

The structure **4b** is shown in Figure 2. It contains a Ni-C(O)-C(Me)-C(Me) metallacyclobutenone ring that is π -bonded to the molybdenum through carbons C(2) and C(3). This ring is close to planar, the maximum deviation of any atom from the mean square plane NiC(2)C(3)C(4) being 0.055 Å. The μ - η^2 , η^2 -1,3- σ /2,3- π bonding mode of the C(R)C(R)C(O) ligand has been observed in only a few other cases, all involving homonuclear metals.⁹

In complex **4b**, the Mo-C(2) and Mo-C(3) bonds are unequal [Mo-C(2) = 2.179 (2) Å; Mo-C(3) = 2.290 (2) Å]. Asymmetric π -bonding of the C(R)-C(R) fragment to the metal has been reported¹⁰⁻¹² in all structurally characterized complexes of this type. In each case, as occurs here, the significantly longer M-C bond occurs for that carbon atom bonded to the ketonic CO. The Ni-Mo bond length of 2.5859 (2) Å is in the same range observed for other simple Ni-Mo single bonds.¹⁴

Complexes **4a**, **5a**, and **5b** are believed to have similar structures to **4b**.¹⁷ All the compounds lose CO slowly when allowed to stand in solution at ambient temperatures, over a period of 1-2 days. The yields of complexes **4a**, **4b**, **5a**, and **5b** from reactions of the complexes **1a** and **1b** with alkynes are thus time-dependent and decrease with time significantly. Clean conversion into the corresponding alkyne complex **2a**, **2b** or **3** is observed when samples of **4a**, **1b**, or **5a,b** are heated in a sealed NMR tube. The complexes **5a** and **5b** are not regenerated by bubbling CO through solutions of **3** under ambient conditions. However, **4a** is formed by bubbling CO through toluene solutions of **2a** at 25 °C.

Bubbling CO through solutions of **4b** for 12 h does not afford **4b**. It is not clear to us why a nickelacyclobutenone π -bonded to Mo rather than molybdenacyclobutenone π -bonded to Ni is obtained. However, the carbonyl ligand may be required by the nickel to reduce its electron density. In this regard it is interesting to note that in the alkyne complexes, a carbonyl ligand on the Mo appears to semibridge to the Ni, rather than remain terminal.

Subtle electronic and steric factors appear to have drastic effects on the ease of formation and stability of the π -bonded metallacycle. We have been able to synthesize Ni-Cr and Ni-W analogues to complexes **2a**, **2b**, and **3** similarly, but have not yet observed the formation of any Ni-Cr or Ni-W complex of a structure similar to **4a,b** or **5a,b**. Further studies are in progress.

Acknowledgment. We thank Research Corporation, the Jesse H. Jones Faculty Research Fund, and the University of Notre

Dame for generous financial support.

Supplementary Material Available: Complete listings of atomic positional and thermal parameters and bond distances and angles for compound **4b** (3 pages). Ordering information is given on any current masthead page.

On the Stability of Cubic P₈

Georges Trinquier,* Jean-Pierre Daudey, and Najia Komih†

Laboratoire de Physique Quantique
(C.N.R.S., U.A. 505), Université Paul-Sabatier
31062 Toulouse Cedex, France

Received July 8, 1985

The stable molecular form of elemental phosphorus, which occurs in white phosphorus, is the P₄ tetrahedron, which undergoes considerable ring strain due to the 60° valence angles at all atoms. In some polymerized modifications such as black or red phosphorus, the valence angles are closer to nonhybridized values. Indeed, in black phosphorus, which is directly derived from a simple cubic system, the angles at the phosphorus atoms are 102° and 96°; in red phosphorus, they are 101°. The question of whether or not the cubic P₈ molecule could be stable has been put forward several times. Such a structure would give 90° angles at all phosphorus atoms and should induce reduced ring strain.

Fluck, Pavlidou, and Janoschek have calculated P₈ (O_h) to be less stable than 2P₄ by 47 kcal/mol, using the experimental P-P bond length (2.21 Å) of P₄ in both molecules.¹ In a previous work we have optimized the geometry of P₈ with a double- ζ basis set.² In this way, P₈ was found to be more stable than 2P₄ by 10 kcal/mol but we already suggested that this result might be reversed by including d orbitals in the basis set, which should favor the more compact and constrained P₄ systems. Halevi, Bock, and Roth recently reported a MNDO study in which all geometries were optimized and which gives P₈ more stable than 2P₄ by 68 kcal/mol.³ These authors show neatly that the simplest D_{3d} coupling 2P₄ \rightleftharpoons P₈ is forbidden in the ground state. However, as pointed out by Kutzelnigg,⁴ both an ab initio SCF calculation with d orbitals in the basis set and a calculation of the force field, in order to demonstrate that P₈ is a real minimum on the potential surface, are still needed. These two points are the main object of the present report. Possible ways of reaching this intermediate by coupling two electronically excited P₄ molecules will be also examined.

