

45 kcal/mol above the tetrahedral  $^1A_1$  ground state  $P_4$  for the  $^3E_g$  triplet state and 119 kcal/mol for the  $^3E_g$  quintet state. The full exploration of these excited surfaces is complicated by the existence of many extrema and plateaux. There is little doubt that  $D_{4h}$   $^5E_g$  is the lowest minimum on the quintet surface, but the shape of the triplet surface is quite different. According to our first results, the  $D_{4h}$  square-planar form,  $^3E_g$ , is only a saddle point between two nearly square-planar  $D_{2d}$  forms, which in turn are plateau points corresponding to transition states between two bicyclo-butyl-diradical-like  $C_{2v}$  stable forms.<sup>16,17</sup> Further exploration of these surfaces is under way.

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(16) The UHF (DZd) geometries: quintet state  $D_{4h}$   $^5E_g$ ,  $d_{P-P} = 2.302$  Å; triplet state  $D_{4h}$   $^3E_g$ ,  $d_{P-P} = 2.152$  Å;  $D_{2d}$   $^3E$   $d_{P-P} = 2.150$  Å,  $\angle PPP = 87.7^\circ$ , dihedral  $\angle PPP, PPP = 148.1^\circ$  (puckering =  $31.9^\circ$ );  $C_{2v}$   $^3B_1$ ,  $d_{P-P} = 2.208$  Å,  $d_{P-P}(\text{bridge}) = 2.218$  Å,  $\angle PPP = 60.3^\circ$ , dihedral  $\angle PPP, PPP = 107.0^\circ$  (puckering =  $73.0^\circ$ ). The UHF relative energies for the  $C_{2v}$ ,  $D_{2d}$ , and  $D_{4h}$  forms of the triplet state are calculated at 0, +13.2, and +16.8 kcal/mol, respectively.

(17) This problem is analogous to that of the  $C_4H_4$  potential surface. It has been shown that both  $D_{2h}$  cyclobutadiene and  $T_d$  tetrahedrane are real minima on the singlet surface.<sup>18-20</sup> It has not been demonstrated which kind of stationary points the  $D_{4h}$  and  $C_{2v}$  triplet structures belong to. Another related problem is tetraphosphabicyclobutane  $P_4H_2$ . A puckered bicyclo structure is preferred for the singlet ground state, whereas a planar monocyclic structure is preferred for the triplet state.<sup>21</sup>

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## X-ray and Neutron Diffraction Study of $H_5Ir[P(i-Pr)_3]_2$

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In the past decade, many metal-polyhydride complexes of the type  $H_xML_y$  (where L is a tertiary phosphine), first prepared by Chatt, Shaw, and co-workers in the 1960's, have been structurally characterized.<sup>1-3</sup> In particular, polyhydride complexes of iridium and rhenium (e.g.,  $H_3IrL_2$  and related compounds) have received considerable attention because of their ability to activate C-H bonds in saturated and unsaturated hydrocarbons.<sup>4</sup> In this paper

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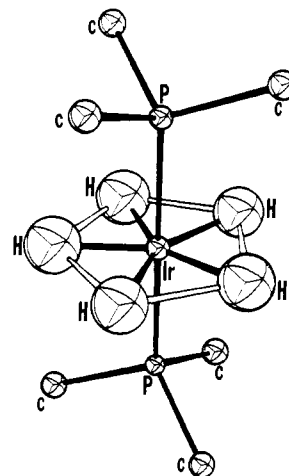


Figure 1. Structure of the core of  $H_5Ir[P(i-Pr)_3]_2$  as obtained from the neutron diffraction analysis. Atoms are drawn at the 50% probability level. For clarity, only the ipso carbon atoms of the isopropyl groups are shown. The hollow connecting lines between the H atoms do not represent bonds but represent nonbonding contacts between the hydride ligands.

