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IRIDIUM: A NOVEL IRIDIUM(V)

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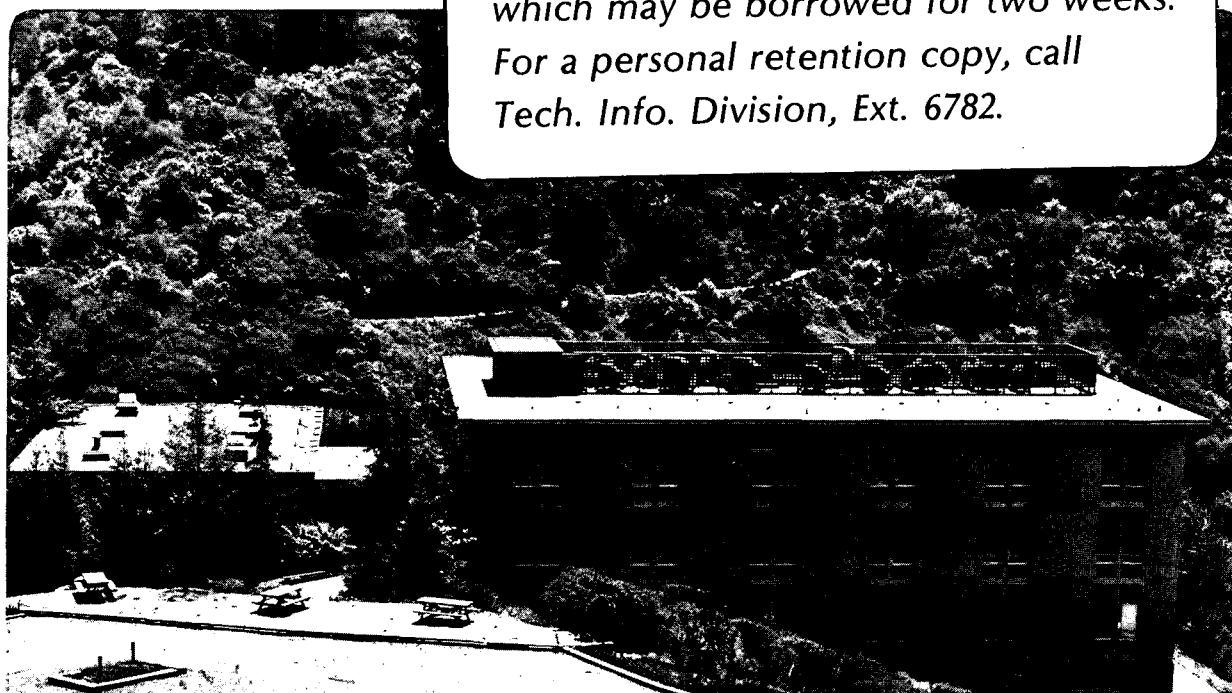
PREPARATION AND REACTIONS OF TETRAHYDRIDO(PENTAMETHYL-
CYCLOPENTADIENYL)IRIDIUM: A NOVEL IRIDIUM(V)
POLYHYDRIDE

T.M. Gilbert and R.G. Bergman

June 1983

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**PREPARATION AND REACTIONS OF TETRAHYDRIDO(PENTAMETHYL-
CYCLOPENTADIENYL)IRIDIUM: A NOVEL IRIDIUM(V) POLYHYDRIDE**

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PREPARATION AND REACTIONS OF TETRAHYDRIDO(PENTAMETHYL-
CYCLOPENTADIENYL)IRIDIUM: A NOVEL IRIDIUM(V) POLYHYDRIDE

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Summary: The complex $(C_5(CH_3)_5)IrH_4$ (2), has been synthesized and characterized by spectroscopic and analytical methods, including a single crystal X-ray diffraction study. This compound is a rare example of a formal iridium(V) species; it can be converted to $[C_5(CH_3)_5](PMe_3)IrH_2$ on irradiation in the presence of PMe_3 , leads to $C_5(CH_3)_5$ -substituted chloro- and hydridochloroiridium dimers on treatment with CCl_4 , gives $[C_5(CH_3)_5]Ir(CO)_2$ with CO, and undergoes thermal and photochemical H/D exchange in the presence of D_2 gas.

