRATE

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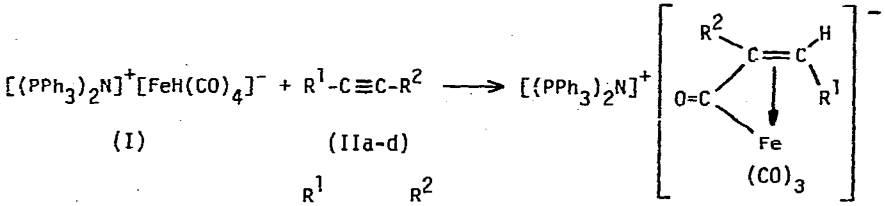
Summary

The crystal structure of a bis(triphenylphosphine)iminium salt of the 1:1 adduct of $[FeH(CO)_4]^-$ and dimethyl acetylenecarboxylate has been determined from three-dimensional X-ray data collected by the counter method. Single crystals belong to the triclinic space space group $P\bar{1}$, with two units of $[C_{36}H_{30}NP_2]^+[C_{10}H_7FeO_8]^-$ in a cell of dimensions: $\underline{a}$ = 13.918(2), $\underline{b}$ = 15.669(5), $\underline{c}$ = 9.909(2) Å, $\underline{\alpha}$ = 91.22(3), $\underline{\beta}$ = 94.83(2), and $\underline{\gamma}$ = 77.62(2)°. The structure was refined to a conventional $\underline{R}$ of 0.068 for 5373 observed $[|\underline{F}_o| > 3\underline{\sigma}(\underline{F})]$ reflections. The resulting structure indicates that the complex anion is η^3-[trans-2,3-bis(methoxycarbonyl)acryloyl]tricarbonylferrate, the coordination around the iron atom being described as a considerably distorted trigonal bipyramid. A comparison of the present structure with the structures of related complexes suggests that the η^3-acryloyl portion is best represented as an intermediate of (η^3-allyl) with the oxygen atom and (η^2-olefin + η^1-acyl). The short Fe-C(acyl) length of 1.897(5) Å implies an enhanced back-donation of electrons from the iron atom to the acyl group.

Introduction

The reactions of $[(PPh_3)_2N]^+[FeH(CO)_4]^-$ (I) with acetylenic compounds (IIa-d) in CH_2Cl_2 at room temperature yield 1:1 adducts, the structure of which have been inferred to be unusual η^3-acryloyltricarbonylferrates (IIIa-d) (scheme 1) [1]. In these reactions no alkenyltetracarbonylferrates were produced; the insertion of a carbonyl group into an intermediate alkenyl-iron bond and the coordination of the olefinic group to the vacant site on the iron atom were inferred to take place. To elucidate the molecular structures of the novel complexes (IIIa-d) we undertook an X-ray study of (IIIa).

Scheme 1



(I)

(IIa-d)

(IIIa-d)

	R^1	R^2
a	COOMe	COOMe
b	H	COOMe
c	H	COMe
d	H	CHO

Experimental

Recrystallization from a methylene chloride-ether solution afforded yellow single crystals. Specimens used for the X-ray work were sealed in argon-filled glass capillary tubes to prevent decomposition. Preliminary oscillation and Weissenberg photographs indicated that the space group was either P1 or P$\bar{1}$; P$\bar{1}$ was later proved to be correct on the basis of the successful analysis. Accurate cell parameters were determined by a least-squares treatment of $2\underline{\theta}$ angles of 21 reflections in the range 18° < $2\underline{\theta}$ < 25° measured on a computer-controlled four-circle diffractometer with Mo Kα radiation ($\underline{\lambda}$ = 0.71069 Å).

A specimen, approximately 0.37 × 0.21 × 0.19 mm^3, was used for X-ray data collection on the diffractometer. Integrated intensities of the independent reflections for 2θ less than 50° were measured with the ω - 2θ scan mode at an ω scan rate of 2° min^{-1} by use of graphite- monochromated Mo Kα radiation. The scan width in ω was $(1.0 + 0.34\tan\theta)°$ with stationary background counts of 10 s duration on either side of the peak. As a check of the deterioration of the specimen the intensities of five reflections were measured after every 50 reflections. No remarkable variation was observed for these monitoring intensities during the data collection. The intensities were corrected for the Lorentz and polarization effects. No corrections were made for absorption or extinction. Of the 6706 reflections measured, only the 5373 reflections with $|F_o| > 3\sigma(F)$ were considered observed and used for the structure determination.

