Anal. Calcd for $\mathrm{C_{19}H_{11}MoO_6Re}$: C, 36.96; H, 1.79. Found: C, 37.03; H, 1.81.

$\mathrm{CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_3}$ (22). Yellow crystals; mp 113–115 °C (chloroform–pentane); IR ($\mathrm{CCl_4}$) 2025 vs, 2015 vs, 1955 vs, 1937 vs $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.28 (t, 2 H, J = 1.9 Hz), 5.52 (t, 2 H, J = 1.9 Hz), 4.69 (t, 2 H, J = 1.8 Hz), 5.03 (t, 2 H, J = 1.8 Hz), 0.53 (s, 3 H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 223.83, 214.87, 94.48, 92.06, 89.11, 87.06, 83.39, 82.06, 81.03, 80.18, −28.54. Anal. Calcd for $\mathrm{C_{19}H_{11}MnO_6W}$: C, 39.75; H, 1.93. Found: C, 39.71; H, 1.98.

$\mathrm{CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3}$ (23). Yellow crystals; mp 143–145 °C (chloroform–pentane); IR ($\mathrm{CCl_4}$) 2025 vs, 2015 vs, 1940 vs $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.29 (t, 2 H, J = 2.2 Hz), 5.51 (t, 2 H, J = 2.2 Hz), 5.29 (t, 2 H, J = 2.2 Hz), 5.44 (t, 2 H, J = 2.2 Hz), 0.53 (s, 3 H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 214.73, 192.76, 94.57, 94.49, 89.33, 88.50, 83.95, 83.49, 82.02, 80.83, −28.87. Anal. Calcd for $\mathrm{C_{19}H_{11}O_6ReW}$: C, 32.35; H, 1.57. Found: C, 32.49; H, 1.62.

$\mathrm{(CO)_3Mn(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3}$ (24). Orange crystals; mp 196–198 °C (chloroform–pentane); IR ($\mathrm{CCl_4}$) 2020 vs, 1950 vs $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.69 (t, 2 H, J = 2.0 Hz), 5.00 (t, 2 H, J = 2.0 Hz), 5.28 (t, 2 H, J = 2.1 Hz), 5.62 (t, 2 H, J = 2.1 Hz); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 223.84, 192.89, 88.06, 86.62, 84.27, 83.93, 82.11, 81.80, 80.69, 79.86. Anal. Calcd for $\mathrm{C_{18}H_8O_6MnRe}$: C, 38.51; H, 1.43. Found: C, 38.35; H, 1.48.

$\mathrm{CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_2P(C_6H_5)_3}$ (26). Yellow crystals; mp 158–160 °C (chloroform–pentane); IR ($\mathrm{CCl_4}$) 2019 vs, 1946 vs, 1930 vs, 1886 vs $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.45–7.35 (15 H), 5.48 (2 H), 4.26 (2 H), 4.61 (2 H), 4.09 (2 H), 0.54 (3 H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 231.42, 228.23, 215.09, 137.69, 137.15, 132.95, 132.81, 129.57, 128.19, 128.07, 94.5, 94.14, 88.22, 86.65, 86.12, 83.14, 78.95, 77.89, 77.43, 77.00, 76.58, −27.34. Anal. Calcd for $\mathrm{C_{36}H_{26}MnO_5PW}$: C, 53.40; H, 3.42. Found: C, 52.83; H, 3.35.

Acknowledgment. We gratefully acknowledge the financial support of the Department of Energy (Grant DE-FG02-85ER13340), Consiglio Nazionale delle Ricerche Roma-Italy (through the Grant "Formazione permanente del Personale" to Claudio Lo Sterzo) and the "Fundation Blanceflor Buoncompagni-Ludovisi", Stockholm, Sweden. The palladium was provided under the Johnson-Matthey Metal Loan Program. High-resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-8211164).

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen coordinates, and thermal parameters for **26** (2 pages); a listing of observed and calculated structure factors for complex **26** (27 pages). Ordering information is given on any current masthead page.

