only the presence of the main components (I and V) but part of the absorption of I masked the presence of the $P(CH_2)_3$ coordinated ligand in V. Moreover the couplings and chemical shifts for the PO_3 coordinated ligand were indeed different from those reported for II or III.[1] They do, however, correspond within experimental error with those of V (see Experimental Section). A parent ion at 320 seen in the mass spectrum can now be attributed to II and the absence of a similar peak at 444 for V can be rationalized on the basis of its lesser volatility under the conditions the spectrum was run. It was during the search for a better synthesis of the "nonaxial mono substituted isomer" that V was identified and found to be responsible (along with II as an impurity) for the spurious data.

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The Crystal and Molecular Structure of Bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II)

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The orange crystals of bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) are monoclinic with a = 7.606 (9) Å, b = 12.332 (12) Å, c = 12.956 (14) Å, and β = 104.25 (4)°. The space group is $P2/c$ and with two molecules per cell, d_{measd} = 1.15 g/cm^3 and d_{calcd} = 1.157 g/cm^3. Diffractometer data were measured using monochromatized Mo Kα radiation and a θ–2θ scan technique. The structure was solved by the heavy-atom method and refined by least-squares methods to a final R of 0.056 for the 1598 observed reflections used in the analysis. The molecule is required to have C_2 symmetry by the space group. The distances and angles are normal for a π-pentadienyl system. The final orientation of the π-pentadienyl system minimizes the steric interaction between the methyl groups while maximizing the number of bonds in the π system which are eclipsed. These results suggest that interligand interactions are important in π complexes. In addition, the methyl groups and hydrogen atoms appear to be bending inward toward the metal atom, an effect which is not observed frequently. Finally, the absence of the C–H stretch at 2730–2830 cm^{-1} has been shown to indicate an endo hydrogen atom and suggests that this band can be a useful diagnostic tool.

Introduction

Structural data on organometallic compounds containing cyclohexadiene as a ligand are limited to a few examples,[1-4] all of which have at least one carbonyl group bonded to the metal atom. Two controversial features of these cyclohexadiene compounds are (1) whether the symmetric nature of the π-pentadienyl group is an intrinsic property of the ligand and (2) the relative orientation of two cyclohexadienyl rings compared to the corresponding bis-π-cyclopentadienide complexes.[5-7] These points have been resolved by our study of bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II), the first example of a cyclohexadienyl complex containing no carbonyl groups.

Experimental Section

Orange crystals of the compound were kindly supplied by Helling and Braitsch.[8] Preliminary precession photographs indicated monoclinic symmetry. The systematic absences of $h0l$ if $l = 2n + 1$ indicated that the probable space groups were Pc (C_s^2) or $P2/c$ (C_{2h}^4). Although the intensity statistics were inconclusive, the space group $P2/c$ was confirmed by the structure analysis.

The intensity crystal was made approximately spherical (0.25 mm in diameter) by rotation of the crystal in cyclohexane. The unit cell dimensions were obtained from a least-squares fit of 2θ, ω, φ, and χ values for nine reflections measured on the Syntex P$\bar{1}$ diffractometer. The final values are a = 7.606 (9) Å, b = 12.332 (12) Å, c = 12.956 (14) Å, β = 104.25 (4)°. The density calculated for two molecules of $Fe(C_{13}H_{21})_2$, mol wt 410.47, per unit cell is 1.157 g/cm^3, in good agreement with the value of 1.15 g/cm^3 measured by flotation.

The intensity data were measured on a computer-controlled Syntex P$\bar{1}$ diffractometer, using graphite-monochromatized Mo Kα radiation (λ 0.71069 Å). A θ–2θ scan at 4°/min was used to measure all the independent reflections up to a 2θ limit of 50°. The background was measured for a time equal to one-quarter of the total scan time at a point 1° to each side of the α_1 and α_2 peaks. [The intensity, I, was equal to [total scan counts − (backgrounds/background to scan ratio)](scan rate), with a standard deviation equal to [total scan counts + (backgrounds/background to scan ratio)^2]$^{1/2}$(scan rate)]. Four standard reflections were measured after every 50 reflections and were used to correct for a small variation (maximum 2%) of the standard reflections with time. The 1598 reflections which had an intensity $I \geq 1.3\sigma(I)$ were considered observed and the 422 reflections which failed to meet the criterion were considered unobserved and flagged with a negative sign. These data were reduced to a set of structure amplitudes on an arbitrary scale by the usual methods. Since the value of μr was only 0.08 (μ is 6.3 cm^{-1} for Mo Kα radiation) and the crystal was approximately spherical, no absorption corrections were applied.