Solution and Refinement of the Structure

The structure was solved by the heavy-atom method. The Fe and two P atoms were located from a Patterson map. An iterative application of Fourier and diagonal least-squares calculations gave a reasonable set of coordinates and isotropic thermal factors of all the non-hydrogen atoms. At this stage the residual index, $R = \Sigma|\Delta F|/\Sigma|F_o|$, where $\Delta F = |F_o| - |F_c|$, was 0.11. In the least-squares calculations the function minimized was $\Sigma w(\Delta F)^2$, where w was the weight (see below). Many peaks on a difference Fourier map then calculated were assignable to those due to the hydrogen atoms. However, only one H atom, H[C(4)] (see Table 1), important to the stereochemistry of the complex anion, was accepted to include and to refine the position and the isotropic thermal factor in the subsequent cycles. The other H atoms were ignored.

In the final three cycles of the block-diagonal least-squares calculations the weighting scheme, $1/w = \sigma^2(F_o) + 0.0024|F_o|^2$, was used. The final residual indices are: $R = 0.068$ and $R_w = [\Sigma w(\Delta F)^2/$

$\Sigma w|F_o|^2]^{1/2}$ = 0.095. The isotropic temperature factor of H[C(4)] was: B = 1.0(1.0) Å^2. In the final refinement cycle no individual parameter shift exceeded one-fifth of the corresponding standard deviation. The averages of $\Sigma w(\Delta F)^2$ for several subgroups of increasing $|F_o|$ were reasonably constant.

Atomic scattering factors were those of Cromer and Waber [2]. The anomalous dispersion corrections for Fe and P were included in the structure factor calculations: for Fe, $\Delta f'$ = 0.301 and $\Delta f''$ = 0.845; for P, $\Delta f'$ = 0.090 and $\Delta f''$ = 0.095 [2]. All computations were carried out on FACOM 270/20 and 230/38 computers of Kwansei Gakuin University.

Results

The crystal data are summarized as follows:

$[C_{36}H_{30}NP_2]^+[C_{10}H_7FeO_8]^-$, M_r = 849.59; triclinic, space group $P\bar{1}$; a = 13.918(2), b = 15.669(5), c = 9.909(2) Å, α = 91.22(3), β = 94.83(2), γ = 77.62(2)°; V = 2103.2(8) Å^3; Z = 2; D_x = 1.341 g cm^{-3}; μ = 5.10 cm^{-1}(Mo Kα).

Table 1 lists the final atomic coordinates. Tables of the anisotropic thermal parameters and the observed and calculated structure amplitudes are available from NAPS* .

The crystals consist of the bis(triphenylphosphine)iminium cations and the mononuclear η^3-[trans-2,3-bis(methoxycarbonyl)-acryloyl]tricarbonylferrate anions (IIIa). In Fig. 1 is shown the crystal structure, in which no unusual intermolecular contacts were found. The structures of the cation and the complex anion are illustrated in Figs. 2 and 3, respectively, with the atomic labelling scheme. Bond lengths and angles are given in Table 2.

(Continued on p.119)

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* The table of structure factors has been deposited as NAPS Document No.03329 (29 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $7.25 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES ($x10^4$; FOR H $x10^3$).