Multiple-Bond Character in $\mathrm{Cp_3U{=}CHPMe_3}$: First Low-Temperature Neutron Diffraction Analysis of a Uranium Organometallic Complex

Raymond C. Stevens and Robert Bau*

Department of Chemistry, University of Southern California, Los Angeles, California 90089

Roger E. Cramer, Dawood Afzal, and John W. Gilje*

Chemistry Department, 2545 The Mall, University of Hawaii, Honolulu, Hawaii 96822

Thomas F. Koetzle*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

Received July 29, 1989

The structure of $\mathrm{Cp_3U{=}CHPMe_3}$ has been determined from neutron diffraction data at 20 K. Crystal data: space group $P\bar{1}$, a = 10.352 (2) Å, b = 11.326 (2) Å, c = 8.235 (1) Å, α = 91.23 (1)°, β = 93.14 (1)°, and γ = 64.291 (9)°; V = 869.5 Å^3; Z = 2. Data were collected at the Brookhaven High Flux Beam Reactor, with a single-crystal specimen of approximate dimensions 4.3 × 1.4 × 1.2 mm. Final agreement factors are $R(F^2)$ = 0.029 and $R(wF^2)$ = 0.038 for 2227 independent reflections and 421 parameters varied. The neutron diffraction study was undertaken to investigate a possible metal–hydrogen interaction and the metal–carbon–phosphorus geometry. Bond distances and angles of interest include U–C = 2.293 (1)Å, C–H = 1.082 (2)Å, C–P = 1.692 (2)Å, U⋯H = 2.859 (3)Å, U–C–P = 141.49 (7)°, and U–C–H = 110.6 (2)°. The α-hydrogen atom is not agostic, and the short U–C bond distance and large U–C–P bond angle indicate multiple-bond character.

Introduction

The compounds $\mathrm{Cp_3U{=}CHPR_3}$ have a rich insertion chemistry, and the products from the insertion of CO, RCN, RNC, RNCO, and several metal carbonyls into the uranium–carbon bond have been reported.[1] On the basis of short U–C bond distances and large U–C–P bond angles found in the X-ray structures of $\mathrm{Cp_3U{=}CHPMe_2Ph}$ and $\mathrm{Cp_3U{=}CHPMe_3}$, it has been suggested that the U–C bonds in these molecules possess multiple-bond character.[2-5] This assignment, which implies a two-electron, three-center π bond between the $\mathrm{Cp_3U}$ and $\mathrm{CHPR_3}$

---

(1) (a) Gilje, J. W.; Cramer, R. E. *Inorg. Chim. Acta* **1987**, *139*, 177. (b) Gilje, J. W.; Cramer, R. E.; Bruck, M. A.; Higa, K. T.; Panchanatheswaran, K. *Inorg. Chim. Acta* **1985**, *110*, 139.

(2) In saturated alkyluranium(IV) complexes the U–C(alkyl) distances are 2.43 (3) Å in $\mathrm{Cp_3U(\textit{n}\text{-}C_4H_9)}$ (Perego, G.; Cesari, M.; Farina, F.; Lugli, G. *Acta Crystallogr.* **1976**, *B32*, 3034.), 2.43 (2) Å in $\mathrm{Cp^*{}_2UMe_2}$ ((a) Roth, S. Ph.D. Dissertation, University of Hawaii, 1988. (b) Marks, T. J.; Day, V. W., private communication), and 2.41 (1) Å in $\mathrm{(dmpe)_2(CH_2C_6H_5)_3UMe}$ (Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293). U–C multiple bond lengths obtained from X-ray structures are 2.274 (8) Å for $\mathrm{Cp_3U{=}CHPMe_3}$ and 2.29 (3) Å for $\mathrm{Cp_3U{=}CHPMe_2Ph}$.[3,4] The significance of these and other distances to the nature of the U–C bond has been discussed (ref 3–6 and; Cramer, R. E.; Mori, A. L.; Maynard, R. B.; Gilje, J. W.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1984**, *106*, 5920.)

