prediction is in modest agreement with the observed values of 0.09 (1α) and 0.10 Å (1β).

Although 1 is the first reported example of an indenylmetallacarborane, there exist in the literature[11,25] examples of polycyclic (arene)ferracarboranes. Structural studies of 1-(η^6-Ar)-2,3-Et_2-1,2,3-$FeC_2B_4H_4$ (Ar = $C_{10}H_8$ and $C_{14}H_{10}$) have both shown cisoid conformations of the carbon atoms in the C_2B_3 face relative to the bridge atoms of the polycyclic arene. Clearly these apparent conformational preferences could be related to those in indenylmetallacarboranes. In addition, the naphthalene complex shows a distinct slipping distortion in the expected direction.[25] The enhanced reactivity toward arene substitution by CO or $P(OMe)_3$ in [3-(η^6-$C_{10}H_8$)-1,2-Me_2-3,1,2-$FeC_2B_9H_9$] over its C_6H_6 analogue has, moreover, been ascribed to naphthalene slippage.[11] It is interesting, however, that no slipping distortion is apparent in the structure of 1-(η^6-$C_{14}H_{10}$)-2,3-Et_2-1,2,3-$FeC_2B_4H_4$.[25]

Electrochemical studies on 1 reveal two reversible one-electron reductions at −0.8 and −1.82 V. The difference between these potentials is the same as that reported by Geiger et al.[26] for 2, suggesting that the reductions are metal-based. The electrochemical synthesis of the 19ve monoanion of 1 may prove to be feasible, but the formation of the 20ve dianion is clearly a less attractive proposition and the analogous system 3-(η^5-C_9H_7)-3,1,2-$NiC_2B_9H_{11}^-$ seems a more realistic target.

The 19- and 20ve analogues of 1 are important because of potential conformational changes, cf. bis(carborane) complexes, and selective or concerted slipping distortions. Complexes of this type will be subject to future contributions in this series.

Acknowledgment. We are very grateful to Dr. G. A. Heath for performing the electrochemical studies and for related discussion. D.E.S. thanks the S.E.R.C. for the award of a research studentship.

Registry No. 1, 100839-11-0; 2, 37100-20-2; $Co(acac)_3$, 21679-46-9; $Tl_2C_2B_9H_{11}$, 97102-40-4; Li[C_9H_7], 32334-19-3.

Supplementary Material Available: Tables of calculated H atom coordinates, thermal parameters, bond distances involving H atoms, bond angles, and least-squares plane data, packing diagrams, and lists of observed and calculated structure factors (69 pages). Ordering information is given on any current masthead page.

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Some Chemistry of Alkyl Complexes of Bis(1,2-bis(diphenylphosphino)ethane)iridium(I)

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New five-coordinate Ir(I) alkyl complexes have been prepared by the addition of LiR (R = CH_3, C_5H_5) to [Ir(dppe)$_2$]Cl (dppe = 1,2-bis(diphenylphosphino)ethane). IrMe(dppe)$_2$ is found to be very reactive toward acid, forming *cis*-IrH(Me)(dppe)$_2^+$, and toward CO and CO_2. In contrast, the cyclopentadienyl complex [Ir(dppe)$_2$]Cp is ionic and shows the reactivity of the Ir(dppe)$_2^+$ cation. That this complex is ionic is apparently not a result of steric constraints. A X-ray structural study of IrMe(dppe)$_2$ indicates that the coordination geometry about the Ir center is that of a distorted trigonal bipyramid with the Me group in an axial position; Ir–Me = 2.189 (8) Å.

Introduction

Transition-metal alkyl complexes play a large role in organo-transition-metal catalyzed transformations of organic molecules. These complexes are involved in such processes as hydrogenation,[1,2] hydroformylation,[3] olefin isomerization,[4] and polymerization.[5]

The square-planar, four-coordinate ions Ir(P–P)$_2^+$, P–P = dppe (1,2-bis(diphenylphosphino)ethane), dmpe (1,2-bis(dimethylphosphino)ethane), and depe (1,2-bis(diethylphosphino)ethane), have shown remarkable activity toward a variety of small molecules, including hydrogen, oxygen, carbon monoxide, hydrogen halides, and carbon dioxide.[6-11] But there appear to be no reports of the reactions of these ions with alkyl groups. Here we report the preparation, structure, and some reaction chemistry of Ir(Me)(dppe)$_2$; we also contrast the chemistry of the Me complex with the corresponding Cp complex, which is the ionic compound [Ir(dppe)$_2$]Cp.

Experimental Section

All reactions were performed under purified dinitrogen with the use of standard Schlenk-line techniques. Manipulations of

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[1] For a general survey of homogeneous catalysis see: (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980. (b) Schrauzer, G. N. "Transition Metals in Homogeneous Catalysis"; Marcel Dekker: New York, 1971. (c) Taqui Kahn, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974.

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air-sensitive compounds were carried out in an argon-filled glovebox. All solvents were thoroughly dried and deoxygenated by refluxing under a dinitrogen atmosphere over Na/benzophenone and were then degassed immediately prior to use. Glassware was dried by heating under vacuum before use.

Chemical analyses were performed by Galbraith Lab. Inc. and by Dornis & Kolbe Microanalytical Lab. The NMR spectra were recorded on a JEOL FX90Q spectrometer. Positive $^{31}P\{^1H\}$ chemical shifts are downfield from 85% H_3PO_4. IR spectra, obtained as Nujol mulls, were recorded on a Perkin-Elmer Model 283 spectrophotometer.