ATOM	x	y	z	ATOM	x	y	z
Fe	4277.1(6)	1614.8(5)	1113.7(7)	C(B2)	8506(4)	3330(4)	666(5)
O(1)	5363(3)	2648(3)	3024(4)	C(B3)	8107(5)	3033(4)	-549(6)
C(2)	4679(4)	2395(4)	2426(5)	C(B4)	7129(5)	2915(4)	-642(6)
C(3)	3664(3)	2376(3)	2624(5)	C(B5)	6561(5)	3111(4)	472(6)
C(4)	3037(4)	2605(3)	1396(5)	C(B6)	6954(4)	3427(4)	1657(6)
C(5)	3003(4)	3391(4)	650(5)	C(C1)	7471(4)	4734(3)	3979(5)
O(6)	2402(3)	3649(3)	-311(4)	C(C2)	7004(4)	4564(4)	5102(6)
O(7)	3686(3)	3846(3)	1114(4)	C(C3)	6240(5)	5212(5)	5566(7)
C(8)	3752(5)	4600(4)	364(7)	C(C4)	5958(5)	6016(5)	4899(8)
C(9)	3345(4)	1952(4)	3749(5)	C(C5)	6423(6)	6178(5)	3777(8)
O(10)	2512(3)	1877(4)	3891(5)	C(C6)	7196(5)	5530(4)	3305(6)
O(11)	4104(3)	1631(3)	4667(4)	C(D1)	10175(4)	1947(3)	5850(5)
C(12)	3901(5)	1120(5)	5764(7)	C(D2)	10281(4)	2622(4)	6777(6)
C(13)	5364(5)	873(5)	1690(6)	C(D3)	11087(5)	2469(5)	7766(6)
O(14)	6098(4)	414(4)	2093(6)	C(D4)	11748(5)	15[illegible]9(5)	7829(7)
C(15)	4617(4)	1915(4)	-473(6)	C(D5)	11628(4)	999(5)	6924(7)
O(16)	4841(4)	2141(4)	-1477(4)	C(D6)	10841(4)	1143(4)	5903(6)
C(17)	3529(5)	815(4)	746(6)	C(E1)	9402(4)	1601(3)	3114(5)
O(18)	3044(4)	312(3)	571(5)	C(E2)	10295(4)	1657(4)	2593(6)
H[C4]	242(3)	242(3)	131(5)	C(E3)	10463(5)	1384(4)	1244(6)
P(1)	8424.3(9)	3877.7(8)	3371.7(12)	C(E4)	9747(6)	1050(4)	464(7)
P(2)	9099.6(9)	2136.9(8)	4678.1(12)	C(E5)	8881(5)	980(4)	1001(7)
N	8672(3)	3150(3)	4503(4)	C(E6)	8685(5)	1251(4)	2329(6)
C(A1)	9492(4)	4298(3)	3034(5)	C(F1)	8214(4)	1642(3)	5421(5)
C(A2)	9431(4)	4919(4)	2023(6)	C(F2)	8520(4)	953(4)	6326(6)
C(A3)	10282(5)	5208(4)	1753(6)	C(F3)	7810(4)	583(5)	6879(7)
C(A4)	11187(4)	4846(4)	2464(6)	C(F4)	6826(4)	893(5)	6537(7)
C(A5)	11237(4)	4234(4)	3441(7)	C(F5)	6521(5)	1571(5)	5633(8)
C(A6)	10394(4)	3949(4)	3763(5)	C(F6)	7208(4)	1965(4)	5088(6)
C(B1)	7940(3)	3534(3)	1758(5)				

TABLE 2

BOND LENGTHS (IN Å) AND ANGLES (IN °).

(A) BOND LENGTHS IN THE COMPLEX.

BOND	LENGTH	BOND	LENGTH	BOND	LENGTH
Fe - C(2)	1.897(5)	C(2) - C(3)	1.450(7)	C(4) - C(5)	1.440(8)
Fe - C(3)	2.023(5)	C(3) - C(4)	1.440(7)	C(5) - O(6)	1.215(6)
Fe - C(4)	2.093(5)	C(4) - H[C4]	0.97(5)	C(5) - O(7)	1.352(7)
Fe - C(13)	1.759(6)	C(3) - C(9)	1.457(8)	O(7) - C(8)	1.432(9)
Fe - C(15)	1.780(6)	C(9) - O(10)	1.209(7)	C(13) - O(14)	1.162(8)
Fe - C(17)	1.806(7)	C(9) - O(11)	1.352(6)	C(15) - O(16)	1.153(8)
O(1) - C(2)	1.213(6)	O(11) - C(12)	1.445(9)	C(17)-O(18)	1.144(9)

(B) BOND LENGTHS IN THE CATION.

BOND	LENGTH	BOND	RANGE	MEAN
N - P(1)	1.580(4)	P - C	1.786(5) - 1.807(6)	1.799(8)[a]
N - P(2)	1.579(4)	C - C	1.368(8) - 1.418(9)	1.397(13)

(C) BOND ANGLES IN THE COMPLEX.