0276-7333/90/2309-0694$02.50/0 © 1990 American Chemical Society

Table I. Summary of Crystal Data and Refinement Results for $Cp_3U{=}CHPMe_3$ from the Neutron Diffraction Study at 20 K

space group	$P\bar{1}$
formula wt	522.19
a, Å	10.352 (2)
b, Å	11.326 (2)
c, Å	8.235 (1)
α, deg	91.23 (1)
β, deg	93.14 (1)
γ, deg	64.291 (9)
V, Å^3	869.5
density (calc), g cm^{-3}	1.99
cryst dimens, mm	4.3 × 1.4 × 1.2
wavelength Å	1.159 30 (12)
abs coeff, (μ), cm^{-1}	2.632
$(\sin\theta)/\lambda$ limit, Å^{-1}	0.6846
total no. of rflns measd	2620
no. of indep rflns	2227
no. of rflns used in struct anal.	2227
no. of variable parameters	421
final agreement factors	
$R(F^2)$	0.029
$R(wF^2)$	0.038
goodness of fit (F^2)	1.106

moieties, has been supported by EHMO calculations, which show covalency with a significant π component for the U-Cα bond.[6] Also the ^{13}C-H coupling constants for the α-CH group have been reported as 113 Hz for $Cp_3U{=}CHPMePh_2$, 100 Hz for $Cp_3U{=}CHPMe_2Ph$, and 95 Hz for $Cp_3U{=}CHPMe_3$.[5] of particular interest is the 95-Hz coupling constant for the title compound, which lies in the range for electron-deficient alkylidene complexes with agostic metal–hydrogen interactions,[7] suggesting that agostic interactions may be associated with the short U-C bonds and large U-C-P angles in $Cp_3U{=}CHPR_3$. To explore this possibility, we have determined the structure of $Cp_3U{=}CHPMe_3$ by neutron diffraction. To our knowledge, this is the first neutron diffraction study of an organometallic uranium compound to be reported.

Neutron Diffraction

The title compound was prepared and crystallized as previously described.[5] A dark green crystal, coated with a thin dark brown film of decomposed material and of approximate dimensions 4.3 × 1.4 × 1.2 mm, was covered in HaloCarbon grease and mounted, with the grease as adhesive, on an aluminum pin oriented approximately along the a^* direction. The sample was then placed in a specially adapted closed-cycle He refrigerator.[8] Neutron diffraction data were collected at 20 K on an automated four-circle diffractometer[9] at the Brookhaven High Flux Beam Reactor using a Ge(200)-monochromated neutron beam of wavelength 1.159 30 (12) Å, based on KBr, a_0 = 6.6000 Å at 298 K. One reflection (532) was monitored during cooling (298 to 20 K); no unusual variation in intensity was observed. Unit-cell constants, determined from the averaged 2θ values of 16 Friedel pairs, together with other experimental details are given in Table I.

One hemisphere of data was collected by the $\theta/2\theta$ step scan technique, with counts being accumulated at each step for a predetermined monitor count of the incident neutron beam. The measurement of low-angle (5° < 2θ < 60°) data was completed with a fixed 2θ scan width of 3.2° and a step size of 0.04°. For the high-angle (60° < 2θ < 105°) data a variable-scan was used with width ranging from 3.2° for 2θ = 60° to 6.49° for 2θ = 105° and the step size adjusted to yield between 60 and 90 steps/scan. The high-angle reflections selected for measurement were those predicted to have the largest neutron intensity, with data collection being terminated upon reaching a level at which very few of the reflections were observed above background (in all, approximately 75% of the accessible high-angle reflections were sampled). Three intense reflections [(7,3,−4), (7,8,−2), (−6,2,2)] were monitored at 200-reflection intervals, and no significant variations in their intensities were observed. The scan profiles were integrated and background corrections applied on the basis of the counts of approximately seven steps on either end of each scan. The squared observed structure factor and standard deviation (σ) for each reflection were obtained upon applying Lorentz and absorption corrections. The latter were calculated by numerical integration over a Gaussian grid of 288 sampling points, with the crystal shape approximated by eight boundary planes belonging to the forms [(0,−1,1), (110), (−1,2,0), (−1,1,1), (−1,1,2)]. Values for the transmission coefficients ranged from 0.558 to 0.722. The validity of the absorption correction was confirmed by comparison with ψ-scan intensity data. Averaging Friedel pairs yielded data for 2227 independent reflections with an agreement factor of R_{int} = 0.019. Starting coordinates of the non-hydrogen atoms were obtained from the X-ray results.[5] The hydrogen atoms were then located from successive difference Fourier maps. Differential Fourier synthesis was used in the initial stages of refinement until all hydrogen atoms were located. Full-matrix least-squares refinement[10] in which positional and anisotropic thermal parameters were varied for all atoms converged at an R value of 0.029. An anisotropic, type I, extinction correction model with Lorentzian mosiac was employed;[11] the quantity minimized in the least-squares was $\sum w(F_o - F_c^2)^2$, with weights taken as $w = [\sigma_{count}^2(F_o^2) + (0.02F_o^2)]^{-1}$. A final difference map was judged to be devoid of significant features.

