

appears that a major contribution to the decrease in stability for the  $\text{BMe}_3$  adduct vs. the  $\text{BF}_3$  adduct arises from a weaker donor-acceptor bond energy, presumably in part from steric effects. This conclusion and the energy estimates are similar to those for the acetonitrile adducts of  $\text{BCl}_3$  and  $\text{BF}_3$  in which the BN bond was found to be 0.07 Å longer in the  $\text{BF}_3$  complex.<sup>21</sup> In that example a difference in BN bond energies was estimated between 8 and 16 kcal/mol using an extrapolated bond energy-bond length correlation and 18 kcal based on a force constant extrapolation. Reorganization energy calculations for  $\text{BMe}_3$  of comparable quality to those performed for  $\text{BH}_3$  and  $\text{BF}_3$ <sup>17</sup> could provide further support for the above analysis.

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**Registry No.**  $(\text{CH}_3)_3^{11}\text{B}\cdot\text{N}(\text{CH}_3)_3$ , 66750-72-9;  $(\text{CH}_3)_3^{10}\text{B}\cdot\text{N}(\text{CH}_3)_3$ , 66769-47-9;  $(\text{CH}_3)_3^{11}\text{B}\cdot^{15}\text{N}(\text{CH}_3)_3$ , 66750-71-8;  $(\text{CH}_3)_3^{10}\text{B}\cdot^{15}\text{N}(\text{CH}_3)_3$ , 66750-70-7;  $(\text{CH}_3)_3^{11}\text{B}\cdot\text{N}(\text{CD}_3)_3$ , 66750-69-4;  $(\text{CH}_3)_3^{10}\text{B}\cdot\text{N}(\text{CD}_3)_3$ , 66750-68-3;  $(\text{CH}_3)_3^{11}\text{B}\cdot\text{N}(\text{C}^{13}\text{H}_5)_3$ , 66750-67-2;  $(\text{CH}_3)_3^{10}\text{B}\cdot\text{N}(\text{C}^{13}\text{H}_5)_3$ , 66750-65-0;  $\text{Me}_3\text{N}\cdot\text{BMe}_3$ , 1704-27-4.

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- A similar analysis involving TMA-TMB and TMA-BH<sub>3</sub> requires an additional assumption for the dissociation energy of diborane. Following the discussion in ref 17, this leads to a BN bond energy from 2 to 30 kcal greater for the BH<sub>3</sub> adduct. The low value occurs when  $\text{BMe}_3$  is given the higher reorganization energy (27.9 kcal) combined with a low dissociation energy for diborane (28.4 kcal/mol for  $\text{B}_2\text{H}_6$ ). The high value applies when BH<sub>3</sub> and  $\text{BMe}_3$  have identical reorganization energies (15.1 kcal) combined with a high dissociation energy for diborane (59 kcal).
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- (a) Studies prior to 1964 are summarized in T. D. Coyle and F. G. A. Stone, *Prog. Boron Chem.*, **1**, 137 (1964); (b)  $\text{Me}_3\text{N}\cdot\text{BF}_3$  (1.664 ± 0.011 Å =  $r(\text{BN})$ ),  $\text{Me}_3\text{N}\cdot\text{BCl}_3$  (1.659 ± 0.006 Å), ref 5; (c)  $\text{Me}_3\text{N}\cdot\text{BF}_3$  (1.673 ± 0.006 Å), S. Shibata and K. Iijima, *Chem. Lett.*, 29 (1977); (d)  $\text{Me}_3\text{N}\cdot\text{BCl}_3$  (1.575 ± 0.01 Å), H. Hess, *Acta Crystallogr., Sect. B*, **25**, 2338 (1969); (e)  $\text{Me}_3\text{N}\cdot\text{BCl}_3$  (1.611 ± 0.006 Å),  $\text{Me}_3\text{N}\cdot\text{BBR}_3$  (1.606 ± 0.021 Å),  $\text{Me}_3\text{N}\cdot\text{BI}_3$  (1.586 ± 0.026 Å), P. H. Clippard, J. C. Hanson, and R. C. Taylor, *J. Cryst. Mol. Struct.*, **1**, 363 (1971); (f)  $\text{CH}_3\text{CN}\cdot\text{BF}_3$  (1.630 ± 0.004 Å),  $\text{CH}_3\text{CN}\cdot\text{BCl}_3$  (1.562 ± 0.008 Å), ref 21a.