BOND	ANGLE	BOND	ANGLE
C(2) - Fe - C(3)	43.3(2)	Fe - C(4) - C(5)	114.0(4)
C(2) - Fe - C(4)	73.1(2)	Fe - C(4) - H[C4]	115(3)
C(2) - Fe - C(13)	85.7(3)	Fe - C(13) - O(14)	177.0(7)
C(2) - Fe - C(15)	106.8(3)	Fe - C(15) - O(16)	177.2(6)
C(2) - Fe - C(17)	145.8(3)	Fe - C(17) - O(18)	177.0(5)
C(3) - Fe - C(4)	40.9(2)	O(1) - C(2) - C(3)	138.3(5)
C(3) - Fe - C(13)	112.3(3)	C(2) - C(3) - C(4)	111.0(4)
C(3) - Fe - C(15)	129.9(3)	C(2) - C(3) - C(9)	125.1(4)
C(3) - Fe - C(17)	106.4(2)	C(4) - C(3) - C(9)	121.8(5)
C(4) - Fe - C(13)	153.2(3)	C(3) - C(4) - C(5)	122.9(5)
C(4) - Fe - C(15)	101.4(2)	C(3) - C(4) - H[C4]	117(3)
C(4) - Fe - C(17)	92.1(2)	C(5) - C(4) - H[C4]	113(3)
C(13) - Fe - C(15)	100.3(3)	C(4) - C(5) - O(6)	124.9(5)
C(13) - Fe - C(17)	96.7(3)	C(4) - C(5) - O(7)	114.2(4)
C(15) - Fe - C(17)	106.3(3)	O(6) - C(5) - O(7)	120.9(5)

TABLE 2 (Continued)

BOND	ANGLE	BOND	ANGLE
Fe - C(2) - O(1)	146.8(4)	C(5) - O(7) - C(8)	117.7(5)
Fe - C(2) - C(3)	73.0(3)	C(3) - C(9) - O(10)	126.3(5)
Fe - C(3) - C(2)	63.7(3)	C(3) - C(9) - O(11)	112.0(5)
Fe - C(3) - C(4)	72.1(3)	O(10) - C(9) - O(11)	121.7(5)
Fe - C(3) - C(9)	118.2(4)	C(9) - O(11) - C(12)	117.1(5)
Fe - C(4) - C(3)	66.9(3)		

(D) BOND ANGLES IN THE CATION.

P(1) - N - P(2) 140.6(3)

BOND	RANGE	MEAN
N - P - C	106.3(2) - 115.0(2)	111.0(30)[a]
C - P - C	105.8(2) - 110.9(2)	107.9(21)
P - C - C	117.2(4) - 122.8(4)	119.5(17)
C - C - C	117.9(6) - 121.7(7)	120.0(9)

[a] The mean value, $\bar{p}$, and its e.s.d., σ, in parentheses are defined as: $\bar{p} = \Sigma p_i/n$ and $\sigma = [(\Sigma p_i^2 - n\bar{p}^2)/(n - 1)]^{1/2}$, where p_i and n stand for individual observation and number of observations, respectively.

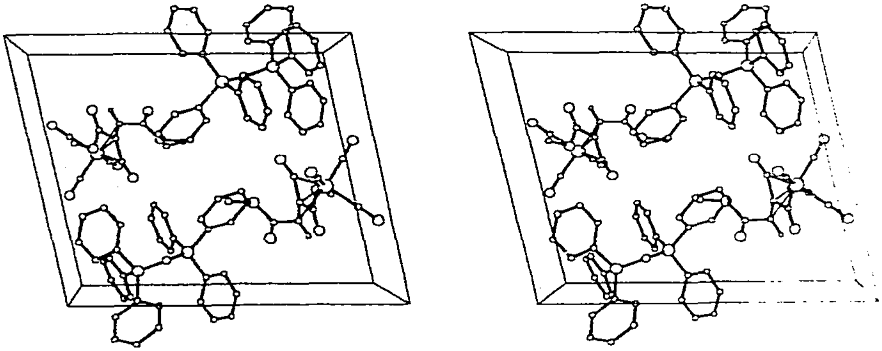


Fig. 1. A stereoscopic drawing of the crystal structure. The origin of the cell is at the upper left corner. The y axis is horizontal, the x axis is vertical, and the z axis points out from the paper.