Structure Determination and Refinement

The position of the iron atom was determined from a sharpened three-dimensional Patterson function. A Fourier synthesis phased on only the iron atom contribution revealed the positions

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(1) M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, **8**, 1950 (1969).

(2) P. J. Van Vurren, R. J. Fletterick, J. Meimwald, and R. E. Hughes, *J. Amer. Chem. Soc.*, **93**, 4394 (1971).

(3) The complex $[C_6(CH_3)_6H]Re(CO)_3$ was studied by P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967), but virtually no distances and angles were given.

(4) The structure of bis(1,3-cyclohexadiene)monocarbonyliron has the olefin acting as a 1,3-diene rather than as a pentadienyl system: C. Kruger and C. H. Tsay, *Angew. Chem., Int. Ed. Engl.*, **10**, 261 (1971).

(5) Data on the orientation of the cyclopentadienide rings in ferrocene derivatives can be found in ref 6 and 7.

(6) G. J. Palenik, *Inorg. Chem.*, **9**, 2424 (1970).

(7) M. R. Churchill and J. Wormald, *ibid.*, **8**, 716 (1969).

(8) J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, **92**, 7207 (1970).

TABLE I

FINAL PARAMETERS FOR THE NONHYDROGEN ATOMS[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0000[b]	1833 (1)	2500[b]	101 (1)	43 (1)	38 (1)	0000[b]	34 (1)	00[b]
C(1)	−302 (5)	1982 (4)	4089 (3)	150 (7)	72 (4)	37 (2)	−11 (9)	42 (7)	11 (5)
C(2)	435 (6)	973 (3)	3892 (3)	201 (9)	59 (3)	47 (3)	−21 (9)	15 (9)	27 (5)
C(3)	2017 (6)	947 (4)	3503 (3)	196 (10)	67 (4)	56 (3)	61 (10)	20 (10)	5 (5)
C(4)	2702 (5)	1949 (5)	3266 (3)	109 (7)	87 (4)	49 (3)	18 (11)	26 (7)	−2 (6)
C(5)	1900 (5)	2932 (3)	3447 (3)	124 (7)	59 (4)	45 (3)	−31 (8)	17 (7)	2 (5)
C(6)	927 (5)	2964 (3)	4352 (3)	172 (8)	60 (4)	39 (3)	22 (9)	31 (7)	−6 (5)
C(7)	−2150 (5)	1997 (5)	4351 (3)	182 (9)	135 (6)	58 (3)	−58 (13)	89 (8)	−9 (7)
C(8)	2858 (8)	−120 (4)	3288 (4)	357 (15)	90 (5)	91 (4)	151 (14)	50 (13)	4 (7)
C(9)	2467 (7)	3988 (4)	3018 (4)	277 (12)	80 (4)	70 (4)	−161 (12)	39 (11)	9 (6)
C(10)	2133 (5)	3080 (4)	5522 (3)	231 (9)	81 (4)	46 (3)	28 (13)	22 (8)	−29 (7)
C(11)	943 (7)	3137 (7)	6310 (3)	335 (13)	205 (7)	54 (3)	16 (16)	75 (11)	−44 (9)
C(12)	3452 (8)	2122 (5)	5837 (4)	360 (15)	134 (7)	65 (4)	125 (16)	−114 (12)	−3 (7)
C(13)	3231 (9)	4120 (6)	5626 (4)	473 (19)	149 (7)	79 (5)	−262 (19)	−42 (16)	−32 (9)

[a] The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. All values are 10^4. [b] Parameters determined by space group symmetry.