Ab initio effective core potential SCF calculations were performed with the PSHONDO algorithm,⁵ using double- ζ (DZ) and

* Permanent address: Faculté de Sciences, Université Mohamed V, Rabat, Morocco.

(1) Fluck, E.; Pavlidou, C. M. E.; Janoschek, R. *Phosphorus Sulfur* **1979**, *6*, 469.

(2) Trinquier, G.; Malrieu, J. P.; Daudey, J. P. *Chem. Phys. Lett.* **1981**, *80*, 552.

(3) Halevi, E. A.; Bock, H.; Roth, B. *Inorg. Chem.* **1984**, *23*, 4376.

(4) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(5) The PSHONDO program results from inclusion of pseudopotentials⁶ in the HONDO program.⁷ These pseudopotentials have now been introduced into the version of HONDO that contains the calculation of analytical energy gradient in both RHF and UHF schemes.⁸

(6) Durand, Ph.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283.

(7) Dupuis, M.; Rys, J.; King, M. F. *J. Chem. Phys.* **1976**, *65*, 383.

(8) Dupuis, M.; King, H. F.; *J. Chem. Phys.* **1978**, *68*, 3998.

(9) Huber, K. P.; Herzberg, G. "Constants of Diatomic Molecules"; Van Nostrand-Reinhold: New York, 1979.

(10) Sutton, L. E. "Interatomic Distances"; Chemical Society: London, 1958; Spec. Publ. No. 11.

(11) McDowell, R. S. *Spectrochim. Acta, Part A* **1971**, *27A*, 773.

(12) Bosworth, Y. M.; Clark, R. J. H.; Rippon, D. M. *J. Mol. Spectrosc.* **1973**, *16*, 240.

(8) Crystal data for complex **4b**, at 21 °C: *a* = 9.075 (2) Å, *b* = 12.416 (3) Å, *c* = 14.873 (3) Å; β = 97.72 (1)°, *Z* = 4, *d*_{calcd} = 1.748 g cm⁻³, Mo K α , space group P2₁/n (No. 14). Of the 5677 unique reflections, 4342 with *F*_o² > 3 σ *F*_o² was used in the refinement. *R*(*F*) = 0.024; *R*_w(*F*) = 0.030. Full details will be reported at a later date.

(9) Three other examples of the μ - η^2 , η^2 -bonding mode of the C(R)C(R)-C(O) ligand have been structurally characterized. These are the complexes [Rh₂(μ -CO)(μ - η^2 , η^2 -C(O)C₂(CF₃)₂)(η -C₅Me₅)₂]¹⁰, [W₂(CO)₄(μ - η^2 , η^2 -C(O)C₂(CO₂Me)₂)(η -C₅H₅)₂]¹¹, and [Pt₂(μ - η^2 , η^2 -C(O)C₂Ph₂)(η -C₅H₅)₂]¹². Isomeric bonding modes, with the terminal C(R) and C(O) groups of this ligand bonded to two different Fe atoms or two distinct Ru atoms, are known.¹³

(10) (a) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *J. Organomet. Chem.* **1982**, *236*, C49-C52. See also: Herrmann, W. A.; Bauer, C.; Weichmann, J. *Chem. Ber.* **1983**, *243*, C21-C26.

(11) Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1783-1788.

(12) Boag, N. M.; Goodfellow, R. J.; Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585-2591.

(13) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. T. *J. Chem. Soc., Dalton Trans.* **1982**, 1297-1307.

(14) Ni-Mo = 2.651 and 2.557 Å in the complex MoNi₂(μ_3 -CPh)(CO)₂(η -C₅H₅)₂,¹⁵ 2.622 Å in the related complex CoMoNi(μ_3 -CMe)(CO)₂(μ -C₅H₅)₂,¹⁵ and 2.616 (2) Å in the alkyne-bridged species FeMoNi(CO)₅(μ -PhC₂CO₂-*i*-Pr)(η -C₅H₅)₂.¹⁶

(15) Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2409-2422.