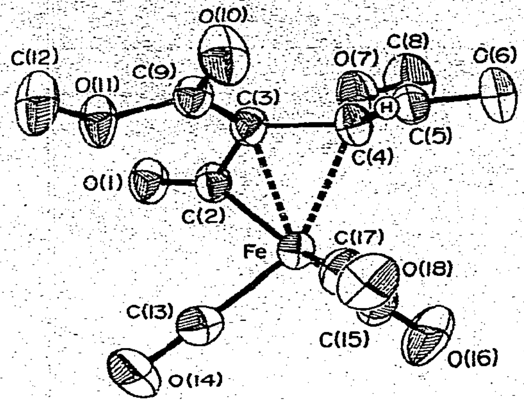


Fig. 2. Molecular structure of η^3-[*trans*-2,3-bis(methoxycarbonyl)acryloyl]tricarbonylferrate, (IIIa), viewed perpendicular to the plane defined by the Fe, C(3), and C(4) atoms. Thermal ellipsoids are drawn at 40% probability level except that of H or H[C(4)], which is drawn by a sphere of an arbitrary radius.

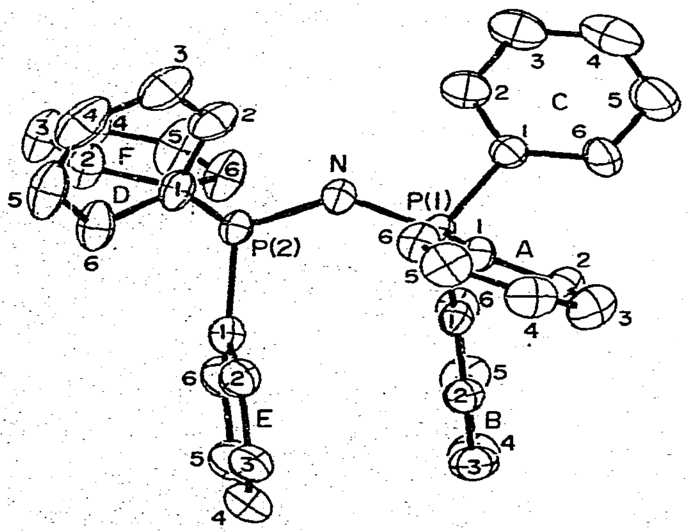


Fig. 3. Molecular structure of bis(triphenylphosphine)iminium, viewed perpendicular to the plane defined by the P(1), N, and P(2) atoms. Thermal ellipsoids are drawn at 40% probability level.

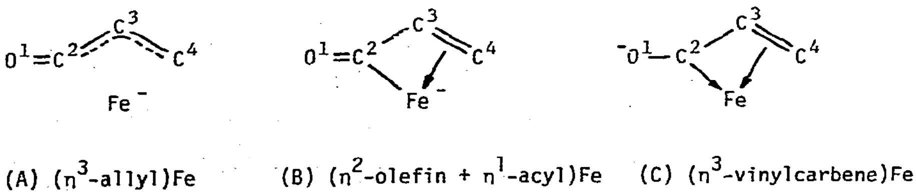
The complex anion contains an η^3-acryloyl ligand having the two methoxycarbonyls in trans configuration with respect to the C(3)=C(4) bond. This finding is quite consistent with the previous prediction [1]. The coordination geometry around the Fe atom may be described as a greatly distorted trigonal bipyramid with the C(2) acyl and the C(17) carbonyl carbons at the axial positions and the other carbonyl carbons, C(13) and C(15), and the olefinic group on the equatorial plane, the C(2)-Fe-C(17) angle being 145.8(3)°.

Discussion

Seemingly, the stereochemistry of the η^3-acryloyl-Fe portion resembles that of a similar portion in $(C_9H_{14}CO)Fe_2(CO)_6$ (IV) [3], $(C_7H_{10}CO)Fe_2(CO)_6$ (V) [3], $PhN:C_6H_4C(CF_3):C(CF_3)COCo(CO)_2$ (VI) [4], or η^3-[trans-1,2-dimethoxycarbonylvinyl)methoxycarbene]tricarbonyliron(0) (VII) [5]. However, a close examination of these structures reveals several remarkable differences to be discussed.