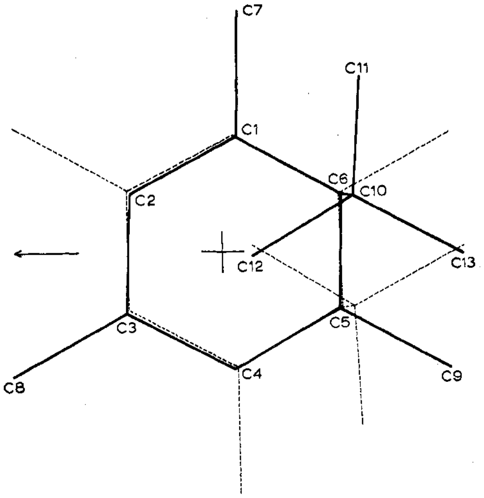

Figure 1.—A view down the centers of the π-pentadienyl system showing the eclipsed nature of the compound. The dashed lines refer to the lower ligand and the heavy lines to the upper one. The twofold axis is shown by an arrow and bisects the bonds C(5)–C(6) and C(2)–C(3) in projection.

of all the carbon atoms, assuming the space group was Pc. The molecule possessed approximately twofold symmetry (which is required in $P2/c$) and an attempted refinement assuming the space group to be Pc led to unreasonable bond lengths. However, when the space group was assumed to be $P2/c$, three full-matrix least-squares cycles with isotropic thermal parameters reduced R, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, to 0.11. An additional three least-squares cycles with anisotropic thermal parameters reduced R to 0.082. A difference Fourier synthesis revealed the positions of all the hydrogen atoms. The hydrogen atom contributions were included in the structure factor calculations (but their parameters were not varied) and two least-squares cycles reduced R to 0.060. An attempt to refine the hydrogen atom parameters resulted in an insignificant change in R, but all the distances and angles involving the hydrogen atoms improved. The final R at this point was 0.056 and the refinement was terminated. The final positional and thermal parameters for the nonhydrogen atoms are tabulated in Table I. The final refined hydrogen atom parameters are given in Table II together with the corresponding C–H distance.[9]

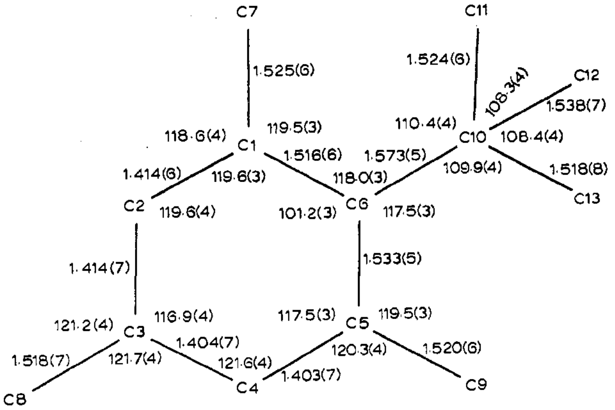

Figure 2.—The atomic numbering and bond distances and angles in bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II). The angles not shown are C(6)–C(10)–C(12) of 111.9 (4)° and C(11)–C(10)–C(13) of 107.8 (4)°. The Fe–C distances are Fe–C(1) of 2.135 (3), Fe–C(2) of 2.047 (4), Fe–C(3) of 2.062 (5), Fe–C(4) of 2.055 (4), Fe–C(5) of 2.135 (4), and Fe–C(6) of 2.714 (4) Å.

The quantity minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$, where

$$\sqrt{w} = |F_o|/4F_M, \text{ if } |F_o| < 4F_M$$

$$\sqrt{w} = 1, \text{ if } 4F_M \leq |F_o| \leq 6F_M$$

$$\sqrt{w} = 6F_M/|F_o|, \text{ if } |F_o| > 6F_M$$

The value of F_M, the mean minimum observable F_o, was 5.0 in this case. The scattering factors for all atoms were taken from the usual source.[10] All calculations were carried out on an IBM-360/65 computer with programs written or modified by one of us (G. J. P.).