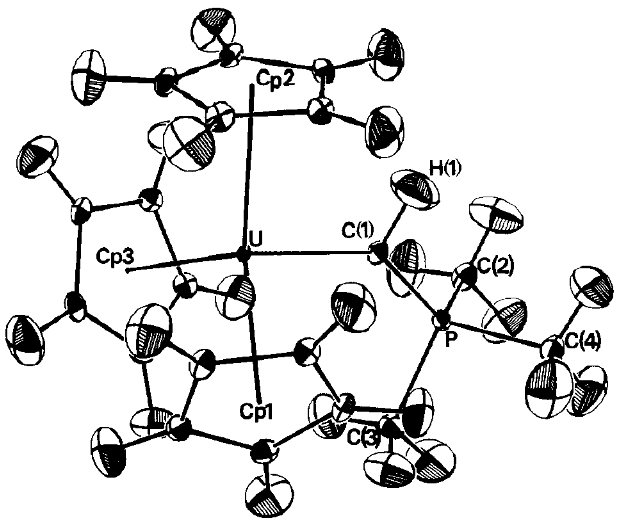


Figure 1. ORTEP[16] diagram of $Cp_3U{=}CHPMe_3$. Thermal ellipsoids are at 75% probability.

Neutron scattering lengths were taken from a compilation of Koester.[12] Computer programs employed include SPEED[13] (selection of reflections for measurements based on predicted intensity), DIFSYN[14] (differential synthesis), a modified version of UPALS[10] (full-matrix least-squares), the absorption correction procedure of Coppens, Leiserowitz, and Rabinovich,[15] Johnson's ORTEP,[16] the SHELXTL system,[17] and locally written programs.

---

[3] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589.

[4] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1983**, *2*, 1336.

[5] Cramer, R. E.; Bruck, M. A.; Edelmann, F.; Afzal, D.; Gilje, J. W.; Schmidbaur, H. *Chem. Ber.* **1988**, *121*, 417.

[6] Tatsumi, K.; Nakamura, A. *J. Organomet. Chem.* **1984**, *272*, 141.

[7] (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[8] Air Products and Chemicals, Inc., Displex Model CS-202.

[9] McMullan, R. K.; Guthy, J.; Stevens, R. C. *NEXDAS, Neutron and X-ray Data Aquisition System*, unpublished work.

[10] Lundgren, J.-O. *Crystallographic Computer Programs*; Report UUIC-B13-4-05; Institute of Chemistry, University of Uppsala, Uppsala, Sweden, 1982.

[11] Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A* **1975**, *A31*, 417.

[12] Koester, L. In *Neutron Physics*; Springer-Verlag: Berlin, Heidelberg, 1977; p 36.

[13] McMullan, R. K., unpublished work.

[14] McMullan, R. K., unpublished work.

[15] Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

Table II. Atomic Coordinates for $Cp_3U{=}CHPMe_3$ from the Neutron Diffraction Study at 20 K