Preparation of $IrMe(dppe)_2$.[12] To $[Ir(dppe)_2]Cl$[6] (0.43 g, 0.42 mmol), suspended in 10 mL of benzene, was added with stirring $LiMe/Et_2O$ solution (1.5 M, Aldrich) until nearly all of the Ir complex dissolved. Excess $LiMe/Et_2O$ should be avoided. After filtration, the solution was slowly evaporated to dryness. The red solid product thus obtained was recrystallized from CH_2Cl_2–hexane. Red needle-like crystals were obtained in 78% yield. Composition was also established by a crystal structure determination (see below). Anal. Calcd for $C_{53}H_{51}IrP_4$: Ir, 19.14; P, 12.34; C, 63.40; H, 5.12. Found: Ir, 19.02; P, 12.18; C, 63.10; H, 5.27.

^1H NMR (benzene-d_6, 30 °C): δ −0.52 (CH_3, qu). ^1H NMR (CD_2Cl_2, 30 °C): δ −0.83 (CH_3, br), 2.38 (methylene, br), 6.9–7.4 (phenyl, m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 30 °C): δ 27.2 (s, br).

Preparation of $[Ir(dppe)_2]Cp{\cdot}THF$. To $[Ir(dppe)_2]Cl$ (0.34 g, 0.33 mmol), suspended in 30 mL of THF, freshly prepared LiCp/THF solution (0.1 M) was added until all the Ir complex dissolved. To this solution was slowly added ethyl ether (20 mL) to precipitate the product. Orange-red crystals of $[Ir(dppe)_2]Cp{\cdot}THF$ were obtained in 81% yield. Recrystallization from other solvents was not successful. Composition was also established by a crystal structure determination.[13] Anal. Calculated for $C_{61}H_{61}IrOP_4$: C, 65.05; H, 5.46; Ir, 17.07; P, 11.00. Found: C, 65.59; H, 5.52; Ir, 15.79; P, 10.39.

^1H NMR (CD_2Cl_2): δ 1.8 (β-CH_2 in THF, qu), 2.1 (CH_2 in dppe, t), 3.7 (α-CH_2 in THF, t), 6.4 (Cp, m). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 50.0 (s).

Preparation of $[Ir(dmpe)_2]Cp$. This compound was prepared in the same manner as the dppe analogue with the substitution of $[Ir(dmpe)_2]Cl$[7] for $[Ir(dppe)_2]Cl$. The crystalline product was brownish yellow in color.

^1H NMR (CD_2Cl_2): δ 1.6–1.9 (CH_3, m), 2.0 (CH_2, t), 6.4 (Cp, m). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 50.2 (s).

***cis*-$[IrH(Me)(dppe)_2][BF_4]$.** To a solution of $IrMe(dppe)_2$ in CH_2Cl_2 was added $HBF_4{\cdot}Et_2O$ dropwise with stirring until the red color of the solution disappeared. Addition of ethyl ether precipitated an off-white solid. Attempts to purify the product by recrystallization were not successful because the compound slowly decomposes in solution. Spectra of a fresh solution of the product in CD_2Cl_2 show the following data: ^1H NMR: δ −11.3 (hydride, pseudo dq, J_{H-P}(cis) = ca. 14.5 Hz, J_{H-P}(trans) = 125 Hz), −0.31 (CH_3, pseudo dq, J = 7.9, 4.2 Hz), 2.4 (CH_2, br), 6.3 (phenyl, dd, J = 7.6, 16.8 Hz), 6.5–7.7 (phenyl, m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_A 32.5, δ_B 26.1, δ_C 19.9, δ_D 3.9; J_{AB} = 332.3 Hz, J_{AC} = 0.5 Hz, J_{AD} = 8.0 Hz, J_{BC} = 9.7 Hz, J_{BD} = 0.5 Hz, J_{CD} = 8.5 Hz. IR: ν(Ir–H) 2140 cm^{-1}.

Determination of the Structure of $IrMe(dppe)_2$. Preliminary examination of the crystals on a CAD-4 diffractometer established that the material crystallizes in the orthorhombic space group C_{2v}^{19}—$Fdd2$. A suitable crystal was transferred from the CAD-4 diffractometer to the cold stream of a Picker FACS-1 diffractometer for data collection, as the resolution on the FACS-1 is higher and the cell, even though F-centered, is very large. Data collection proceeded by methods standard in this laboratory.[14] The intensities of 6 standard reflections, monitored every 100 reflections, showed only the expected statistical fluctuations. Data collection was terminated at 2θ = 56.6°, for at that angle only about $^1/_5$ of the reflections were observed to be above the 3σ limit. Table I lists crystal data and other pertinent details.

Table I. Crystal Data and Experimental Details for $IrMe(dppe)_2$

formula	$C_{53}H_{51}IrP_4$
fw	1004.09
a, Å	46.847 (16)
b, Å	30.429 (11)
c, Å	12.191 (5)
V, Å^3	17378
d_{calcd}, g/cm^3	1.535 (−160 °C)[a]
space group	C_{2v}^{19}—$Fdd2$
cryst shape	needle crystal bounded by {110} and {001}; width ≈ 0.08 mm, length ≈ 0.57 mm
cryst vol, mm^3	0.0039
radiation	graphite-monochromatized Mo Kα ($\lambda(K\alpha_1)$ = 0.7093 Å)
μ, cm^{-1}	32.41
transmission factors	0.724–0.824
takeoff angle, deg	3.1
scan speed, deg in 2θ/min	2.0
receiving aperture	4.0 mm wide × 5.0 mm high; 34 cm from crystal
scan width, deg	0.85 below Kα_1 to 0.75 above Kα_2
background counts	10 s with rescan option[b]
data collected	$h,k,\pm l$, $3.3 \le 2\theta \le 20°$; h,k,l, $20° \le 2\theta \le 56.6°$
no. of unique data ($l \ge 0$)	5470
no. of unique data ($F_o^2 \ge 3\sigma(F_o^2)$)	4545
no. of variables	522
p for estimation of $\sigma(F_o^2)$	0.03
R on F_o^2	0.064
R_w on F_o^2	0.079
R on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.039
R_w on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.037
error in observn of unit wt	1.05 e^2

[a] The low-temperature system is based on a design by: Huffman, J. C., Ph.D. Thesis, Indiana University, 1974. [b] The diffractometer was run under the disk-oriented Vanderbilt system: Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570.