Few examples exist of organometallic complexes of late transition metals in high oxidation states. Comparison with high-valent complexes of early transition metals suggests that such compounds, especially those of Group VIII B, might be expected to possess unique properties and reactivities.

Phosphine-stabilized iridium(V) hydrides have been known since the early 1970's,¹ and were shown somewhat later to catalyze H/D exchange with deuterated solvents at elevated temperatures.² Recently, Maitlis and coworkers demonstrated the accessibility of pentamethylcyclopentadienyl-substituted organo-iridium(V)³ and organo-rhodium(V)⁴ complexes, noting intriguing products upon pyrolysis of the former. However, examples of this type of complex are still relatively rare.

As part of continuing studies of the synthesis and reactivity of iridium

hydride complexes,⁵ we wish to report the synthesis of the photoactive complex $(C_5(CH_3)_5)IrH_4$ (2, Scheme 1). This material represents an unusual example of an iridium(V) organometallic polyhydride, and exhibits several interesting thermal and photochemical reactions.

A search of the available literature indicated that no neutral iridium compounds containing only pentamethylcyclopentadienyl and hydride ligands were known. In 1973, however, White, Oliver and Maitlis⁶ reported the synthesis of the cationic salt $[(C_5(CH_3)_5)Ir]_2H_3PF_6$, (1), which seemed a viable precursor for a neutral complex of the proper formula. Accordingly, we treated a hexane:benzene slurry of the cation at ambient temperature with 5.6 equivalents of $LiEt_3BH$,⁷ and allowed the resulting orange-red solution to stir overnight. Rapid chromatography through alumina III (air-free conditions) followed by removal of solvent gave a yellow-white residue, from which a colorless, moderately air-sensitive solid could be sublimed (40°C, 30 mTorr) in 55% yield. Spectroscopic and elemental analysis data for this compound indicate it to be the monomeric $(C_5(CH_3)_5)IrH_4$, (2). Data for 2: 1H NMR (C_6D_6) 1.99 (s, $C_5(CH_3)_5$), δ -15.43 (s, Ir-H); ^{13}C NMR (C_6D_6 , 1H decoupled) δ 96.5 ($C_5(CH_3)_5$), 10.0 ($C_5(CH_3)_5$); IR (KBr) 2150 (s), 2140 (shoulder cm^{-1}); MS, m/e 332, 330, 328, 326, 324, 322; molecular weight (Signer isothermal distillation method⁸, CH_3OCH_3 solvent, 25°C) 327 ± 15 , Calc. 331. Anal for $C_{10}H_{19}Ir$: Calc. C 36.24; H 5.78. Found C 35.98; H 5.83.

The polyhydride 2 is highly soluble in most common solvents, which hampered the isolation of X-ray diffraction-quality crystals. However, extremely slow sublimation (5 mTorr) on a warmed surface in a Pyrex NMR tube yielded crystals suitable for a diffraction study.

The single crystal X-ray structure determination was performed at -150°C.⁹ Even at this temperature, complex decomposition was observed in the

X-ray beam over the data collection period. Three data sets were collected. An initial low angle set was discarded during refinement due to difficulties caused by the decomposition. Both a high angle and a low angle set were taken on a second crystal; of these, the high angle data set proved most amenable to a reasonable solution of the structure. The atoms were located through a combination of Fourier and search techniques, and their positions determined accurately through several full-matrix least squares cycles. Refining two iridium atoms and twenty carbon atoms with anisotropic thermal parameters (199 parameters, 1446 observations), the final residuals are $R = 3.65\%$, $wR = 4.63\%$.

The crystal structure consists of two independent molecules of $(C_5(CH_3)_5)IrH_4$ in the asymmetric unit (Figure 1). The average Ir-C distance is $2.244(19) \text{ \AA}$ (range $2.224(10)$ - $2.271(11) \text{ \AA}$). Although the crystal decomposition problems mentioned above prevented our locating the hydrogen atoms directly, it is clear that they must lie on the "open" side of the Ir atoms. The closest intermolecular contacts to the Ir atoms are in the range 4.4 to 4.6 \AA to the methyl groups of neighboring molecules.

Treatment of a benzene solution of **2** with excess CCl_4 at ambient temperature immediately caused the colorless solution to become bright purple; analysis of the 1H NMR spectrum of the reaction mixture demonstrated that the compounds **3**¹⁰ and **4**¹¹ were present. Heating the mixture to $60^\circ C$ for 14 hours gave the well-known dimer **5**¹², which was isolated in 92% yield and characterized by 1H NMR.