(16) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Naceur, J. B.; Mentzen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123-1130.

(17) Two other isomeric forms of **5a,b**, with a molybdenacyclobutenone ring π -bonded to the nickel cannot be ruled out. However, based on the similar spectroscopic and chromatographic behavior of **5a** and **5b** to **4a**, and in view of the structure of **4b**, we believe that the assigned structures are more likely.

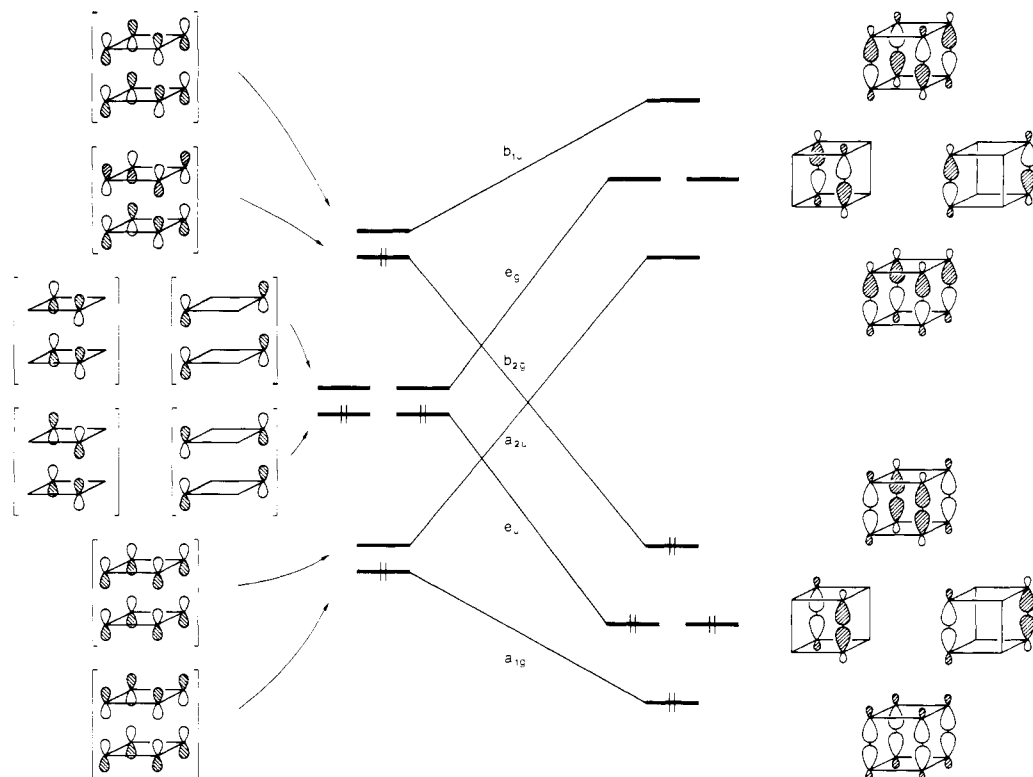


Figure 1. Simplified orbital correlation diagram for the D_{4h} least-motion coupling of two square-planar P_4 molecules. Orbital occupation corresponds to the coupling of quintet states with opposite spins on each fragment.

Table I. Summary of the Results on P_2 , P_4 (T_d), and P_8 (O_h)^a

		DZ	DZd	exptl
P_2	r_{P-P}	1.962	1.865	1.893 ^c
	k_e	5.7	7.2	5.6 ^c
P_4	r_{P-P}	2.370	2.190	2.21 ^d
	k_{A_1}	1.5	2.2	1.75, ^e 1.68 ^f
P_8	r_{P-P}	2.420	2.274	
	k_{A_1g}	1.5	2.1	
$2P_2 \rightarrow P_4$	ΔE	+3.0	-29.4	
	ΔH ^b	+4.3	-28.1	-52 ^g
$2P_4 \rightarrow P_8$	ΔE	-10.3	+26.3	
	ΔH	-8.1	+28.5	
$4P_2 \rightarrow P_8$	ΔE	-4.2	-32.4	
	ΔH	+0.5	-27.7	

^aUnits: r in Å, k in mdyn/Å, ΔE and ΔH in kcal/mol. ^b ΔH is ΔE corrected by the differences in zero-point vibration energies calculated from Table II. ^cReference 9. ^dReference 10. ^eReference 11. ^fReference 12. ^gReference 13.