The structure was solved and refined by methods standard in this laboratory.[14] The position of the Ir atom was obtained by inspection of a normal Patterson function. The remaining nonhydrogen atoms were located on a difference electron density map. Initial refinement by full-matrix least-squares methods was on F_o. After correction for absorption effects the sense of the polar axis was determined in the following way. Isotropic refinement of the non-hydrogen atoms was carried out for (a) the parameters as determined and (b) the parameters with signs reversed. The respective R, R_w indices for these two refinements were 0.047, 0.050 and 0.058, 0.074. These indices strongly favor model a. Conclusive proof for the correctness of model a was established by a comparison of the $|F_o|$ and $|F_c|$ values of the hkl and $hk\bar{l}$ reflections; these reflections are not equivalent in $Fdd2$. There were 104 comparisons for reflections having F_c greater than 20e and $|F_o(hkl)|$ and $|F_o(hk\bar{l})|$ differing by more than 5%; model a predicted the correct inequality in 101 cases. In ensuing refinements only those reflections with $l > 0$ were used, in order to avoid excessive contributions from low-angle data.

After two cycles of anisotropic refinement of the non-hydrogen atoms the positions of the H atoms of the methyl group were established from a difference electron density map. These positions were idealized (C–H = 0.95 Å, $B_H = B_C + 1.0$ Å^2). The positions of the phenyl and methylene H atoms were calculated from known geometry. These 51 H atoms were added as fixed contributions in the final cycles of refinement, which were carried out on F_o^2 and included those reflections for which $F_o^2 < 0$. Table II lists the final positional parameters for the non-hydrogen atoms. Table III[15] presents the anisotropic thermal parameters and the positions of the H atoms while Table IV[15] lists structure amplitudes (×10). A negative entry in Table IV indicates that $F_o^2 < 0$. After the final refinement an analysis of $\sum w(F_o^2 - F_c^2)^2$ as

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[12] Abbreviations: dppe = $Ph_2PCH_2CH_2PPh_2$; dmpe = $Me_2PCH_2CH_2PMe_2$; Cp = C_5H_5; Me = CH_3; Ph = C_6H_5; s = singlet; d = doublet; t = triplet; q = quartet; qu = quintet; m = multiplet; br = broad.

[13] Kershner, D.; Swepston, P., unpublished results.

[14] See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

[15] Supplementary material.

Table II. Positional Parameters for the Non-Hydrogen Atoms of IrMe(dppe)$_2$

atom	x	y	z
Ir	0.161232 (6)	0.066257 (10)	0
P(1)	0.11758 (4)	0.09809 (7)	−0.00530 (23)
P(2)	0.17779 (4)	0.13653 (7)	0.01606 (21)
P(3)	0.19709 (4)	0.03578 (7)	−0.10016 (18)
P(4)	0.17844 (4)	0.02855 (7)	0.14994 (18)
C(1)	0.13808 (18)	0.00690 (28)	−0.0487 (8)
C(2)	0.12060 (20)	0.1575 (3)	−0.0197 (7)
C(3)	0.14725 (17)	0.17331 (27)	0.0392 (7)
C(4)	0.09307 (19)	0.0825 (3)	−0.1167 (8)
C(5)	0.10191 (18)	0.0903 (3)	−0.2244 (7)
C(6)	0.08619 (20)	0.0765 (3)	−0.3129 (9)
C(7)	0.06056 (23)	0.0536 (4)	−0.2976 (9)
C(8)	0.05110 (21)	0.0465 (4)	−0.1902 (10)
C(9)	0.06690 (19)	0.0614 (3)	−0.1003 (8)
C(10)	0.09312 (20)	0.0915 (3)	0.1121 (8)
C(11)	0.09650 (19)	0.0571 (3)	0.1829 (8)
C(12)	0.07795 (19)	0.0480 (3)	0.2690 (9)
C(13)	0.05436 (19)	0.0752 (3)	0.2826 (8)
C(14)	0.05058 (20)	0.1107 (3)	0.2140 (9)
C(15)	0.06939 (18)	0.11903 (29)	0.1295 (7)
C(16)	0.19474 (19)	0.1624 (3)	−0.1044 (8)
C(17)	0.22200 (19)	0.1805 (3)	−0.1023 (8)
C(18)	0.23363 (21)	0.2005 (3)	−0.1957 (9)
C(19)	0.21850 (20)	0.2027 (4)	−0.2917 (9)
C(20)	0.19111 (20)	0.1836 (3)	−0.2935 (8)
C(21)	0.18000 (18)	0.16336 (28)	−0.2037 (8)
C(22)	0.20231 (18)	0.15548 (29)	0.1236 (8)
C(23)	0.22626 (18)	0.12951 (28)	0.1486 (8)
C(24)	0.24565 (18)	0.1422 (3)	0.2279 (7)
C(25)	0.24132 (19)	0.1799 (3)	0.2856 (8)
C(26)	0.21785 (22)	0.2064 (3)	0.2623 (10)
C(27)	0.19869 (20)	0.1943 (3)	0.1806 (9)
C(28)	0.21248 (15)	−0.00871 (25)	−0.0134 (8)
C(29)	0.21253 (17)	0.00267 (29)	0.1076 (7)
C(30)	0.22865 (17)	0.06444 (28)	−0.1489 (7)
C(31)	0.22882 (16)	0.08314 (26)	−0.2545 (9)
C(32)	0.25288 (19)	0.1049 (3)	−0.2941 (7)
C(33)	0.27701 (17)	0.10859 (28)	−0.2304 (8)
C(34)	0.27764 (18)	0.0900 (3)	−0.1266 (8)
C(35)	0.25381 (17)	0.06808 (28)	−0.0868 (7)
C(36)	0.18888 (17)	0.00590 (26)	−0.2277 (7)
C(37)	0.04490 (17)	0.22080 (28)	−0.0143 (7)
C(38)	0.05101 (18)	0.2005 (3)	−0.1131 (8)
C(39)	0.07325 (19)	0.2171 (3)	−0.1766 (8)
C(40)	0.08927 (18)	0.2518 (3)	−0.1423 (7)
C(41)	0.16641 (17)	0.02156 (29)	0.7076 (7)
C(42)	0.15936 (17)	−0.01908 (27)	0.2058 (7)
C(43)	0.14440 (18)	−0.01569 (29)	0.3042 (7)
C(44)	0.12914 (18)	−0.0497 (3)	0.3480 (9)
C(45)	0.12824 (20)	−0.0898 (3)	0.2924 (9)
C(46)	0.14287 (21)	−0.09432 (29)	0.1956 (9)
C(47)	0.15827 (18)	−0.05951 (28)	0.1531 (8)
C(48)	0.18770 (17)	0.05675 (25)	0.2778 (6)
C(49)	0.17364 (18)	0.09564 (27)	0.3023 (7)
C(50)	0.18000 (18)	0.11923 (28)	0.3963 (7)
C(51)	0.19992 (18)	0.1027 (3)	0.4681 (7)
C(52)	0.21364 (20)	0.0628 (4)	0.4475 (8)
C(53)	0.20774 (18)	0.0403 (3)	0.3526 (7)