The polyhydride complex shows high photoactivity under reaction conditions similar to those described by Janowicz and Bergman.⁵ Irradiation ($\lambda \geq 275 \text{ nm}$; high pressure Hg lamp, Pyrex filter) of **2** in the presence of $P(CH_3)_3$ in toluene smoothly generates **6** in quantitative 1H NMR yield. Continued irradiation results in extrusion of dihydrogen and insertion of the

intermediate into the carbon-hydrogen bonds of the solvent.⁵ A similar irradiation of 2 in the presence of CO leads to $(C_5(CH_3)_5)Ir(CO)_2$ ¹², (7), as demonstrated by ¹H NMR and IR. An intermediate was seen in the ¹H NMR during this experiment, which spectral analysis indicated might be $(C_5(CH_3)_5)Ir(CO)H_2$,¹³ corresponding to the phosphine complex discussed above. These two experiments suggest that complex 2 extrudes dihydrogen upon irradiation, leading to the intermediate " $(C_5(CH_3)_5)IrH_2$ ", which is then trapped by the dative ligand.

The complex is capable of undergoing H/D exchange under photolysis conditions. Irradiation of 2 in toluene under 5 atm of D₂ for two hours, followed by removal of solvent and sublimation of the reaction mixture led to a colorless compound, which spectral analysis indicated was a partially (ca. 57% by ¹H NMR integration) deuterated analogue of 2, in 76% yield. The extent of deuteration is limited by competitive formation of a burgundy material during irradiation; this material seems to be a hydride deficient iridium species but as yet has defied isolation due to its extreme solubility.

A fully deuterated analogue of 2 may be prepared through thermal H/D exchange. Heating 2 at 60°C in toluene for 26 hours under D₂ (1.5 atm), followed by the workup described above led to 8 in 80% yield. The complex 8 was demonstrated to be 83% deuterated by ¹H NMR integration of the hydride resonance against the $C_5(CH_3)_5$ resonance; lack of deuteration on the ring was confirmed by ²H NMR and IR.¹⁴ Data for 8: ²H NMR (C₆H₆) δ -15.34 (s); IR (KBr) 1555 (s), 1545 (shoulder) $v_H/v_D = 1.38$. Interestingly, however, no reaction occurs between 2 and the normally powerful dative ligand $P(CH_3)_3$ under these conditions; only upon elevation of the temperature to 110°C and heating for 44 hr is conversion of tetrahydride 2 to 6 observed. This indicates that the thermal hydrogen exchange reaction must take place by some mechanism (e.g.,

partial detachment of the Cp ligand; loss of hydrogen atoms in a radical chain process) other than simple reductive elimination of H₂ followed by oxidative addition of D₂.

Both the chemistry and structure of tetrahydride 2 are under further study. It is our hope that the method utilized in the synthesis of 2 will be applicable to other transition metal systems, and that 2 might also be employed as a precursor to additional iridium(V) complexes.

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Supplementary Material Available. Experimental writeup by Dr. Hollander, data collection and refinement parameters, positional parameters and their esd's, general temperature factor expressions and their esd's, raw interatomic distances and angles for 2, listing of F_o and F_c and packing diagrams for the crystal (28 pages). Supplied with the archival edition of the journal, available in many libraries; alternatively, ordering information is given on any current masthead page.

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- 7) Use of less than five equivalents of hydride reagent results in incomplete consumption of starting material and decreased yields of **2**; no other product is isolated under such conditions.
- 8) (a) Signer, R. Justus Liebigs Ann. Chem. 1930, 478, 246. (b) Clark, E. P. Ind. Eng. Chem., Anal. Ed. 1941, 13, 820.
- 9) Crystal Data: Monoclinic, $P2_1/n$, $a = 16.7466(25) \text{ \AA}$, $b = 7.6224(15) \text{ \AA}$, $c = 17.0821(30) \text{ \AA}$, $\beta = 101.406(13)$, $V = 2137.5(12) \text{ \AA}^3$, $Z = 8$, $d(\text{calc}) = 2.060 \text{ g/cm}^3$ @ -150°C . Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$, $45^\circ \leq 2\theta \leq 55^\circ$, 2103 reflections, $1446 F^2 > 3\sigma(F^2)$. Corrected for decay; empirically corrected for absorption.
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- 14) More recent experiments suggest that deuterium may be incorporated into the $C_5(CH_3)_5$ ring when higher pressures or longer reaction times are employed. This result will be considered more fully in future descriptions of this work.