For the best representation of the interaction of the O(1)-C(2)-C(3)-C(4) system with the Fe atom in (IIIa) three extreme views, shown in Scheme 2, should be considered. In (A) the C(2)-C(3)-C(4) fragment is represented as an η^3-allyl unit with O(1) attached to the terminal atom, C(2). The scheme (B) consists of the η^2-olefin- and η^1-acyl-Fe bonds. In the last scheme (C), a localized minus charge resides on the acyl oxygen atom; thus the ligand may be regarded as an η^3-vinylcarbene unit.

Scheme 2



(A) (η^3-allyl)Fe (B) (η^2-olefin + η^1-acyl)Fe (C) (η^3-vinylcarbene)Fe

The model (A) is consistent with the finding that C(2)-C(3) and C(3)-C(4) lengths [1.450(7) and 1.440(7) Å] are equal to each other within experimental errors, indicating that the p-π-electrons are delocalized over the C(2)-C(3)-C(4) system. The corresponding bond distances in (IV) and (V) differ significantly from each other. The C(2)-C(3) and C(3)-C(4) lengths are somewhat longer than those found in some other (η^3-allyl)-metal complexes, probably due to an extension of the π-electron delocalization to the methoxycarbonyl groups: the C(3)-C(9) and C(4)-C(5) lengths are slightly shorter than the usual C(sp^2)-C(sp^2) length. However, the atoms bonded to the C(2)-C(3)-C(4) fragment deviate considerably from the plane defined by these atoms: C(5) and C(9) deviate by 0.97 and -0.34 Å, respectively, from the plane.

The Fe-C(2) length of 1.897 Å is significantly shorter than any of the corresponding lengths in the usual Fe-acyl complexes (1.96 - 1.97 Å) [6-8] and also shorter than any found in (V) [1.945(4) Å] and (VI) [1.961(7) Å], but longer than the Fe-C(carbene) length in (VII) [1.819(3) Å]. This shortening should partly be due to an enhanced back-donation of electrons from the Fe atom to the acyl group. Thus the model (A) is not sufficient. Owing to the short Fe-C(2) bond, the three Fe-C distances [1.897(5), 2.023(5), and 2.093(5) Å] deviate from the long-short-long pattern usually found in the (η^3-allyl)-metal system [9], and the C(2)-C(3)-C(4) angle is reduced to 110.0(4)° from the usual value (115-124°) for the normal η^3-allyl ligands [9].

The scheme (B) explains the short Fe-C(2) bond, except that the additional shortening, described above, due to the back-donation of electrons is not involved. However, the delocalization of π-electrons over the C(2)-C(3)-C(4) portion is not shown explicitly in this scheme. Finally, the scheme (C) is not satisfied also with the C(2)-O(1) length [1.216(6) Å], which corresponds to the C=O double-bond length. The C-O^- bond should be as long as ca. 1.28 Å found in $[NMe_4]^+[(\pi\text{-}C_5H_5)(CO)_2MnC(O)Ph]$ containing a $Mn \leftarrow \dot{C}\text{-}O^-$ fragment [10], or longer than ca. 1.25 Å observed in many phenolate groups [11]. Moreover, if (C) is the major contribution for this system, the bond lengths and angles around the acryloyl portion should be more similar to those in (VII).

In conclusion, evidently, the bonding scheme of the present acryloyl-Fe portion is not represented by any single scheme; an adequate one is an intermediate between (A) and (B), with more(A) than (B). Further details of the bonding scheme will be obtained from molecular orbital treatment. In view of the complicated structures of (IV), (V), and (VI), the present structure can be taken as a typical one for the η^3-acryloyl-metal system.*

The geometry of the $[(PPh_3)_2N]^+$ moiety is very similar to that commonly found in many ionic complexes: the P-N-P linkage is bent and both the P-N-P angle and the N-P lengths are in the known ranges (P-N-P = 134.6 - 141.8° and N-P = 1.571 - 1.586 Å) as compiled by Wilson and Bau [14].

Acknowledgement

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* Formation of η^3-acryloyl complexes of Co [12] and W [13] has been reported, the structures of which have not yet been established.

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