a function of setting angles, $|F_o|$, and indices revealed no unexpected trends.

Attempted Reaction of IrMe(dppe)$_2$ with H$_2$. A sample of IrMe(dppe)$_2$ was dissolved in CD_2Cl_2 and H_2 was bubbled through the solution. No color change occurred, and the NMR spectrum of the solution remained that of IrMe(dppe)$_2$.

Reaction of IrMe(dppe)$_2$ with CO. A sample of IrMe(dppe)$_2$ was dissolved in CD_2Cl_2 and CO was bubbled through the solution. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a very broad resonance at 30.3 ppm and a sharp singlet assigned to free dppe at −12.7 ppm. A new methyl resonance appears in the ^1H spectrum (0.42 ppm (br)) as do phenyl resonances for free (7.25 ppm) and coordinated (7.08 ppm) dppe. Methylene resonances for free and coordinated dppe appear at 2.05 (br) and 2.35 ppm (d, J_{H-P} = 18.3 Hz), respectively. A solution infrared spectrum of the material obtained from the NMR tube shows two C≡O stretches at 1962 and 1915 cm^{-1}, consistent with the formulation of this compound as IrMe(CO)$_2$(dppe). The product could not be isolated in pure form.

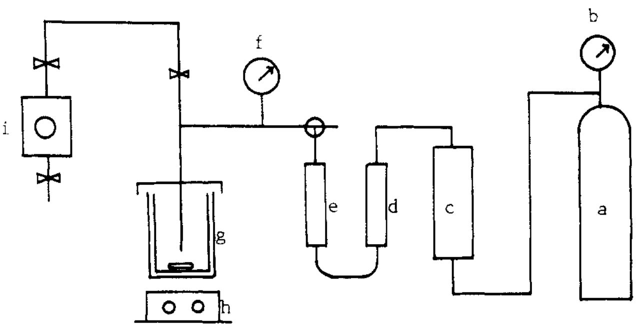

Figure 1. A schematic diagram for liquid CO_2 experiments: a, CO_2 cylinder; b, regulator; c, flow meter; d, O_2 removal tube; e, H_2O removal tube; f, reactor pressure gauge; g, reactor with quartz liner; h, magnetic stirrer; i, high-pressure IR cell with ZnS window.

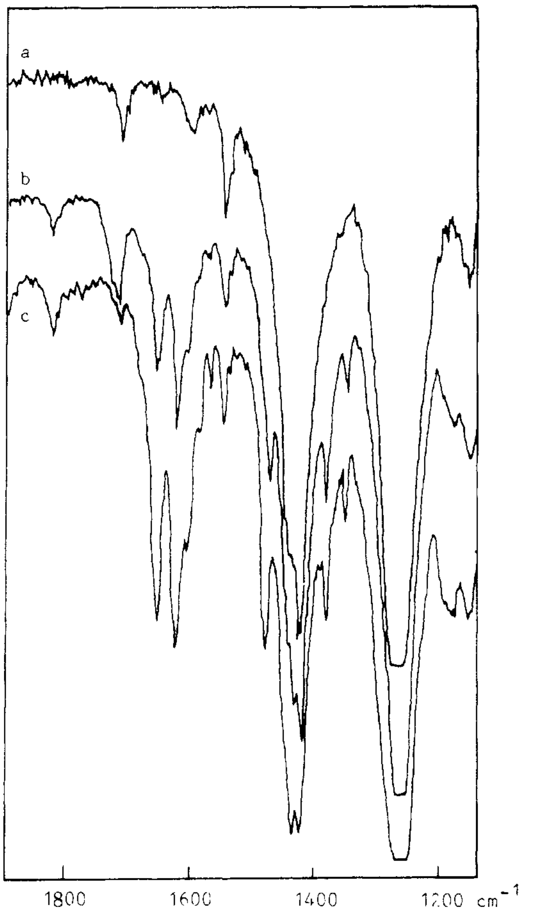

Figure 2. IR spectra of IrMe(dppe)$_2$ in liquid CO_2–CH_2Cl_2 (1:1): (a) solvent only; (b) 1 h; (c) 7 h.