## Notes

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### Preparation and Molecular Structure of $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)]\text{Cl}\cdot\text{CH}_3\text{CN}$

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Despite the stability of organometallic compounds of vanadium(II) and vanadium(0) (e.g.,  $(\eta\text{-C}_5\text{H}_5)_2\text{V}^3$  and  $\text{V}(\text{CO})_6^4$ ), no reports of the isolation of di- or zerovalent tantalum or niobium complexes have appeared,<sup>5</sup> excepting  $(\text{LiPh})_4\text{MPh}_2(\text{ether})_{3.5}$  ( $\text{M} = \text{Nb}, \text{Ta}$ )<sup>6</sup>. We recently reported the preparation of  $\text{TaCl}_2(\text{dmpe})_2$  ( $\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$ ), a well-characterized molecular Ta(II) complex.<sup>7</sup> The availability of this material led us to explore its chemistry with nucleophilic reagents in an attempt to find simple metathetical reactions leading to organometallic compounds of Ta(II). We report the reaction of  $\text{TaCl}_2(\text{dmpe})_2$  with cyclopentadienide ion, which apparently proceeds by disproportionation, and the crystal structure of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}\cdot\text{CH}_3\text{CN}$ .

### Experimental Section

Solvent purification, manipulations, and instrumental measurements

were performed as previously described.<sup>7</sup>  $\text{Na}(\text{C}_5\text{H}_5)\cdot\text{DME}^8$  (DME = dimethoxyethane) and  $\text{TaCl}_2(\text{dmpe})_2$  were prepared by literature methods. A positive <sup>31</sup>P chemical shift represents a resonance at lower field than 85%  $\text{H}_3\text{PO}_4$ .

$[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}$ . A 10-mm Pyrex tube, fitted with a stopcock, was charged with 1.00 g (1.81 mmol) of  $\text{TaCl}_2(\text{dmpe})_2$  and 0.700 g (3.98 mmol) of  $\text{Na}(\text{C}_5\text{H}_5)\cdot\text{DME}$ . The tube was evacuated and cooled to -196 °C, and ca. 5 mL of THF condensed onto the solids. After being sealed in vacuo and heated to 100 °C overnight, the vessel was opened and the solids were collected by filtration. Extraction of the residue with  $\text{CH}_2\text{Cl}_2$  and evaporation of the solvent afforded 0.44 g (0.89 mmol, 49%) of the crude product. An analytical sample was recrystallized from  $\text{CH}_2\text{Cl}_2$ -heptane at -78 °C: <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ )  $\tau$  5.07 (t,  $J_{\text{PH}} = 2.2$  Hz, 10 H), 8.4 (br, m, 16 H)— $\text{dmpe}$  methyl and methylene resonances are overlapping and poorly resolved; <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CD}_3\text{CN}$ ) 14.0 ppm (s). Anal. Calcd for  $\text{C}_{16}\text{H}_{26}\text{ClP}_2\text{Ta}$ : C, 38.69; H, 5.28. Found: C, 38.44; H, 5.18.

Extraction of the reaction mixture with  $\text{CH}_3\text{CN}$  or recrystallization of the purified product from  $\text{CH}_3\text{CN}$  gave the acetonitrile adduct  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}\cdot\text{CH}_3\text{CN}$  (vide infra).

$[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})_2]\text{Cl}$ . A mixture of 1.50 g (2.73 mmol) of  $\text{TaCl}_2(\text{dmpe})_2$  and g 0.96 (5.46 mmol) of  $\text{Na}(\text{C}_5\text{H}_5)\cdot\text{DME}$  was reacted similarly, except that the sealed tube was allowed to stand for 24 h at room temperature. An identical workup gave 0.85 g (1.38 mmol, 51%) of yellow crystals: <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ )  $\tau$  5.55 (quintet,  $J_{\text{PH}} = 3.2$  Hz, 5 H), 8.5 (br, m, 32 H)— $\text{dmpe}$  methyl and methylene resonances are overlapping and poorly resolved; <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CD}_3\text{CN}$ ) 5.78 ppm (s). Anal. Calcd for  $\text{C}_{17}\text{H}_{37}\text{Cl}_2\text{P}_4\text{Ta}$ : C, 33.08;