Results and Discussion

The molecule possesses exact C_2 symmetry (*i.e.*, required by the space group) with the Fe atom on the twofold axis. A view down the ring centers, Figure 1, shows that the twofold axis in projection bisects the C(2)–C(3) and C(5)–C(6) bonds. The atomic numbering is given in Figure 1 and also in Figure 2 where distances and angles in the 6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl ligand are illustrated.

The C–C distances in the delocalized π-pentadienyl portion of the ligand vary from 1.403 to 1.414 Å, with a

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(9) Tables II and III which contain the hydrogen atom parameters, the bond distances, and angles involving the hydrogen atoms have been deposited as supplementary material. These tables together with a listing of the observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2809. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(10) "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, p 202.

mean value of 1.409 (6) Å. The π-pentadienyl system is more symmetrical than in other π-pentadienyl complexes such as the following: π-cyclohexadienyltricarbonylmanganese,[1] range 1.388–1.415 Å with a mean of 1.401 (14) Å; dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron,[2] range 1.371–1.434 Å with a mean of 1.401 (24) Å; and guaiazulenehexacarbonyldimolybdenum,[11] range 1.394–1.410 Å with a mean of 1.403 (6) Å. In all cases the mean values are identical within the experimental error. These results suggest that the dimensions of a π-pentadienyl system are relatively constant, a result which is not unexpected.

The distances involving C(6) and the ring atoms, C(1)–C(6) of 1.516 (6) and C(5)–C(6) of 1.533 (5) Å, are probably not significantly different and are only slightly longer than the value of 1.510 (5) Å expected for a C(sp^2)–C(sp^3) bond distance. Similarly, the ring-*exo*-methyl C–C distances average 1.521 Å, and are slightly but not significantly longer than expected. The C(6)–C(10) distance of 1.573 (5) Å is somewhat longer than the usual C–C single bond and indicates steric strain involving the *tert*-butyl group. The fact that the C(6)–C(10)–C(11), C(6)–C(10)–C(12), and C(6)–C(10)–C(13) angles are all larger, average 110.7°, than the tetrahedral value, while the three angles involving the methyl groups C(11), C(12), and C(13), average 108.2°, are all smaller than the tetrahedral value supports the hypothesis of steric strain.

The bond angles in the cyclohexadienyl ring show some deviations from the expected values. The C(1)–C(6)–C(5) angle of 101.2 (3)° is much smaller than the ideal tetrahedral value of 109.46°. Similarly, small angles have been observed in the other two cyclohexadienyl structures, 104.1° in $C_6H_7Mn(CO)_3$[1] and 104.6° in $C_8H_8COFe(CO)_2$,[2] and may result from an attempt to maximize the overlap of the metal orbitals with those on the terminal carbon atoms of the π-pentadienyl system. The angle C(2)–C(3)–C(4) of 116.9 (4)° is also smaller than the expected value of 120°. The decrease in this angle may be related to a steric strain resulting from the flattening of the normal boat conformation of a cyclohexadiene ring. In fact, there is still a slight boat shape to the molecule as is indicated by the calculations of various planes through the ring.

A number of least-squares planes were calculated and some are tabulated in Table IV. The atoms C(1), C(2), C(4), and C(5) define a plane, with C(3) and C(6) bent up from the plane by 0.038 and 0.657 Å, respectively, in an overall boat conformation. The conformation is similar to that found in $C_6H_7Mn(CO)_3$[1] where the corresponding four atoms are required to be coplanar by symmetry and the remaining two atoms are also above the plane by 0.027 and 0.626 Å, respectively. Therefore, the π-cyclohexadienyl ligand is best described as having a boat conformation, with the two ends making dihedral angles of 3.0 and 42.8°, respectively, with the four coplanar central atoms.