Table I. Selected Distances and Angles in  $H_5Ir[P(i-Pr)_3]_2$ <sup>a</sup>

Bond Distances, Å			
Ir-H <sub>1</sub>	1.606 (5)	H <sub>1</sub> ...H <sub>2</sub>	1.90 (1)
Ir-H <sub>2</sub>	1.630 (4)	H <sub>2</sub> ...H <sub>3</sub>	1.89 (1)
Ir-H <sub>3</sub>	1.615 (5)	H <sub>3</sub> ...H <sub>4</sub>	1.83 (1)
Ir-H <sub>4</sub>	1.587 (5)	H <sub>4</sub> ...H <sub>5</sub>	1.84 (1)
Ir-H <sub>5</sub>	1.578 (4)	H <sub>5</sub> ...H <sub>1</sub>	1.93 (1)
av	1.603 (9)	av	1.882 (2)
Ir-P	2.309 (1)	C-H (methyl) (av)	1.086 (1)
P-C (av)	1.859 (1)	C-C (av)	1.528 (1)
C-H (ipso) (av)	1.100 (2)		
Bond Angles			
H <sub>1</sub> -Ir-H <sub>2</sub>	72.0 (5)°	Ir-P-C (av)	114.1 (5)°
H <sub>2</sub> -Ir-H <sub>3</sub>	68.8 (5)°	P-C-H (av)	102.4 (10)°
H <sub>3</sub> -Ir-H <sub>4</sub>	70.5 (5)°	C-C-H (av)	111.2 (4)°
H <sub>4</sub> -Ir-H <sub>5</sub>	75.4 (5)°	C-C-C (av)	110.0 (3)°
H <sub>5</sub> -Ir-H <sub>1</sub>	73.0 (5)°	P-C-C (av)	114.2 (10)
av	71.9 (11)°	C-P-C (av)	104.5 (30)
H-Ir-P (av)	89.7 (3)°	H-C-H (av)	107.6 (2)°

<sup>a</sup> Results of the 80 K neutron diffraction study. The esd's of average values were calculated as  $\sigma(\bar{x}) = [\sum_{i=1}^n (\bar{x} - x_i)^2 / (n-1)]^{1/2}$ .

we report the preparation and single-crystal X-ray and neutron-diffraction analysis of  $H_5Ir[P(i-Pr)_3]_2$  (*i-Pr* = isopropyl).

$H_5Ir[P(i-Pr)_3]_2$  was synthesized in a manner similar to that employed by Chatt et al. to make other iridium polyhydrides:<sup>5</sup> to a deep red solution of  $HIrCl_2[P(i-Pr)_3]_2$ <sup>6,7</sup> (0.61 g, 1.04 mmol) in THF, 0.15 g (3.9 mmol) of  $LiAlH_4$  was added in portions. An

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(6) (a)  $HIrCl_2[P(i-Pr)_3]_2$  was prepared via a procedure very similar to that described in ref 6b: 1 g (2.83 mmol) of  $IrCl_3 \cdot 3H_2O$  and 0.5 mL of 12 M HCl were added to 50 mL of isopropyl alcohol and the suspension was heated for 1 h. To this green-brown suspension was added 0.907 mL (5.6 mmol) of the triisopropylphosphine, which resulted in a yellow-green precipitate. The mixture was refluxed at 80 °C for 18 h, during which time a red crystalline solid was deposited. The compound was extracted with toluene ( $5 \times 10$  mL), concentrated, and cooled to -10 °C to give a crystalline solid. Its structure has been analyzed by single-crystal X-ray diffraction methods which reveal a square-planar, *trans*- $IrCl_2P_2$  skeleton, implying a square pyramidal overall geometry with the "missing" H atom in the axial position (Garlaschelli, L.; Khan, S. I.; Bau, R., unpublished results). (b) Masters, C.; Shaw, B. L.; Stainbock, R. E. *J. Chem. Soc., Dalton Trans.* **1972**, 664.