atom	x	y	z
U	0.10904 (8)	0.21554 (8)	0.20606 (8)
P	0.3846 (1)	0.3444 (1)	0.3000 (1)
C(1)	0.2203 (1)	0.3459 (1)	0.2820 (1)
C(2)	0.3999 (1)	0.4804 (1)	0.2021 (1)
C(3)	0.5222 (1)	0.2000 (1)	0.2132 (1)
C(4)	0.4550 (1)	0.3487 (1)	0.5057 (1)
C(11)	−0.1879 (1)	0.3136 (1)	0.1884 (1)
C(12)	−0.1616 (1)	0.4262 (1)	0.1803 (1)
C(13)	−0.1069 (1)	0.4440 (1)	0.3351 (1)
C(14)	−0.0966 (1)	0.3418 (1)	0.4385 (1)
C(15)	−0.1485 (1)	0.2617 (1)	0.3480 (1)
C(21)	0.1826 (1)	0.0586 (1)	0.4800 (1)
C(22)	0.1457 (1)	−0.0141 (1)	0.3584 (1)
C(23)	0.2544 (1)	−0.0586 (1)	0.2448 (1)
C(24)	0.3573 (1)	−0.0120 (1)	0.2941 (1)
C(25)	0.3136 (1)	0.0591 (1)	0.4405 (1)
C(31)	0.0066 (1)	0.2129 (1)	−0.1171 (1)
C(32)	0.1240 (1)	0.0890 (1)	−0.0908 (1)
C(33)	0.2509 (1)	0.1079 (1)	−0.0751 (1)
C(34)	0.2116 (1)	0.2433 (1)	−0.0909 (1)
C(35)	0.0598 (1)	0.3091 (1)	−0.1143 (1)
H(1)	0.1463 (3)	0.4343 (3)	0.3400 (4)
H(2A)	0.3769 (3)	0.4780 (3)	0.0714 (3)
H(2B)	0.3217 (3)	0.5720 (2)	0.2517 (3)
H(2C)	0.5074 (3)	0.4742 (3)	0.2231 (3)
H(3A)	0.6229 (3)	0.2084 (2)	0.2150 (4)
H(3B)	0.5394 (3)	0.1149 (2)	0.2843 (3)
H(3C)	0.4901 (3)	0.1877 (3)	0.0885 (3)
H(4A)	0.3802 (3)	0.4362 (3)	0.5664 (3)
H(4B)	0.4657 (4)	0.2630 (3)	0.5726 (3)
H(4C)	0.5602 (3)	0.3492 (3)	0.5045 (3)
H(11)	−0.2324 (3)	0.2752 (3)	0.0898 (3)
H(12)	−0.1789 (3)	0.4873 (2)	0.0744 (3)
H(13)	−0.0797 (3)	0.5238 (2)	0.3692 (3)
H(14)	−0.0578 (3)	0.3273 (2)	0.5646 (2)
H(15)	−0.1573 (3)	0.1761 (2)	0.3936 (3)
H(21)	0.1238 (3)	0.1040 (2)	0.5860 (2)
H(22)	0.0527 (3)	−0.0341 (3)	0.3548 (3)
H(23)	0.2590 (3)	−0.1180 (2)	0.1382 (3)
H(24)	0.4543 (2)	−0.0311 (3)	0.2328 (3)
H(25)	0.3700 (3)	0.1064 (3)	0.5106 (3)
H(31)	−0.1049 (3)	0.2315 (3)	−0.1369 (3)
H(32)	0.1176 (3)	−0.0041 (2)	−0.0882 (3)
H(33)	0.3590 (2)	0.0322 (2)	−0.0552 (3)
H(34)	0.2841 (3)	0.2896 (3)	−0.0867 (3)
H(35)	−0.0043 (3)	0.4138 (2)	−0.1298 (3)

Table III. Selected Bond Distances and Angles for $Cp_3U{=}CHPMe_3$

	Distances (Å)		
U–C(1)	2.293 (2)	C(2)–P	1.824 (2)
P–C(1)	1.692 (2)	C(3)–P	1.803 (2)
H(1)–C(1)	1.082 (2)	C(4)–P	1.815 (2)
U···H(1)	2.859 (3)		
	Angles (deg)		
H(1)–C(1)–U	110.6 (2)	P–C(1)U	141.49 (7)
H(1)–C(1)–P	107.4 (2)		

Discussion

Two drawings of $Cp_3U{=}CHPMe_3$ are shown in Figures 1 and 2. Atomic coordinates are given in Table II, bond distances and angles of interest in Table III, and H···H contacts less than 2.55 Å in Table IV.

The neutron and X-ray structures[5] of $Cp_3U{=}CHPMe_3$ are very similiar, the greatest difference being that the neutron results are of higher precision, particularly for the lighter atoms. In general, the bond lengths determined by neutron diffraction are slightly longer than the corresponding X-ray values. This effect has been observed in other studies and reflects the nuclear position determination by neutron diffraction and the minimization of librational foreshortening effects at the reduced temperature of the neutron study. In any event, in all of the structure determinations of $Cp_3U{=}CHPR_3$ type molecules, the U=C bond distance is very close to 2.29 Å and the U–C–P angle is slightly greater than 140°.