**Table I.** Data for the X-ray Diffraction Study of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]\text{Cl}\cdot\text{CH}_3\text{CN}$ 

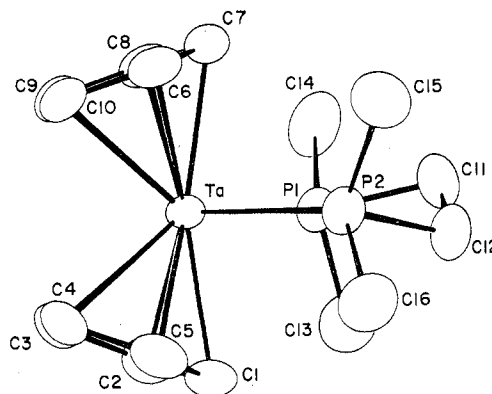
(A) Crystal Data at 23 (1) °C	
crystal system: monoclinic	$V = 2033.4 \text{ \AA}^3$
space group: $P2_1/c [C_2h^5; \text{No. 14}]$	$Z = 4$
$a = 9.347 (2) \text{ \AA}$	formula wt 537.8
$b = 13.891 (3) \text{ \AA}$	$\rho(\text{calcd}) = 1.757 \text{ g cm}^{-3}$
$c = 15.733 (3) \text{ \AA}$	$\rho(\text{obsd})^a = 1.76 (1) \text{ g cm}^{-3}$
$\beta = 96.84 (5)^\circ$	$\mu(\text{calcd}) = 59.8 \text{ cm}^{-1}$
	(Mo K $\alpha$ )
Cell constant detrmn: 12 pairs of $\pm(hkl)$ and refined $2\theta$ , $\omega$ , $\phi$ , and $\chi$ values in the range $40 <  2\theta  < 47^\circ$ ( $\lambda(\text{Mo K}\alpha_1) = 0.70926 \text{ \AA}$ )	
(B) Collection of Intensity Data	
radiation	Mo K $\alpha$ , highly oriented graphite monochromator
reflens measd	$+h, +k, \pm l$ (to $2\theta = 48^\circ$ )
scan type; speed	$\theta$ - $2\theta$ ; variable, 1.95-6.51°/min
scan range	symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]^\circ$
bgd measurement	stationary, for one-fourth of scan time at each of scan limits
no. of reflens measd	3864 total; 3211 in unique set
standard reflens	800, 004, 080 measd after every 50 reflens; devn $< \pm 3\sigma(I)$ for each
automatic recentering of crystal	every 850 reflens
(C) Treatment of Intensity Data <sup>b</sup>	
absorp cor	empirical, normalized transmission factors 0.642-1.000, based on 100, 200, 300, 500, 800 reflens
data reduction	intensities as before; <sup>10</sup> esd's of $ F_o $ values calcd by method of finite differences <sup>11</sup>
statistical information	$R_s = 0.012$ ; $R_{av} = 0.013$ ( $0kl$ reflctn)
(D) Refinement, <sup>c</sup> with 2767 Data for Which $F > 3.92\sigma(F)$	
wgtng of reflens	$w = [\sigma^2( F_o ) + (\rho F_o )^2]^{-1}$ ; $\rho = 0.030$
Patterson solns	Ta, 2P, Cl; $R = 0.182$
isotropic refinement, all nonhydrogen atoms	$R = 0.047$ , $R_w = 0.065$
anisotropic refinement, all nonhydrogen atoms	$R = 0.033$ , $R_w = 0.049$
anisotropic refinement, all atoms, extinction cor	$R = 0.020$ , $R_w = 0.030$
structure factor calcn, all 3211 data	$R = 0.028$ , $R_w = 0.032$
standard devn of an obsvsn of unit wt	0.842
final difference map	0.45 e/ $\text{\AA}^3$ near Cl; other peaks random and $< 0.33 \text{ e/\AA}^3$

<sup>a</sup> Measured by flotation in bromoform-hexane. <sup>b</sup>  $R_s = \Sigma \sigma(|F_o|) / \Sigma |F_o|$ ;  $R_{av} = [(\Sigma ||I| - |I_{av}|) / \Sigma |I|]$ . <sup>c</sup>  $R = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|$ ;  $R_w = \{\Sigma w[|F_o| - |F_c|]^2 / \Sigma w|F_o|^2\}^{1/2}$ . Standard deviation of an observation of unit weight =  $\{\Sigma w[|F_o| - |F_c|]^2 / (m - n)\}^{1/2}$ , where  $m$  (=2767) is the number of observations and  $n$  (=208) is the number of parameters varied.