(7) It has recently come to our attention that Werner and co-workers have also reported the synthesis of  $HIrCl_2(PR_3)_2$ ,  $H_2IrCl(PR_3)_2$ , and  $H_2RhCl(PR_3)_2$  (Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.*, **1985**, *287*, 395).

immediate color change occurred, from red to pale yellow. The mixture was then stirred for 2 h at room temperature, at which point the solution became colorless. Excess  $\text{LiAlH}_4$  was hydrolyzed with 10 mL of wet THF (10%  $\text{H}_2\text{O}$ ). The solvent was removed in vacuo and the residue extracted with toluene. The toluene solution was dried again in vacuo and the resulting pale-yellow solid dissolved in heptane. After cooling to  $-10^\circ\text{C}$  (ethylene glycol bath), large pale yellow crystals appeared. IR data  $\nu(\text{Ir-H})$   $1950\text{ cm}^{-1}$  (in heptane);  $^1\text{H NMR}$  triplet at  $\tau = 21$  with  $J_{\text{PH}} = 12\text{ Hz}$ .

The title compound crystallizes in the triclinic space group  $P\bar{1}$ ,  $Z = 1$ , with  $a = 7.837(1)\text{ \AA}$ ,  $b = 10.700(1)\text{ \AA}$ ,  $c = 7.424(1)\text{ \AA}$ ,  $\alpha = 106.99(1)^\circ$ ,  $\beta = 104.22(1)^\circ$ ,  $\gamma = 72.55(1)^\circ$ , at  $T = 80\text{ K}$ .<sup>8</sup> A room temperature single-crystal X-ray analysis<sup>9a</sup> was first performed on a small crystal of  $\text{H}_3\text{Ir}[\text{P}(i\text{-Pr})_3]_2$  yielding the positions of the non-hydrogen atoms [ $R(F) = 0.023$  for 2210 reflections]. Neutron diffraction data subsequently were collected at the Brookhaven High Flux Beam reactor on a crystal of dimensions  $0.75 \times 1.36 \times 3.78\text{ mm}$  at  $80\text{ K}$ .<sup>9b</sup> All the H atoms were located from a series of difference Fourier syntheses; full-matrix least-squares refinement of a structure model with anisotropic thermal parameters for all atoms (332 variable parameters) then led to an agreement factor of  $R(F^2) = 0.071$  for all 4457 measured reflections [ $(\sin \theta)/\lambda_{\text{max}} = 0.78\text{ \AA}^{-1}$ ].

The  $\text{H}_3\text{Ir}(\text{PC}_3)_2$  core of the molecule (a pentagonal bipyramid with five equatorial H atoms) is shown in Figure 1. Selected distances and angles are given in Table I. Since the iridium atom is situated at an inversion center, what is actually observed is a disordered superposition of two pentagons of H atoms (i.e., a decagon of half-hydrogens). The  $\text{H}\cdots\text{H}$  separations are sufficiently large, however, to enable the individual half-hydrogens to be readily resolved; the H parameters refined without any difficulty. The result (Table I) is an average Ir-H distance of  $1.603(9)\text{ \AA}$  and an average nonbonding  $\text{H}\cdots\text{H}$  distance of  $1.87(1)\text{ \AA}$ . As additional consequences of the crystallographic inversion center at the Ir atom, the P-Ir-P axis is required to be linear, and the six ipso-carbon atoms are staggered with respect to this axis.

The terminal Ir-H distance of  $1.603(9)\text{ \AA}$  compares well with the values of  $1.59\text{ \AA}$  found in  $[\text{H}_4\text{IrPt}(\text{PEt}_3)_4]^+ 10a$  and  $1.594(3)\text{ \AA}$  in  $\text{H}_2\text{Ir}(\text{SiEt}_3)_2(\text{C}_5\text{Me}_5)$ ,<sup>10b</sup> the only other iridium hydride complexes (with terminal hydrides) analyzed to date by single-crystal neutron diffraction, and is slightly shorter, as expected, than the average Os-H distance of  $1.659(3)\text{ \AA}$ , which we measured several years ago in the complex  $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$ .<sup>2b</sup> The compound  $\text{Sr}_2\text{IrD}_3$ , studied by powder neutron diffraction methods, showed an Ir-D distance of  $1.714(5)\text{ \AA}$ .<sup>11</sup> In  $\text{H}_3\text{Ir}[\text{P}(i\text{-Pr})_3]_2$  the entire  $\text{IrH}_3$  equatorial group is planar within  $\pm 0.02\text{ \AA}$ , thus showing no evidence for any "rippling" or "doming" effect.