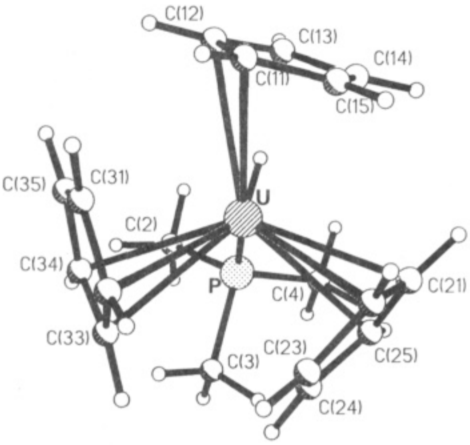


Figure 2. Projection down the U–C(1) axis in which only those U–C(Cp) distances less than the average U–C(Cp) distance for each Cp group are represented as bonds.

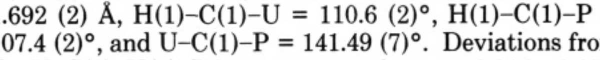
Table IV. H•••H Contacts Less Than 2.55 Å for $Cp_3U{=}CHPMe_3$[a]

	Intramolecular Contacts		
H(1)···H(13)	2.13	H(12)···H(35)	2.40
H(3B)···H(24)	2.21	H(14)···H(21)	2.43
H(3C)···H(34)	2.36	H(15)···H(22)	2.46
H(4B)···H(25)	2.41	H(23)···H(32)	2.33
H(11)···H(31)	2.27	H(24)···H(33)	2.51
	Intermolecular Contacts		
H(3A)···H(11)	2.25	H(3A)···H(15)	2.53

[a] H–H contacts within CH_3 groups are 1.75–1.79 Å. Esd's are less than 0.01 Å.

A significant result of the present neutron study is the location of the α hydrogen (H(1)) in a position that indicates no agostic interaction with the uranium. Bond distances and angles within the U–C(H)–P unit are H(1)–C(1) = 1.082 (2) Å, U–C(1) = 2.293 (1) Å, C(1)–P = 1.692 (2) Å, H(1)–C(1)–U = 110.6 (2)°, H(1)–C(1)–P = 107.4 (2)°, and U–C(1)–P = 141.49 (7)°. Deviations from the U, C(1), H(1), P least-squares plane are 0.014, −0.051, 0.019, and 0.018 Å, respectively, indicating near coplanarity of the four atoms. While the U–C(1)–P angle is expanded from the 120° characteristic of an sp^2-hybridized carbon atom, the H(1)–C(1)–P angle is significantly smaller than the H(1)–C(1)–U angle and the U···H(1) distance is 2.859 (3) Å. There is thus no evidence for any unusual interaction between the uranium and H(1).[18]

We had previously discussed[4,5] the bonding in $Cp_3U{=}CHPR_3$ in terms of several resonance structures:



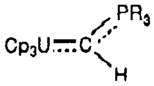
The combination of these resonance forms

---

(16) Johnson, C. K. Oak Ridge Natl. Lab., [Rep.] ORNL (U.S.) 1976, ORNL-5138.

(17) Sheldrick, G. M. SHELXTL-Plus; Nicolet X-ray Instruments: Madison, WI, 1988.

(18) While this structure confirms that no agostic interactions occur in the solid state, it is possible that the low J_{C-H} is the result of an agostic interaction when the compound is in solution. A similiar situation has been encountered in $TiMe_2(dmpe)_2$: Jensen, J. A.; Wilson, S. R.; Schultz, A. J.; Girolami, G. S. *J. Am. Chem. Soc.* **1987**, *109*, 8094.



accounts for the short U–C(1) and P–C(1) bonds. While this model necessarily would be altered if there is additional bonding between the $[Cp_3U]^+$ and $[CHPR_3]^-$ groups, the neutron data, which indicate a normal α-C(1)H(1) group, support the bonding description summarized above. The closest intramolecular nonbonding contacts are 2.13 Å, H(1)⋯H(13), and 2.21 Å, H(3B)⋯H(24) (Figure 2). Both are considerably less than 2.4 Å, twice the van der Waals radius for hydrogen, and suggests that $Cp_3U{=}CHPR_3$ is sterically crowded. These contacts thus may indicate that the large U–C–P angle is not due to electronic effects alone but rather also reflects repulsion between PMe_3 and Cp groups; Figure 2 illustrates the crowding effect.