H, 6.04; Cl, 11.49. Found: C, 33.06; H, 6.37; Cl, 10.36.

**Collection and Reduction of Diffraction Data.** Clear, deep red prismatic crystals were grown by slow cooling of an acetonitrile solution and mounted in capillary tubes sealed under  $\text{N}_2$ . Laue, Weissenberg, and precession photographs of one of these ( $0.32 \times 0.24 \times 0.28 \text{ mm}$ ) established the crystal system, space group, and crystal quality. The crystal was transferred to a goniometer and centered optically on a Syntex  $P2_1$  diffractometer. Most operations were carried out as described previously;<sup>10</sup> other operations are described below. Details of the structure analysis, in outline form, are given in Table I.<sup>11</sup> All operations and refinement were carried out using locally modified versions of the machine-language or Fortran diffractometer programs,<sup>12a</sup> and the Syntex XTL Structure Determination System (24K Nova configuration).<sup>12b</sup>

The data were corrected for absorption by an empirical method. Several  $h00$  reflections ( $\chi = 86^\circ$ , Table IC) were measured at rotation intervals of  $10^\circ$  about the diffraction vector (from  $\psi = 0^\circ$  to  $\psi = 350^\circ$ ). A set of normalized absorption curves, interpolated in  $\phi$ , were derived and checked for consistency. There was little variation from curve to curve in (a) the position of maxima and minima and (b) the ratio of maximum and minimum values.

**Figure 1.** Molecular structure of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]^+$  viewed from the edge of the Ta-P1-P2 plane.

**Solution and Refinement of Structure.** The analytical scattering factors of Cromer and Waber were used;<sup>13a</sup> real and imaginary components of anomalous scattering were included in the calculations for Ta, P, and Cl.<sup>13b</sup> At the conclusion of anisotropic refinement of all nonhydrogen atoms, a difference Fourier synthesis revealed the positions of *all* hydrogen atoms. These were not used directly but were used in the following manner to determine calculated positions for the hydrogen atoms. The program HPOSN<sup>12c</sup> was used to generate "tetrahedral" positions for the methylene protons and idealized in-plane positions for the cyclopentadienyl protons. The program METHYL<sup>14</sup> was used to generate positions for methyl H atoms at  $10^\circ$  intervals about the P-C and C-C (acetonitrile) bond axes. Calculated H atom positions were then selected, which were the "best fit" to a given set of three observed proton positions. The hydrogen atoms were included, as fixed contributions to  $F_c$  (with C-H = 0.95 Å), in subsequent cycles of least-squares refinement. The calculation procedure above was repeated after each cycle of refinement. All data were corrected for secondary extinction by applying an empirical correction of the form  $|F_o|_{\text{cor}} = |F_o|(1.0 + gI_o)$  where  $g$  (determined graphically) =  $2.86 \times 10^{-7}$ . At convergence  $[(\Delta/\sigma)_{\text{max}} \leq 0.02]$ , a weighting scheme analysis revealed no systematic dependence of  $w[|F_o| - |F_c|]^2$  on  $|F_o|$ ,  $(\sin \theta)/\lambda$ , Miller indices, or sequence number. Table II lists the positional and anisotropic thermal parameters for all nonhydrogen atoms. Table III, available as supplementary material, lists the positional and isotropic thermal parameters for hydrogen atoms.

## Results and Discussion

Treatment of  $\text{TaCl}_2(\text{dmpe})_2$  with  $\text{Na}(\eta\text{-C}_5\text{H}_5)\cdot\text{DME}$  affords the tantalum(III) complexes  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}$  and  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})_2]\text{Cl}$  as the only isolable products. Formation of the former is favored at elevated temperatures; the latter at ambient conditions. No substituted Ta(II) species were isolated or detected by ESR. It seems likely that reaction of the Ta(II) precursor with cyclopentadienide ion, commonly considered a one-electron reductant, gives the Ta(III) complexes by disproportionation. We were unable to isolate Ta(I) or further reduced products, but the poor yields of the Ta(III) complexes are consistent with their presence.