Reaction of IrMe(dppe)$_2$ with Liquid CO$_2$.[16] A diagram of the apparatus used for this reaction is shown in Figure 1. A typical experiment was carried out as follows. A solid sample of the Ir complex (0.1–0.3 g) was put in the quartz-lined, 45-mL, reaction vessel (Parr Instruments, Inc.) and 5–10 mL of solvent (CH_2Cl_2) were introduced into the vessel in order to increase the solubility of the complex in liquid CO_2. The high-pressure IR cell with 19-mm ZnS windows (Harrick Scientific Corp.) was connected to the reaction vessel and was evacuated. A measured amount of CO_2(g) (to yield 5–10 mL of liquid CO_2) was condensed into the vessel cooled in a liquid N_2 bath. After completion of the CO_2 condensation the vessel was closed and warmed to room temperature. The reaction mixture was stirred for 1 day. The

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[16] Mason, M. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5153–5157.

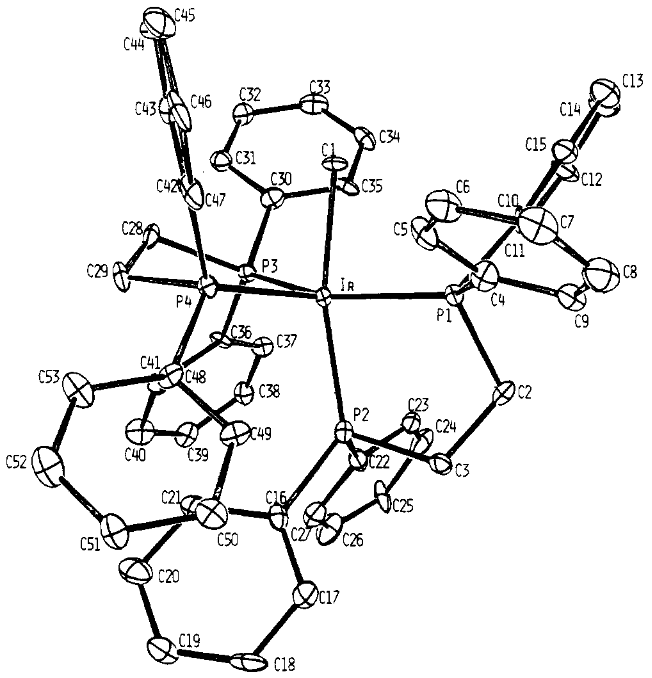

Figure 3. The molecular structure of $IrMe(dppe)_2$, showing thermal ellipsoids at their 50% probability levels and the labeling scheme. Hydrogen atoms have been omitted for the sake of clarity.

reaction mixture was then transferred to the IR cell, and the pressure vessel was disconnected. Time-dependent IR spectra of $IrMe(dppe)_2$ (3×10^{-2} M) in an equivolume liquid CO_2–CH_2Cl_2 solvent are shown in Figure 2.

Reaction of $[Ir(dppe)_2]Cp \cdot THF$ with H_2. To a solution of $[Ir(dppe)_2]Cp \cdot THF$ in CH_2Cl_2 was bubbled dry H_2. In minutes the orange-red solution became light yellow. *n*-Hexane was added to this reaction solution to precipitate a white solid; it was recrystallized from a CH_2Cl_2–hexane pair. The IR spectrum of this compound is identical with an authentic sample of $[IrH_2(dppe)_2]Cl$.[6]

Reaction of $[Ir(dppe)_2]Cp \cdot THF$ with HBF_4. To a solution of $[Ir(dppe)_2]Cp \cdot THF$ in CH_2Cl_2 was added $HBF_4 \cdot Et_2O$ until the color of the solution changed from red to light yellow. To this solution was added *n*-hexane to precipitate an off-white solid established to be $[IrHCl(dppe)_2][BF_4]$ from its NMR spectra and by comparison of its IR spectrum with that of an authentic sample.[6] ^1H NMR: δ −19.9 (Ir–H, qu), 2.4 (CH_2, br), 2.8 (CH_2, br), 7.1–7.4 (Ph, m). $^{31}P\{^1H\}$ NMR: δ 21.1 (s). IR: ν(Ir–H) 2203 cm^{-1}, ν(B–F) 1065, 1036 cm^{-1}.

Results and Discussion

Preparation of $IrMe(dppe)_2$. The complex $IrMe(dppe)_2$ is conveniently synthesized by the reaction of $[Ir(dppe)_2]Cl$ and LiMe in benzene (eq 1). The use of

$$[Ir(dppe)_2]Cl + LiMe \xrightarrow{C_6H_6} IrMe(dppe)_2 + LiCl \qquad (1)$$

alkyllithium reagents in the preparation of transition-metal alkyls from the corresponding chloro complexes is widespread.[17] However, the presence of chloride as a counterion, as in $[Ir(dppe)_2]Cl$, as opposed to being directly bound to the metal, greatly facilitates this method. A similar procedure for the synthesis of $IrMe(PMe_3)_4$ has been reported.[18]

The compound $IrMe(dppe)_2$ is very air sensitive in the solid state and in solution. It is soluble in benzene, THF, CH_2Cl_2, and $CHCl_3$ but has only limited solubility in ether and hexane.