The Fe–C distances show that the iron atom is approximately equidistant from the three central atoms of the π-pentadienyl system (av Fe–C distance is 2.054 Å) and somewhat further away (av Fe–C distance of 2.135 Å) from the two terminal carbon atoms. A similar displacement of the metal atom toward the central carbon atoms has been observed in other π-pentadienyl systems: $C_6H_7Mn(CO)_3$,[1] 2.141 *vs.* 2.219 Å; azulenehexacarbonyldimanganese,[12] 2.123 *vs.* 2.279 Å; and $C_{10}H_8COFe(CO)_2$,[2] 2.11 *vs.* 2.22 Å. These Fe–C distances, when compared to the displacement of the Fe atom from "the center of the ring," suggest that the Fe–C distances are more important than locating the Fe atom at the ring center. The mean Fe–C distance of 2.087 Å is longer than the corresponding mean Fe–C distance of 2.040 Å given for unperturbed π-cyclopentadienyl complexes.[13] However, more recent studies have reported slightly longer Fe–C distances: 2.046 Å in diacetylferrocene,[6] 2.044 Å in bis(π-azulene)iron,[7] and 2.058 Å in ferrocene in the gas phase.[14] These results coupled with the shorter C–C distances in the π-pentadienyl system (1.409 Å) compared with those in π-cyclopentadienyl compounds (1.43 Å)[15] suggest that the metal–ring interactions are weaker in π-pentadienyl systems.

TABLE IV

LEAST-SQUARES PLANES[a]

Atoms	Planes 1	2	3	4	5
C(1)	14*	30	9*	0*	91
C(2)	−22*	−7*	−9*	−946	0*
C(3)	17*	21*	38	−1484	0*
C(4)	−4*	−7*	9*	−966	0*
C(5)	−5*	−6	−9*	0*	54
C(6)	669	678	657	0*	765
C(7)	−233	−205	−246	716	−115
C(8)	−9	−7*	31	−2509	−86
C(9)	−258	−268	−271	709	−178
H(2)	−232	−212	−214	−1137	−224
H(4)	−205	−215	−185	−1209	−230
Fe	−1572	−1565	−1566	574	−1535
	Parameters for the Planes ($\times 10^4$)				
l	3706	3639	3763	−5977	3455
m	0286	0261	0182	5727	0590
n	9284	9311	9263	−5611	9366
p	42553	42571	42150	−5646	43330

[a] The deviations from the plane (Å × 10^3) are given for the specified atom. Equation of the plane: deviation (A) $= lX + mY + lZ - p$ where X, Y, Z, are the orthogonal coordinates (in Å) relative to a, b, c^* and p is the distance of the plane from the origin. The atoms used to define the planes are noted by an asterisk following the deviation. Dihedral angles of interest are 1 to 3 of 0.7°, 3 to 4 of 42.8°, and 3 to 5 of 3.0°.

The two most important results of our study concern the conformation of the molecule and the deviations from planarity of the atoms attached to the ring. A view down the ring centers, Figure 1, shows an almost eclipsed conformation with the methyl groups on opposite rings being staggered relative to each other. The conformation represents the minimum steric repulsion between groups on the two rings. A more fundamental question is why does the molecule not assume the conformation where the iron atom would be at a center of symmetry? The centrosymmetric structure would have exactly the same staggered arrangement of methyl groups so that steric considerations cannot be the answer. A comparison of the centrosymmetric arrangement with the conformation found in our study

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[11] M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1545 (1968).

[12] M. R. Churchill and P. H. Bird, *ibid.*, **7**, 1793 (1968).

[13] P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 1 (1967).

[14] A. Haaland and J. E. Nikson, *Chem. Commun.*, 88 (1968).

[15] Although the average value of 1.419 is cited in ref 13, the values of 1.426, 1.430 and 1.431 Å were reported in ref 6, 7, and 14, respectively. The value 1.43 Å is more reasonable in view of the higher precision in these latter studies.

reveals a difference in the number of bonds in the π-pentadienyl system which will overlap in the two cases. In the observed conformation there are three bonds which overlap, while in the centrosymmetric case, only two bonds are overlapped. If the bonding in these systems involves appreciable inter-ring overlap, then the observed conformation is preferred. Therefore, the present structure gives the first indication that an interaction between two π systems may be important and may control the observed configuration. However, the effect of packing forces cannot be ascertained although the centrosymmetric structure would have been predicted *a priori*. Nevertheless, the Fe–ring distance of 1.57 Å is slightly shorter than the predicted value of 1.60 Å,[2] in support of an inter-ring interaction. Clearly, the nature of the bonding in bis(cyclohexadienyl)metal and ferrocene systems is not well understood and additional studies must be carried out.