Scheme 1

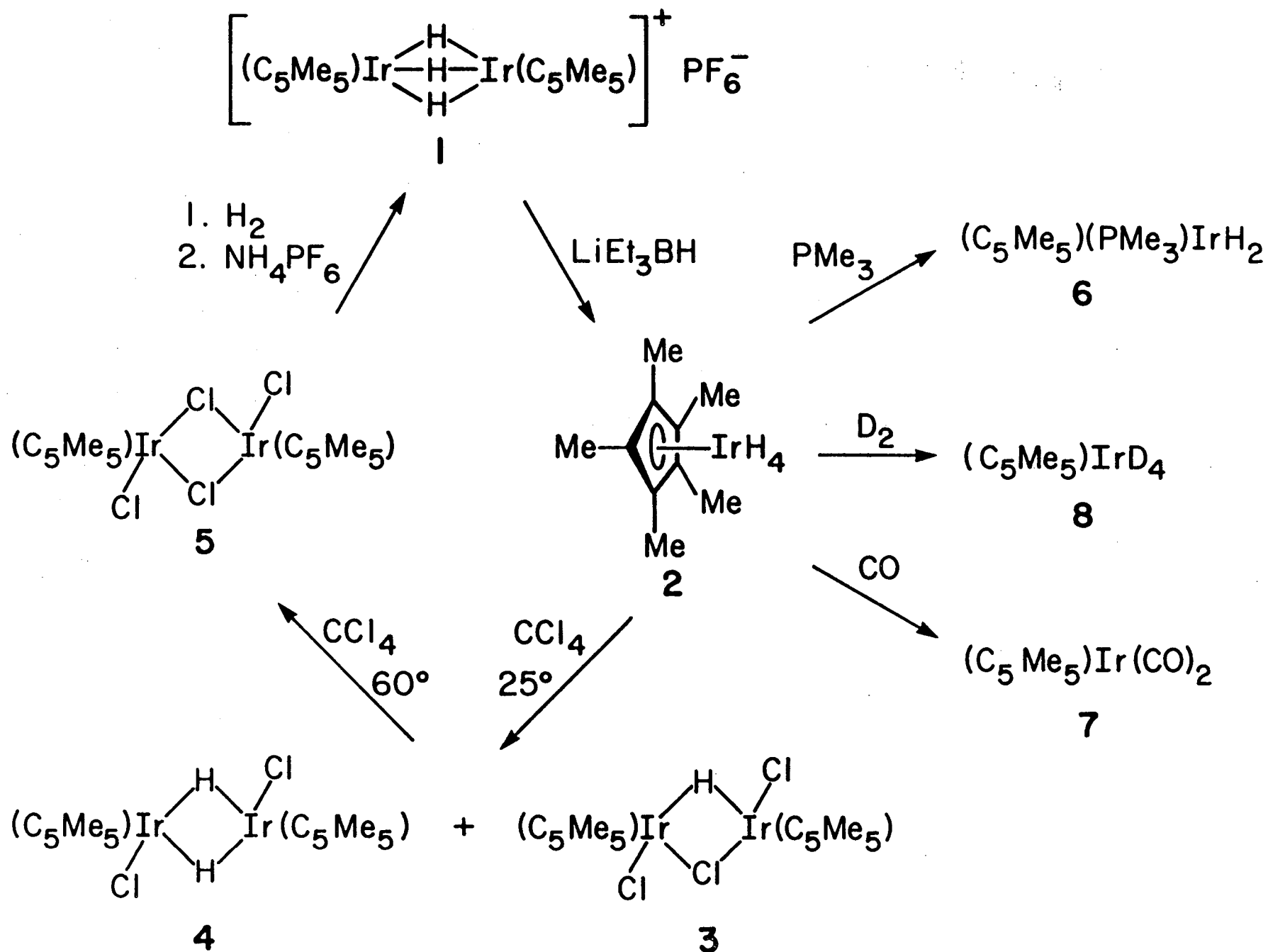
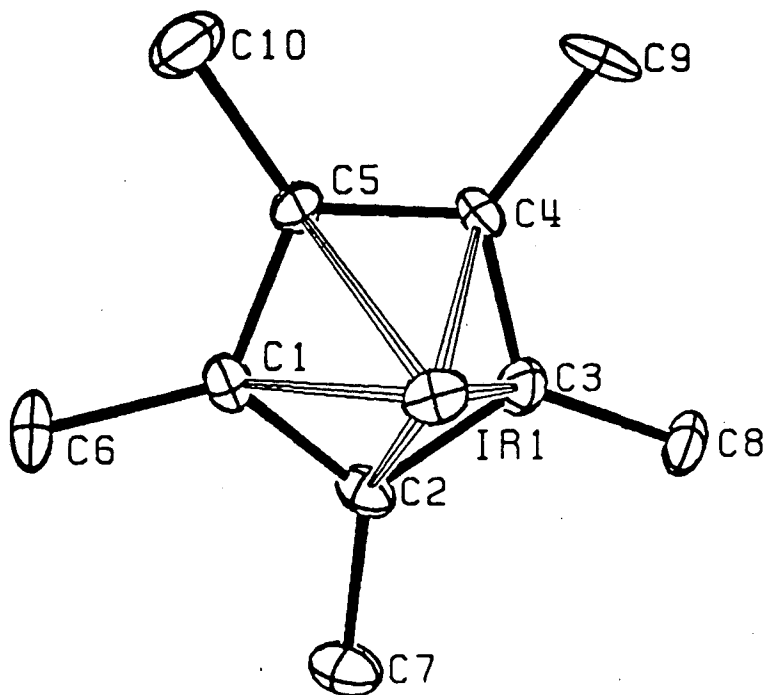
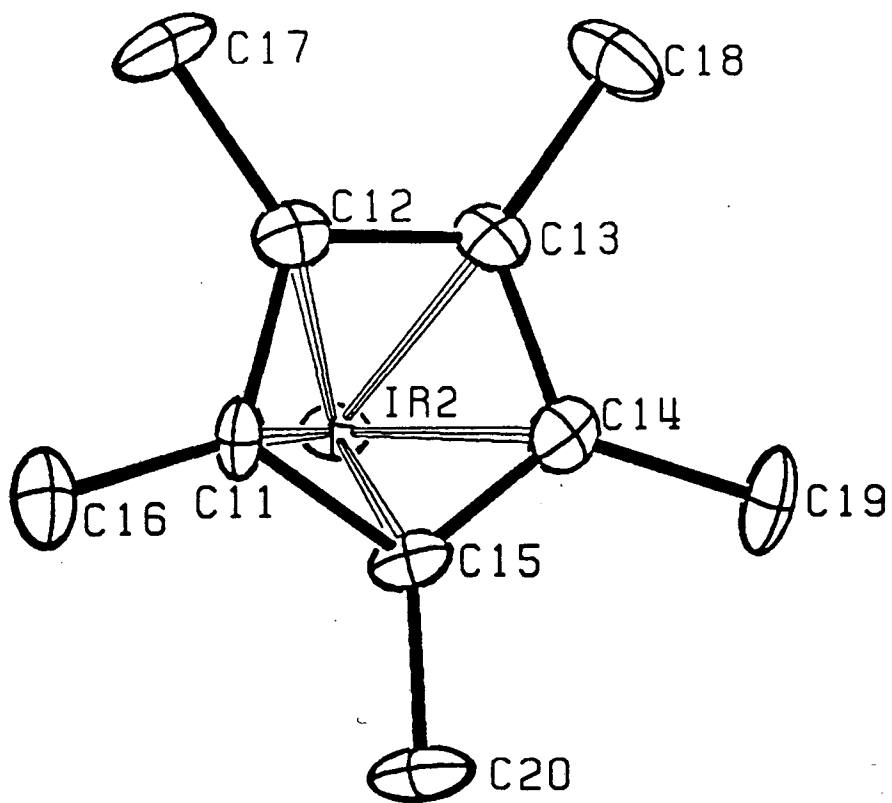


Figure Caption

Figure 1. ORTEP drawing of $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{IrH}_4$ (2).

FIGURE 1



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