Table V. Selected Bond Distances (Å) and Angles (deg) in $IrMe(dppe)_2$

Ir–C(1)	2.189 (8)	C(1)–Ir–P(1)	84.1 (2)
Ir–P(1)	2.264 (2)	C(1)–Ir–P(2)	164.7 (2)
Ir–P(2)	2.283 (2)	C(1)–Ir–P(3)	83.3 (2)
Ir–P(3)	2.274 (2)	C(1)–Ir–P(4)	88.7 (3)
Ir–P(4)	2.304 (2)	P(1)–Ir–P(2)	84.75 (7)
P(1)–C(2)	1.821 (9)	P(1)–Ir–P(3)	145.73 (9)
P(2)–C(3)	1.838 (8)	P(1)–Ir–P(4)	123.50 (9)
P(3)–C(28)	1.863 (9)	P(2)–Ir–P(3)	100.20 (8)
P(4)–C(29)	1.854 (9)	P(2)–Ir–P(4)	106.24 (8)
C(2)–C(3)	1.519 (12)	P(3)–Ir–P(4)	87.96 (8)
C(28)–C(29)	1.515 (13)	Ir–P(1)–C(2)	110.9 (3)
P(1)–C(4)	1.841 (10)	P(1)–C(2)–C(3)	109.4 (6)
P(1)–C(10)	1.844 (10)	C(2)–C(3)–P(2)	112.0 (6)
P(2)–C(16)	1.846 (10)	C(3)–P(2)–Ir	108.6 (3)
P(2)–C(22)	1.836 (9)	Ir–P(3)–C(28)	106.1 (3)
P(3)–C(30)	1.817 (8)	P(3)–C(28)–C(29)	112.8 (6)
P(3)–C(36)	1.842 (9)	C(28)–C(29)–P(4)	111.5 (6)
P(4)–C(42)	1.834 (9)	C(29)–P(4)–Ir	107.0 (3)
P(4)–C(48)	1.831 (8)	Ir–P(1)–C(4)	118.3 (3)
$(C–C)_{av}$	1.387 (13)[a]	Ir–P(1)–C(10)	119.5 (3)
		Ir–P(2)–C(16)	118.5 (3)
		Ir–P(2)–C(22)	124.6 (3)
		Ir–P(3)–C(30)	125.5 (3)
		Ir–P(3)–C(36)	120.0 (3)
		Ir–P(4)–C(42)	121.2 (3)
		Ir–P(4)–C(42)	121.6 (3)

[a] Standard deviation of a single observation as calculated from the 48 C–C bond lengths in the 8 phenyl rings. The agreement between this value and those from the inverse matrix (0.011–0.014) suggests that standard deviations have been correctly estimated.

Structure of $IrMe(dppe)_2$. The crystal structure of $IrMe(dppe)_2$ consists of the packing of 16 well-separated molecules in the unit cell. The closest H···H approach is 2.26 Å between atoms H2C(28) and H1C(52). Figure 3 displays the molecular structure, thermal ellipsoids of the non-hydrogen atoms, and the labeling scheme. The geometry about the Ir center may be described as distorted trigonal bipyramidal, as can be deduced from the distances and angles of Table V. The present structure is the second exception to the general trend that in $IrX(P–P)_2$ species the X ligand occupies an equatorial site of a trigonal bipyramid. For the present structure (X = Me) and for X = H and P–P = dppe[19] the X group occupies an axial position created as a result of the equatorial–equatorial ligation of one P–P ligand, as opposed to the usual equatorial–axial coupling. In $IrH(dppe)_2$ the Ir–P distances range from 2.245 (2) to 2.279 (2) Å, with the Ir–P distance of the P atom trans to H being 2.278(2) Å. In $IrMe(dppe)_2$ the Ir–P distances range from 2.264 (2) to 2.304 (2) Å with Ir–P(2), trans to Me, being 2.283 (2) Å. Other distances and angles within $IrMe(dppe)_2$ are unexceptional.

Spectroscopic Properties of $IrMe(dppe)_2$. The ^1H NMR spectrum of $IrMe(dppe)_2$ in benzene-d_6 shows a quintet for the methyl resonance at −0.52 ppm. In CD_2Cl_2 (+30 °C) this resonance occurs at −0.83 ppm and is very broad and featureless. When the sample is cooled to −90 °C, this resonance shifts to −1.12 ppm but remains featureless. The $^{31}P\{^1H\}$ spectrum in CD_2Cl_2 is also temperature dependent (Figure 4). At +30 °C a broad singlet occurs at 27.2 ppm. When the sample is cooled, this resonance broadens and splits into a complex pattern. The limiting low-temperature spectrum could not be obtained in this solvent, but it is evident that the temperature dependence of these spectra is a result of the stereochemical nonrigidity of the complex. Such nonrigidity is a characteristic of many five-coordinate transition-metal com-

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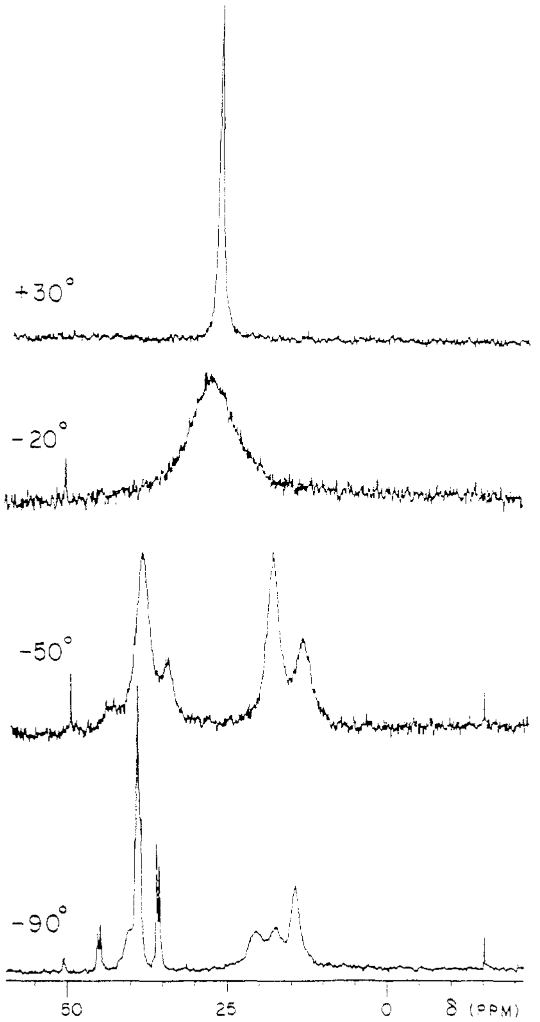