A second important point is the question of whether substituent groups on π systems should bend inward or outward. Inspection of the deviations in Table IV indicates that the substituents on the planar four-membered system C(1), C(2), C(4), and C(5) are all bent toward the iron atom. Similar displacements of the hydrogen atoms are found in *N*-formylaminomethylferrocene;[16] in diacetylferrocene,[6] one methyl group and one oxygen atom on the opposite rings are displaced toward the metal atom, and in $C_6H_7Mn(CO)_3$,[1] two of the three hydrogen atoms are displaced toward the metal atom. In contrast, the chlorine atoms in decachlororuthenocene[17] are all displaced away from the center of the rings so that the Cl···Cl distances are larger than anticipated for van der Waals contacts. These observations together with a consideration of the orientation of the rings, *vide supra*, suggest that interligand interactions may be important and will influence both the orientation of the rings as well as the planarity of groups on the π system.

The three cyclohexadienyl complexes whose structures have been determined[1-3] all have a broad C–H stretch in the region of 2730–2830 cm^{-1}. This band has been assigned to the exo hydrogen atom on the tetrahedral carbon atom in the cyclohexadienyl ring. The present compound does not have a C–H stretch in this region; therefore, the *tert*-butyl group was assumed to be exo, with the hydrogen atom in the endo position.[18] This suggestion has been verified in the present study. Therefore, the presence of this absorption band is indeed a useful diagnostic tool for the conformation at the saturated carbon atom. Furthermore, the exo orientation of the *tert*-butyl group is easily rationalized on the basis of steric repulsions between groups on the two rings. The shortest intermolecular forces were surveyed and did not indicate any unusual interactions. With the lack of hydrogen bonding or other similar attractive force, the molecular packing is governed by van der Waals forces.

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[16] L. H. Hall and G. M. Brown, *Acta Crystallogr., Sect. B*, **27**, 81 (1971).

[17] G. M. Brown, F. L. Hedberg, and H. Rosenberg, *Chem. Commun.*, 5 (1972).

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The Crystal and Molecular Structure of Nitrosylcarbonylbis(triphenylphosphine)iridium, $Ir(NO)(CO)(P(C_6H_5)_3)_2$

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The structure of nitrosylcarbonylbis(triphenylphosphine)iridium, $Ir(NO)(CO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system with four molecules in a unit cell of dimensions a = 11.271 (3) Å, b = 18.036 (6) Å, c = 18.240 (6) Å, and β = 119.23 (2)°. The observed and calculated densities are 1.55 (±0.02) and 1.59 g cm^{-3}, respectively. Least-squares refinement has led to a final value of the conventional R factor (on F) of 0.030 for the 2946 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of well-separated molecules, and the coordination around the iridium atom is distorted tetrahedral. Structural parameters describing this geometry are the P–Ir–P angle of 103.9 (1)°, the N–Ir–C angle of 128.8 (2)°, and the dihedral angle between the P–Ir–P and N–Ir–C planes of 84.3 (2)°. The nitrosyl ligand is coordinated to the metal in a nearly linear fashion, with an Ir–N bond length of 1.787 (8) Å and an Ir–N–O bond angle of 174.1 (7)°. The compound is therefore formulated as an NO^+ complex of iridium($-$I). Other important bond distances in the molecule are as follows (Å): Ir–P, 2.323 (2), 2.324 (2); Ir–C, 1.873 (11); C–O, 1.144 (11); and N–O, 1.180 (9).

Introduction

In recent years, five- and six-coordinate nitrosyl complexes of the transition metals have been well described.[1] Two distinct modes of coordination of the nitrosyl ligand have been identified. In the first, the nitrosyl is formally coordinated as NO^+, while in the second it may be described as NO^-. A structural difference is associated with these two types of coordination. The NO^+ species has a formal triple bond with sp hybridization; it is therefore linearly coordinated to the metal. The NO^- ligand, however,

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[1] For a recent review of monomeric transition metal nitrosyl complexes see B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci. Inorg. Chem., Ser. One, 1972.*