No paramagnetic species were detected by ESR on treating a THF/HMPA solution of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}$  with 1 equiv of sodium in HMPA at  $-30^\circ\text{C}$ . A slurry of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}$  in THF slowly reacted with a Na dispersion, yielding a red solution which did not give ESR signals. No crystalline products were isolated. However, the oily residue obtained by evaporation of the solvent exhibits a sharp cutoff in its mass spectrum corresponding to  $(\text{C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})\text{H}$ .

Recrystallization of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}$  from  $\text{CH}_3\text{CN}$  gave red crystals of the acetonitrile adduct. The crystal structure consists of discrete ions and solvent molecules. The structure of the  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]^+$  unit is shown in Figure 1; selected bond distances and angles are tabulated in Table IV.

Table II. Positional and Anisotropic Thermal Parameters for  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{Cl}]\text{Cl}\cdot\text{CH}_3\text{CN}^a$ 

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ta	0.188 761 (17)	0.094 057 (11)	0.200 066 (10)	0.03097 (12)	0.02494 (12)	0.02689 (12)	0.00093 (7)	0.00344 (8)	-0.00031 (7)
P1	0.085 96 (13)	0.090 39 (8)	0.341 62 (7)	0.03834 (65)	0.03761 (69)	0.03327 (61)	-0.00307 (52)	0.00949 (50)	-0.00264 (49)
P2	0.409 55 (13)	0.120 71 (10)	0.307 38 (8)	0.03225 (62)	0.04312 (70)	0.04177 (68)	-0.00191 (52)	0.00191 (52)	-0.00252 (55)
C1	0.290 71 (15)	0.079 92 (10)	0.879 49 (9)	0.05512 (77)	0.05638 (81)	0.05468 (76)	0.00387 (63)	0.00975 (61)	0.01409 (63)
C2	0.166 71 (57)	0.259 43 (35)	0.210 31 (31)	0.0608 (33)	0.0266 (26)	0.0522 (30)	0.0100 (22)	0.0022 (25)	0.0020 (21)
C3	0.028 49 (54)	0.225 54 (38)	0.177 53 (32)	0.0491 (29)	0.0465 (29)	0.0482 (28)	0.0178 (25)	0.0043 (23)	0.0040 (25)
C4	0.038 17 (59)	0.186 84 (38)	0.096 15 (32)	0.0618 (34)	0.0487 (31)	0.0396 (27)	0.0140 (26)	-0.0077 (24)	0.0088 (24)
C5	0.259 58 (62)	0.242 08 (37)	0.146 92 (35)	0.0627 (34)	0.0387 (28)	0.0572 (33)	0.0004 (25)	0.0104 (27)	0.0164 (24)
C6	0.321 89 (53)	-0.039 08 (35)	0.162 77 (34)	0.0481 (29)	0.0330 (26)	0.0614 (33)	0.0049 (23)	0.0118 (25)	-0.0102 (24)
C7	0.234 59 (64)	-0.066 91 (36)	0.229 86 (33)	0.0743 (37)	0.0291 (25)	0.0400 (26)	0.0056 (25)	0.0015 (26)	-0.0034 (22)
C8	0.089 18 (59)	-0.062 71 (35)	0.194 35 (32)	0.0607 (33)	0.0327 (26)	0.0444 (28)	-0.0159 (24)	0.0154 (24)	-0.0125 (22)
C9	0.084 48 (57)	-0.033 66 (37)	0.111 21 (31)	0.0623 (33)	0.0426 (29)	0.0394 (27)	-0.0055 (26)	-0.0010 (24)	-0.0121 (23)
C10	0.226 41 (56)	-0.019 42 (35)	0.091 63 (29)	0.0635 (32)	0.0343 (26)	0.0371 (26)	0.0003 (24)	0.0140 (24)	-0.0093 (21)
C11	0.231 95 (65)	0.081 18 (41)	0.430 39 (33)	0.0628 (35)	0.0645 (36)	0.0353 (26)	0.0023 (28)	0.0036 (25)	0.0066 (25)
C12	0.354 04 (55)	0.144 52 (44)	0.414 16 (31)	0.0465 (29)	0.0684 (37)	0.0374 (27)	-0.0078 (28)	-0.0008 (22)	-0.0093 (26)
C13	-0.010 74 (68)	0.195 10 (47)	0.374 45 (36)	0.0778 (40)	0.0749 (43)	0.0495 (31)	0.0247 (33)	0.0276 (29)	-0.0099 (29)
C14	-0.032 12 (66)	-0.005 83 (46)	0.368 24 (35)	0.0793 (41)	0.0695 (40)	0.0496 (32)	-0.0239 (33)	0.0291 (30)	-0.0035 (29)
C15	0.541 12 (60)	0.025 27 (49)	0.329 26 (43)	0.0479 (33)	0.0740 (44)	0.0906 (47)	0.0166 (31)	-0.0205 (31)	-0.0059 (37)
C16	0.526 40 (58)	0.223 92 (46)	0.298 98 (38)	0.0501 (32)	0.0659 (38)	0.0752 (40)	-0.0225 (29)	0.0053 (28)	-0.0096 (32)
C17	0.425 11 (74)	0.647 53 (52)	0.447 63 (44)	0.0834 (46)	0.0714 (46)	0.0771 (43)	-0.0196 (38)	0.0168 (36)	0.0140 (37)
C18	0.358 68 (73)	0.740 15 (50)	0.440 52 (41)	0.0678 (39)	0.0609 (42)	0.0694 (40)	-0.0219 (34)	-0.0128 (31)	0.0059 (33)
N	0.310 74 (84)	0.814 36 (51)	0.435 10 (53)	0.1283 (62)	0.0710 (46)	0.1482 (68)	0.0031 (44)	-0.0500 (51)	-0.0027 (44)