Figure 4. $^{31}P\{^1H\}$ NMR spectra of $IrMe(dppe)_2$ in CD_2Cl_2 as a function of temperature.

plexes.[20] Several closely related methyl complexes, such as $CoMeL_4$ ($L = P(OMe)_3$,[21] $2L$ = dppe[22]) and IrMe(COD)(dppe)[23] (COD = 1,4-cyclooctadiene), show fluxionality; however, the exact nature of the fluxional processes is not understood. From the ^1H NMR data, Shapley and Osborn[23] suggested that a pseudorotation process occurs for IrMe(COD)(dppe). The appearance of the methyl protons for $IrMe(dppe)_2$ as a broad featureless resonance between -90 and +30 °C in CD_2Cl_2 indicates that Ir–P bond breaking probably occurs in this solvent.

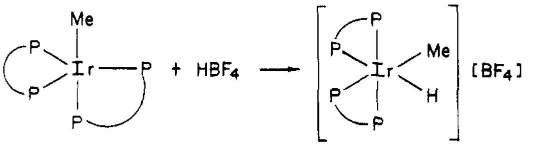
Preparation and Characterization of $[Ir(dppe)_2]Cp$. The complex $[Ir(dppe)_2]Cp$, as the THF solvate, is conveniently prepared by the reaction of $[Ir(dppe)_2]Cl$ and LiCp in THF solution. A crystal structure determination[13] reveals that this material in the solid state is an ionic compound, being composed of the $Ir(dppe)_2^+$ cation and the Cp^- anion. The closest approach of the Cp^- ion to the Ir center is ~4 Å. Very recently there appeared the first example of an isolated Cp^- anion in a crystal structure.[24] Although there appear to be no earlier determinations of the structure of the $Ir(dppe)_2^+$ cation, the structure found in $[Ir(dppe)_2]Cp$[13] closely resembles that of the corresponding Rh cation.[25]

The ^1H and $^{31}P\{^1H\}$ NMR spectra of $[Ir(dppe)_2]Cp{\cdot}THF$ in CD_2Cl_2 are consistent with the ionic formulation, in accordance with the X-ray structure. The ^1H spectrum shows a multiplet centered at 6.4 ppm that corresponds to the resonance of free cyclopentadienyl species.[26] The resonances from the methylene and phenyl groups of the dppe ligand are almost identical with those of the starting material $[Ir(dppe)_2]Cl$ in the same solvent. The $^{31}P\{^1H\}$ spectra of $[Ir(dppe)_2]Cp{\cdot}THF$ shows a sharp singlet at 50.0 ppm, identical with that found in $[Ir(dppe)_2]Cl$ but far from the resonance of $IrMe(dppe)_2$ at 27.2 ppm.

For confirmation of the chemical reactivity of the square-planar $Ir(dppe)_2^+$ cation, two reactions were performed. The reaction of $[Ir(dppe)_2]Cp{\cdot}THF$ in CH_2Cl_2 with $HBF_4{\cdot}Et_2O$ affords $[IrHCl(dppe)_2][BF_4]$.[6] The appearance of this product is reasonable and implies the presence of Cl^- ion in solution. H_2 reacts with a CH_2Cl_2 solution of $[Ir(dppe)_2]Cp{\cdot}THF$ to afford $IrH_2(dppe)_2^+$, presumably as the chloride salt.[6]

That the Cp^- group acts as a counterion rather than a ligand to $Ir(dppe)_2^+$ is surprising. The Cp^- ion, of course, is a strong ligand in transition-metal chemistry, and, indeed, our attempted synthesis of $Ir(Cp)(dppe)_2$ was prompted by curiosity about whether the Cp ligand would σ- or π-bond to the Ir center. Although the Ir center in $Ir(dppe)_2^+$ is surrounded by bulky phenyl groups, it is still coordinatively unsaturated and there appear to be no severe steric impediments to the formation of $Ir(Cp)(dppe)_2$. Indeed when the bulky dppe ligand is replaced by the dmpe ligand, the ionic compound $[Ir(dmpe)_2]Cp$ forms in preference to the molecular compound $Ir(Cp)(dmpe)_2$, as judged by ^1H and $^{31}P\{^1H\}$ NMR spectra, which are almost identical with those of $[Ir(dppe)_2]Cp$. In the other example of an isolated Cp^- ion[24] the cation is $Re(NO)(CH_3)(PMe_3)_4^+$; the Re atom in this cation appears to be more crowded than the Ir atom in $Ir(dppe)_2^+$ or $Ir(dmpe)_2^+$.

Reactivity of $IrMe(dppe)_2$. (i) Reaction of $IrMe(dppe)_2$ with Acid. Protonation of d^8 transition-metal alkyl complexes usually results in the liberation of methane.[21,22,27] This occurs, for example, for $CoMe(dppe)_2$,[22] which is closely analogous to $IrMe(dppe)_2$. However, the reaction of $IrMe(dppe)_2$ with $HBF_4{\cdot}Et_2O$ affords *cis*-$[IrH(Me)(dppe)_2][BF_4]$ (eq 2). This complex is remarkably stable in solution and in the solid state. The cation is analogous to the *cis*-$IrH(Me)(PMe_3)_4^+$ cation.[18]



(2)

In the ^1H spectrum of the hydride complex in fresh CD_2Cl_2 solution the hydride resonance appears as a doublet of pseudoquartets centered at -11.3 ppm. The methyl resonance occurs at -0.31 ppm as a pseudoquartet of doublets. In addition, a doublet of doublets of phenyl group resonances occurring at 6.3 ppm is indicative of the cis geometry.[8] The IR spectrum of solid [IrH(Me)-

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[26] The multiplet in the ^1H NMR spectrum, rather than a singlet as found by Casey et al.,[24] is surprising. However, LiCp dissolved in CD_2Cl_2 shows the same multiplet. Probably Cp^- reacts with CD_2Cl_2 to liberate Cl^- ion.