double- ζ + d (DZd) basis sets ($\eta(d) = 0.57$). Force field calculations were carried out at the DZ level only, which is appropriate for this purpose and which lead to reasonable vibrational frequencies as can be seen for P_2 and P_4 . The results are summarized in Tables I and II. The P-P bond is found to be 0.08-Å longer in P_8 than in P_4 . The inclusion of d orbitals in the basis set shortens this distance by about the same amount in both P_4 and P_8 (-0.18 and -0.15 Å, respectively). As expected² P_8 is calculated to be 26 kcal/mol less stable than $2P_4$ at the DZd level. Correlation effects can be expected to increase this difference by favoring the strained tetrahedra over the near-strain free cube. We have already proposed that the 12 cis parallel repulsions occurring between the P-P bonds in the cube might be responsible for the lower stability of P_8 over $2P_4$.² The calculated vibrational frequencies (Table II) are all real, which means that the O_h structure is a real minimum on the P_8 potential surface. The $P_8 \rightarrow 2P_4$ dissociation being forbidden in the ground state, cubic P_8 might therefore be a viable intermediate, which could actually

(13) Mc Bride, B. J.; Heimel, S.; Ehlers, J. G.; Gordon, S. NASA [Spec. Publ.], SP NASA SP-3001.

Table II. Calculated Harmonic Vibrational Frequencies^a

P_2		P_4 (T_d)			P_8 (O_h)		
exptl ^b		exptl ^c			exptl ^d		
792	781	e	317	367	373	e_u	184
		t_2	422	462	481	t_{2g}	274
		a_1	575	606	619	a_{2u}	374
						t_{1u}	385
						t_{2g}	388
						a_{1g}	409
						t_{2u}	428
						e_g	451

^aIn cm^{-1} (DZ basis set). ^bReference 9. ^cReference 12. ^dReference 11.

be observed, under which conditions?

Since it is not accessible from two tetrahedral ground-state P_4 molecules and since it seems most improbable to build the cube from a simultaneous coupling of four P_2 units, we suggest that a simple way of building cubic P_8 might be the coupling of two square-planar P_4 units, i.e., two electronically excited P_4 molecules. Obviously, D_{4h} least-motion coupling is allowed from quintet states, as illustrated by the simplified orbital correlation diagram of Figure 1. For open-shell triplet or singlet states, the a_{2u} orbital is filled while the b_{2g} orbital is empty. The reaction is formally forbidden; its barrier depends on the CI matrix element between these two orbitals. Note that because of the very nature of a_{2u} and b_{2g} orbitals, a simple C_{4v} , C_4 , D_{2h} , C_{2h} , or C_2 distortion does not make the reaction allowed while a C_{2v} or C_2 distortion does.¹⁴ By means of UHF + CI calculations¹⁵ performed at the DZd level, these two square-planar open-shell states were estimated to lie

(14) Noneclipsed arrangements of two rhomboid P_4 units may define such C_{2v} or C_2 point groups.

(15) The CI calculations were carried out with the CIPSI algorithm: Daudey, J. P.; Malrieu, J. P. In "Current Aspects of Quantum Chemistry"; Carbo, Ed.; Elsevier Scientific Publishing Co.: Amsterdam, 1982. For the open-shell states, the CI was performed from the spin-up set of the UHF wavefunction. Multireference wavefunctions built over 50, 36, and 16 determinants were taken as zeroth-order descriptions for closed-shell singlet and open-shell triplet and quintet states, respectively, and perturbed to the second order in energy.

45 kcal/mol above the tetrahedral 1A_1 ground state P_4 for the 3E_g triplet state and 119 kcal/mol for the 5E_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.^{16,17} Further exploration of these surfaces is under way.

Acknowledgment. We thank Dr Jean-Paul Malrieu for helpful discussions.

(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°); 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°). 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.¹⁸⁻²⁰ 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.²¹

(18) Schweig, A.; Thiel, W. *J. Am. Chem. Soc.* **1979**, *101*, 4742.

(19) Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 2617.

(20) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5292.

(21) Schoeller, W. W.; Lerch, C. *Inorg. Chem.* **1983**, *22*, 2992.