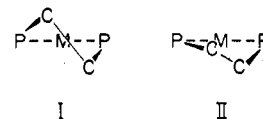
<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses in this and the following table. The form of the thermal ellipsoid is  $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \dots + 2b^*c^*U_{23}kd)]$ .

Table IV. Bond Distances (Å) and Selected Angles (deg) in  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}\cdot\text{CH}_3\text{CN}$ 

Ta-P1	2.534 (1)	P2-C12	1.850 (5)
Ta-P2	2.536 (1)	P2-C15	1.813 (6)
Ta-C1	2.314 (5)	P2-C16	1.817 (6)
Ta-C2	2.362 (5)	C1-C2	1.414 (7)
Ta-C3	2.404 (5)	C1-C5	1.421 (8)
Ta-C4	2.399 (5)	C2-C3	1.404 (7)
Ta-C5	2.345 (5)	C3-C4	1.404 (8)
Ta-C6	2.343 (5)	C4-C5	1.388 (9)
Ta-C7	2.314 (5)	C6-C7	1.463 (8)
Ta-C8	2.366 (5)	C7-C8	1.408 (8)
Ta-C9	2.395 (5)	C8-C9	1.368 (7)
Ta-C10	2.383 (5)	C9-C10	1.411 (7)
C11-C12	1.487 (8)	C6-C10	1.375 (7)
P1-C11	1.840 (6)	C17-C18	1.427 (10)
P1-C13	1.820 (7)	C18-N	1.123 (10)
P1-C14	1.814 (6)		
P2-Ta-P1	77.21 (4)	C17-C18-N	177.7 (8)

The gross stereochemistry of the cation is similar to the pseudotetrahedral arrangement typically found for  $(\eta\text{-C}_5\text{H}_5)_2\text{ML}_2$  complexes.<sup>15</sup> The P-Ta-P angle of 77.21 (4)° is within the range 85.6–74.8° observed for all other structurally characterized dmpe complexes<sup>16</sup> and very close to the bite angles for other Ta-dmpe adducts.<sup>16b,f,g</sup> Further, the observed value is consistent with L-M-L angles (76–82°) reported for other d<sup>2</sup>  $(\eta\text{-C}_5\text{H}_5)_2\text{ML}_2$  structures.<sup>15,17</sup>

The angle formed by the normals to the cyclopentadienyl rings is 138.9°, somewhat larger than the 130–135° typically found for  $(\eta\text{-C}_5\text{H}_5)_2\text{ML}_2$  complexes.<sup>15,17a</sup> This value is, however, not unprecedented; cf. 139.5° for d<sup>2</sup>  $[(\eta\text{-C}_5\text{H}_5)_2\text{ReBr}_2]\text{BF}_4$ .<sup>15</sup> The average metal to ring distance of 2.035 Å is normal. The cyclopentadienyl rings are eclipsed.