[27] Alkyl hydride complexes often decompose to give alkanes, regardless of the synthetic method used to generate them. See, for example: Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

$(dppe)_2][BF_4]$ in a Nujol mull shows an Ir–H stretch at 2140 cm^{-1}. This complex is interesting since alkyl hydride intermediates frequently occur in transition-metal-catalyzed reactions, such as hydrogenation and olefin isomerization.[1,3]

At room temperature and atmospheric pressure IrMe(dppe)$_2$ does not react with H_2.

(ii) Reaction of IrMe(dppe)$_2$ with CO. When CO is bubbled through a solution of IrMe(dppe)$_2$ in CD_2Cl_2, a rapid color change from red to yellow occurs. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution shows that one of the dppe ligands is liberated, as evidenced by a singlet at −12.7 ppm. A new broad singlet occurs at 30.3 ppm and is ascribed to the dppe ligand bound to the Ir center. The ^1H NMR spectrum shows a resonance for an iridium-bound methyl group at 0.42 ppm. The methylene protons of the coordinated dppe ligand appear as a doublet (J_{H-P} = 18.3 Hz) centered at 2.35 ppm and those of free dppe appear at 2.05 ppm. No evidence was found for an acyl methyl group. The infrared spectrum of the material obtained from this reaction shows two C≡O stretches at 1962 and 1915 cm^{-1}. On the basis of the above spectral data, we formulate this product as IrMe(CO)$_2$(dppe) and the stoichiometry of the reaction as that shown in eq 3.

$$IrMe(dppe)_2 + 2CO \rightarrow IrMe(CO)_2(dppe) + dppe \quad (3)$$

The spectral data for IrMe(CO)$_2$(dppe) are very similar to those for the complex IrH(CO)$_2$(dppe).[28] This complex also shows two ν(C≡O) vibrations in the infrared spectrum at 1966 and 1912 cm^{-1}. Methylene protons of the dppe ligand resonate at 2.0 ppm (doublet, J_{P-H} = 17.1 Hz) in the ^1H spectrum. A singlet in the $^{31}P\{^1H\}$ NMR spectrum occurs at 33.8 ppm.

The absence of the acyl complex Ir(COMe)(CO)$_2$(dppe) contrasts to the reaction of CoMe(dppe)$_2$ with CO, which is reported to afford Co(COMe)(CO)$_2$(dppe).[22] It is not clear whether this is a result of slower migratory insertion kinetics for Ir or whether the equilibrium lies toward the methyl complex. A closely related complex IrMe(CO)$_2$(PPh$_3$)$_2$ was found to form Ir(COMe)(CO)$_2$(PPh$_3$)$_2$ when treated with 60 psi of CO at 60 °C for several hours.[29] This suggests that forcing conditions are also required to form the acyl complex from IrMe(CO)$_2$(dppe).

(iii) Reaction of IrMe(dppe)$_2$ with CO$_2$. The complex IrMe(dppe)$_2$ in solution does not react with CO_2 at atmospheric pressure. Nor does it react with liquid CO_2 (900–1000 psi) at room temperature. However, it does react slowly with CO_2 in a liquid CO_2–CH_2Cl_2 mixed solvent. The Ir complex is fairly soluble in this mixed solvent, and the reaction mixture could be examined by IR spectroscopy. Time-dependent infrared spectra of IrMe(dppe)$_2$ in an equivolume mixture of liquid CO_2–CH_2Cl_2 (3×10^{-2} M solution) are shown in Figure 2. The intensities of the two bands at 1628 and 1660 cm^{-1} grow with time and arise from absorption by the reacted CO_2. However, the nature of the product cannot be determined unambiguously from these data. A simple adduct in which CO_2 occupies the sixth coordination site seems unlikely. Insertion of CO_2 into the Ir–Me bond seems more reasonable. There are two possible CO_2 insertion products: (i) an alkylcarboxylic acid type that contains the Ir–OOCCH$_3$ fragment or (ii) a metallo ester type that contains the Ir–COOCH$_3$ fragment.[30] Both types are known for six-coordinate Ir complexes;[31,32] unfortunately their carboxylate frequencies appear in the same region (1600–1700 cm^{-1}).

(iv) Oxidation of IrMe(dppe)$_2$ with Ag$^+$. IrMe(dppe)$_2$ is readily oxidized by 2 equiv of the one-electron oxidant Ag^+.[33] Although the IrMe(dppe)$_2^{2+}$ species was not isolated, NMR spectra and reactivity are consistent with this formulation. The considerable chemistry of this coordinatively unsaturated, five-coordinate d^6 ion is under study.

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Registry No. IrMe(dppe)$_2$, 100228-68-0; [Ir(dppe)$_2$]Cl, 15390-38-2; [Ir(dppe)$_2$]Cp, 100228-69-1; [Ir(dppe)$_2$]Cp·THF, 100228-74-8; [Ir(dmpe)$_2$]Cp, 100228-71-5; [Ir(dmpe)$_2$]Cl, 60314-45-6; *cis*-[IrH(Me)(dppe)$_2$][BF$_4$], 100228-73-7; IrMe(CO)$_2$(dppe), 100243-47-8; [IrH$_2$(dppe)$_2$]Cl, 12124-29-7; [IrHCl(dppe)$_2$][BF$_4$], 79292-53-8.

Supplementary Material Available: Table III (anisotropic thermal parameters and hydrogen atom positions) and Table IV (structure amplitudes) (25 pages). Ordering information is given on any current masthead page.

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