X-ray and Neutron Diffraction Study of $H_3Ir[P(i-Pr)_3]_2$

Luigi Garlaschelli,[†] Saeed I. Khan, and Robert Bau*

Chemistry Department
University of Southern California
Los Angeles, California 90089

Giuliano Longoni

Dipartimento di Chimica Inorganica e Metallorganica
Università Di Milano, Milano 20133, Italy

Thomas F. Koetzle*

Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973

Received July 22, 1985

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.¹⁻³ 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.⁴ In this paper

[†] On leave from the Dipartimento di Chimica Inorganica e Metallorganica, Università di Milano, Milano 20133, Italy.

(1) For a brief review, see: Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *Adv. Chem. Ser.* **1978**, *167*, 73.

(2) (a) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872. (b) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557. (c) Teller, R. G.; Carroll, W. E.; Bau, R. *Inorg. Chim. Acta* **1984**, *87*, 121.

(3) (a) Howard, J. A. K.; Mead, K. A.; Spencer, J. L. *Acta Crystallogr., Sect. C* **1983**, *C39*, 555. (b) Howard, J. A. K.; Greagson, D.; Spencer, J. L.; Turner, D. *Acta Crystallogr., Sect. A* **1981**, *A37*, C240. (c) Gregson, D.; Howard, J. A. K.; Nicholls, J. N.; Spencer, J. L.; Turner, D. G. *J. Chem. Soc., Chem. Commun.* **1980**, 572. (d) Gregson, D.; Mason, S. A.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G. *Inorg. Chem.* **1984**, *23*, 4107. (e) Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012. (f) Clark, G. R.; Skelton, B. W.; Waters, T. N. *Inorg. Chim. Acta* **1975**, *12*, 235.

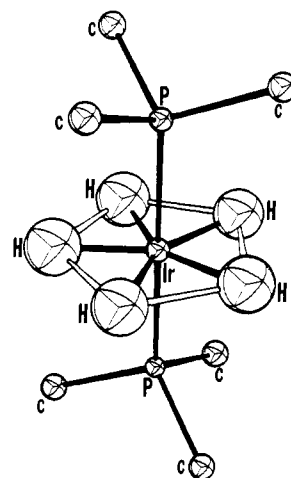


Figure 1. Structure of the core of $H_3Ir[P(i-Pr)_3]_2$ as obtained from the neutron diffraction analysis. Atoms are drawn at the 50% probability level. For clarity, only the ipso carbon atoms of the isopropyl groups are shown. The hollow connecting lines between the H atoms do not represent bonds but represent nonbonding contacts between the hydride ligands.

Table I. Selected Distances and Angles in $H_3Ir[P(i-Pr)_3]_2$ ^a

Bond Distances, Å			
Ir-H ₁	1.606 (5)	H ₁ ...H ₂	1.90 (1)
Ir-H ₂	1.630 (4)	H ₂ ...H ₃	1.89 (1)
Ir-H ₃	1.615 (5)	H ₃ ...H ₄	1.83 (1)
Ir-H ₄	1.587 (5)	H ₄ ...H ₅	1.84 (1)
Ir-H ₅	1.578 (4)	H ₅ ...H ₁	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 ₁ -Ir-H ₂	72.0 (5)°	Ir-P-C (av)	114.1 (5)°
H ₂ -Ir-H ₃	68.8 (5)°	P-C-H (av)	102.4 (10)°
H ₃ -Ir-H ₄	70.5 (5)°	C-C-H (av)	111.2 (4)°
H ₄ -Ir-H ₅	75.4 (5)°	C-C-C (av)	110.0 (3)°
H ₅ -Ir-H ₁	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)°

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

we report the preparation and single-crystal X-ray and neutron-diffraction analysis of $H_3Ir[P(i-Pr)_3]_2$ (*i-Pr* = isopropyl).

$H_3Ir[P(i-Pr)_3]_2$ was synthesized in a manner similar to that employed by Chatt et al. to make other iridium polyhydrides:⁵ to a deep red solution of $HIrCl_2[P(i-Pr)_3]_2$ ^{6,7} (0.61 g, 1.04 mmol) in THF, 0.15 g (3.9 mmol) of $LiAlH_4$ was added in portions. An

(4) (a) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331. (b) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764. (c) Clerici, M. G.; DiGiacchino, S.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* **1975**, *84*, 379. (d) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695. (e) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 606.

(5) Chatt, J.; Coffey, R. S.; Shaw, B. L. *J. Chem. Soc.* **1965**, 7391.

(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 $IrCl_2 \cdot 3H_2O$ 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 × 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.; Staincock, 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).