Although a number of conformations are plausible for the frequently disordered dmpe backbone,<sup>16b</sup> only two are commonly found. II occurs for ordered  $\text{Wl}_2(\text{CO})_3(\text{dmpe})$ <sup>16c</sup> and  $\text{TaCl}(\eta^4\text{-C}_{10}\text{H}_8)(\text{dmpe})_2$ <sup>16f</sup> (approximately, for one of two dmpe ligands).  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}\cdot\text{CH}_3\text{CN}$  and three other ordered examples<sup>16c,d,f</sup> have conformation well represented by I.

There are a number of moderately short C-C contacts between the dmpe methyl and cyclopentadienyl carbon atoms, as well as between the two cyclopentadienyl rings (see Figure 1). The Ta-C distances (Table IV) appear to be related to the severity of these C-C contacts. Thus, the longest Ta-C distances (to atoms C<sub>3</sub>, C<sub>4</sub>, C<sub>9</sub>, and C<sub>10</sub>) are associated with the atoms having the shortest C-C contacts; the shorter Ta-C<sub>1</sub> and Ta-C<sub>7</sub> distances are associated with carbon atoms having the least severe intramolecular contacts.

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**Registry No.**  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{dmpe})]\text{Cl}\cdot\text{CH}_3\text{CN}$ , 66632-54-0;  $\text{TaCl}_2(\text{dmpe})_2$ , 61916-35-6;  $[(\eta\text{-C}_5\text{H}_5)\text{Ta}(\text{dmpe})_2\text{Cl}]\text{Cl}$ , 66632-52-8.

**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes (Table VI), hydrogen atom positions (Table III), and intramolecular contacts (Table V) (12 pages). Ordering information is given on any current masthead page.

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### Crystal Structure of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HFe}_2(\text{CO})_8]^-$

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As part of our continuing studies on transition-metal hydride complexes<sup>1</sup> and metal carbonyl anions,<sup>2</sup> and as a sequel to our earlier work on the isoelectronic  $[\text{Fe}_2(\text{CO})_8]^{2-}$  and  $[\text{FeCo}(\text{CO})_8]^-$  anions,<sup>2c</sup> we wish to report the structure of the  $[\text{HFe}_2(\text{CO})_8]^-$  anion. This anion was first prepared by Hieber and Brendel in 1957 via the alkaline reduction of  $\text{Fe}_2(\text{CO})_9$ .<sup>3</sup> From the results of Mössbauer and vibrational spectroscopic experiments, Greenwood and co-workers suggested that the structure of  $[\text{HFe}_2(\text{CO})_8]^-$  is based on that of  $\text{Fe}_2(\text{CO})_9$ , with one of the CO bridges replaced by a bridging hydride.<sup>4</sup> The solution structure of  $[\text{HFe}_2(\text{CO})_8]^-$  has not been thoroughly investigated until recently, perhaps because of its rapid decomposition in most solvents. It is also probably for this reason (i.e., solution instability) that a definitive single-crystal X-ray study has not been previously reported. In the light of current interest in the chemistry of this anion,<sup>5</sup> it was felt that the solid-state structure of  $[\text{HFe}_2(\text{CO})_8]^-$  was deserving of a definitive and quantitative X-ray study.