It should be noted, incidentally, that all attempts to prepare the analogous  $\text{H}_3\text{Rh}[\text{P}(i\text{-Pr})_3]_2$  failed... instead, the reduction of the corresponding starting material  $\text{HRhCl}_2[\text{P}(i\text{-Pr})_3]_2$  yielded only  $\text{H}_2\text{RhCl}[\text{P}(i\text{-Pr})_3]_2$ .<sup>7,12</sup>

(8) The above unit cell parameters are from the low-temperature neutron diffraction analysis. For the preliminary X-ray diffraction study carried out at room temperature, the corresponding values are  $a = 7.956(1)\text{ \AA}$ ,  $b = 10.840(1)\text{ \AA}$ ,  $c = 7.515(1)\text{ \AA}$ ,  $\alpha = 107.9(1)^\circ$ ,  $\beta = 104.4(2)^\circ$ ,  $\gamma = 72.21(1)^\circ$ .

(9) (a) For the X-ray analysis, data were collected on a Nicolet-Syntex P21 diffractometer with  $\text{Mo K}\alpha$  radiation up to a  $2\theta$  value of  $50^\circ$  ( $\theta/2\theta$  scan). The structure was solved by the standard heavy-atom method. (b) The details of the low-temperature neutron data collection are similar to those described in an earlier publication (ref 2b). Initial phases for the neutron data were calculated on the basis of the non-hydrogen atomic positions derived from the X-ray analysis.

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(12) Both  $\text{HRhCl}_2[\text{P}(i\text{-Pr})_3]_2$  and  $\text{H}_2\text{RhCl}[\text{P}(i\text{-Pr})_3]_2$  have been chemically isolated and structurally characterized by X-ray diffraction (Garlaschelli, L.; Khan, S. I.; Huang, S. H.; Bau, R., unpublished results).

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**Supplementary Material Available:** A listing of the final atomic parameters for  $\text{H}_3\text{Ir}[\text{P}(i\text{-Pr})_3]_2$  (Table A) (1 page). Ordering information is given on any current masthead page.

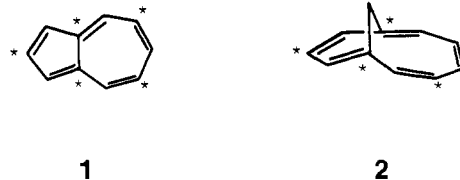
### An Alternant Hydrocarbon $\pi$ -System with Nonalternant Character. Evidence from UV-Vis Spectroscopy for Cyclic Homoconjugation in Homoazulene

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Azulene (1), when subjected to the Coulson "starring" proce-



dure, is found to contain two adjacent atoms of like parity (see asterisks in 1) and is therefore classified as a *nonalternant* hydrocarbon  $\pi$ -system.<sup>1</sup> Many of the peculiar properties of azulene can be traced to the presence of the lone transannular bond that makes this molecule nonalternant.<sup>2</sup> Herein we present the first experimental evidence that even *homoconjugation* between atoms of like parity can impart nonalternant character to a neutral hydrocarbon  $\pi$ -system. Homoazulene 2 and several derivatives thereof constitute the focus of these studies.<sup>3,4</sup>

Among the special "nonalternant properties" of azulene, the response of the UV-vis absorption spectrum of the introduction of substituents on the chromophore is particularly striking. In general, benzenoid aromatics and other alternant hydrocarbons obey Woodward's familiar rules, i.e., ca. +5 nm shift in the long-wavelength absorption maximum for each alkyl substituent.<sup>5</sup> Azulene, however, does not conform. A single alkyl substituent can shift the visible absorption maximum of azulene by as much as +29 nm toward longer wavelength or by as much as -14 nm toward shorter wavelength, depending on the site of attachment. This unusual behavior has required the development of a totally different set of empirical rules, now known as Plattner's rules, to correlate the spectral properties of azulene derivatives.<sup>6</sup> Stronger donor substituents, such as OMe, cause proportionally larger shifts of the same sign.<sup>7</sup>

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