Within the $CHPR_3$ moiety bond angles and distances are normal, and as in other Cp_3U-X type molecules, the geometry about uranium is roughly tetrahedral.[4] The average U–C(Cp) distance of 2.8 Å is normal for U^{IV} systems.[2] Due to the high precision of the neutron results, the small differences in individual U–C(Cp) distances (2.764 (1) –2.819 (1) Å) are statistically significant. A projection down the U–C(1) axis is shown in Figure 2 where only those U–C(Cp) distances that are less than the average U–C(Cp) distance for each Cp group are represented as bonds. In each case, one side of the Cp ring lies closer to the uranium than the other, so that the Cp planes are not perpendicular to the vector joining the uranium with their respective centroids (88.7° for Cp(1), 88.5° for Cp(2), and 89.1° for Cp(3)). The closest intramolecular contacts between the hydrogens on neighboring Cp groups, Table IV, are near or somewhat less than 2.4 Å. Thus, the slight, screwlike canting of the Cp groups is probably a steric effect.

Acknowledgment. The support of this work by the National Science Foundation, Grants CHE 85-12989 (J.W.G. and R.E.C.) and CHE 87-03425 (R.B.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (R.E.C. and J.W.G.), and the W. C. Hamilton Memorial Scholarship (R.C.S.) is gratefully acknowledged. Work at Brookhaven National Laboratory was performed under Contract DE-AC02-76CH00016 with the U.S. Department of Energy, Office of Basic Energy Sciences (T.F.K.). The technical assistance of J. Guthy and D. Rathjen during the neutron diffraction experiment is gratefully appreciated. Finally, we thank L. Brammer for his careful review of the manuscript and helpful suggestions for its improvement.

Supplementary Material Available: Tables S1 (anisotropic temperature factors) and S2 (bond distances (Å) and angles (deg)) (4 pages); Table S3 (observed and calculated squared structure factors) (43 pages). Ordering information is given on any current masthead page.

EPR Spectrum of the $Fe_2(CO)_8^-$ Radical Trapped in Single Crystals of $PPN^+HFe_2(CO)_8^-$ †

Paul J. Krusic

Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

John R. Morton, Keith F. Preston,* Antony J. Williams, and Florence L. Lee

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

Received August 2, 1989

Solid $PPN^+HFe_2(CO)_8^-$ prepared by literature methods exhibits an intense EPR spectrum due to the presence of a paramagnetic impurity. Comparison with the spectrum in frozen solutions of $Na^+Fe_2(CO)_8^-$ in 2-MeTHF shows that the signal is due to the $Fe_2(CO)_8^-$ radical. The EPR signal in single crystals of the material is anisotropic and obeys the symmetry operations of the lattice space group ($P2_1/c$). Measurements made with crystallographically aligned specimens show that, within experimental error, the principal directions of the **g**-tensor (principal values 2.0093, 2.0538, 2.0579) are determined by the local symmetry (C_{2v}) of the host anion. It is concluded that the $Fe_2(CO)_8^-$ radical retains the symmetry of the host anion and thus has two bridging carbonyl ligands. The orientation of the components of **g** and their displacement from the free-spin value conform with the results of extended Hückel calculations, which place the unpaired electron in a b_2 orbital that is antibonding in the Fe–Fe distance.

Introduction

The variety of modes available to carbon monoxide in bonding to transition-metal atoms[1] results in a wealth of structures among the metal carbonyls and raises many possibilities for isomerism. Energy differences between isomers, such as bridged and unbridged versions of the same molecule, are often small, so that subtle changes in environment may sometimes favor one structure over another. $Co_2(CO)_8$, for example, exists as a doubly bridged form in the pure solid[2] and as unbridged forms in solution and frozen matrices.[3-6] An even more striking example

---

† NRCC No. 31043, Du Pont Contribution No. 5305.

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 22.

(2) Sumner, G. F.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

(3) Bor, G.; Noack, K. *J. Organomet. Chem.* **1974**, *64*, 367.

(4) Bor, G.; Dietter, U. K.; Noack, K. *J. Chem. Soc., Chem. Commun.* **1976**, 914.

(5) Sweaney, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 415.

0276-7333/90/2309-0697$02.50/0