#### Experimental Section

$[\text{HFe}_2(\text{CO})_8]^-$  was prepared by the method of Hieber<sup>3</sup> and isolated as its bis(triphenylphosphine)iminium salt. All manipulations were carried out in the absence of air and all solvents were deoxygenated prior to use. A 1.4-g sample (25 mmol) of KOH was dissolved in 25 ml of absolute ethanol. Diiron nonacarbonyl ( $\text{Fe}_2(\text{CO})_9$ ), 1.8 g (5 mmol), was added to the alcoholic KOH solution and the resultant

mixture was stirred for approximately 15 min to allow all of the iron carbonyl to react. The solution was then cooled to  $-78^\circ\text{C}$  by means of a dry ice-acetone bath. Thirty milliliters of a 1 N solution of acetic acid, prepared from glacial acetic acid and absolute ethanol, was cooled to about  $-50^\circ\text{C}$  and then added to the stirring iron carbonyl solution. This was followed by the addition of a solution of 1.8 g (3 mmol) of  $[(\text{Ph}_3\text{P})_2\text{N}]^+\text{Cl}^-$  in 50 mL of absolute ethanol at  $-78^\circ\text{C}$ . The resultant mixture was allowed to warm slowly to room temperature. During the warming period a precipitate of small yellow brown crystals appeared. The mixture was then heated until all of the precipitate just dissolved, and as it cooled again to room temperature, very well formed yellow-brown crystals of  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HFe}_2(\text{CO})_8]^-$  were obtained along with small quantities of crystalline  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HFe}_3(\text{CO})_{11}]^-$ . The crystals were isolated by filtration and washed with water. The compound is remarkably stable in the solid state, showing decomposition only after exposure to air for several days. In solution the compound is unstable, decomposing to  $[\text{HFe}_3(\text{CO})_{11}]^-$  and other products in several hours.<sup>4b,5b</sup> All attempts to recrystallize the isolated material failed. The yellow-brown crystals were identified as  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HFe}_2(\text{CO})_8]^-$  based on the IR spectrum in the carbonyl stretching region (1990 (m), 1920 (s), 1880 (vs), 1790 (m), 1750 (m)  $\text{cm}^{-1}$ ) taken as a fluorocarbon mull. These values are in general agreement with the spectrum obtained by Greenwood et al. for the  $[\text{Et}_4\text{N}]^+$  salt.<sup>4</sup>

#### Crystallographic Section

X-ray diffraction work was carried out on a specimen of dimensions  $0.50 \times 0.27 \times 0.23$  mm, mounted on a glass fiber. Crystals of  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HFe}_2(\text{CO})_8]^-$  are monoclinic, space group  $P2_1/c$ , with  $a = 10.687$  (5) Å,  $b = 20.470$  (10) Å,  $c = 19.421$  (10) Å,  $\beta = 107.72$  (3)°, and  $V = 4047.0$  Å<sup>3</sup>;  $\rho(\text{obsd}) = 1.422$   $\text{g cm}^{-3}$  and  $\rho(\text{calcd}) = 1.435$   $\text{g cm}^{-3}$  for  $Z = 4$ . One quadrant of data was collected with Zr-filtered Mo K $\alpha$  radiation using a  $\theta$ - $2\theta$  scan technique up to a  $2\theta$  limit of  $44^\circ$ . The procedure used in data collection is essentially the same as that described in an earlier publication.<sup>2f</sup> A total of 5162 reflections were collected and corrected for Lorentz and polarization effects. Elimination of the weaker data ( $I \leq 3\sigma$ ) and merging of duplicate reflections resulted in 3330 reflections being retained for the subsequent structure analysis. An absorption correction was not carried out, on the basis of the observation that the intensity of an axial reflection (at  $\chi = 90^\circ$ ) showed no significant variation with spindle angle  $\phi$ . The absorption coefficient ( $\mu$ ) is  $8.72$   $\text{cm}^{-1}$  for Mo K $\alpha$  X-rays.

The positions of the iron atoms were determined from a Patterson map. A difference Fourier map phased by the iron atoms revealed the positions of the phosphorus atoms. The remaining nonhydrogen atoms were located from successive difference-Fourier maps. This was followed by several cycles of least-squares refinement, in which all the atoms except the carbons of the phenyl rings were assigned anisotropic temperature factors. The  $R$  factor at this stage was 0.084.

At this point an attempt was made to locate the bridging hydrogen atom. The coordinates of the phenyl hydrogen atoms were calculated<sup>7</sup> and included in the synthesis of a series of difference-Fourier maps using  $((\sin \theta)/\lambda)^2$  limits of 0.278, 0.175, and 0.110 Å<sup>-2</sup>, the first value representing all of the data. This technique has been used previously to locate hydrogen atoms in close proximity to metal atoms.<sup>8</sup> In the present case the difference-Fourier maps revealed a single peak in a bridging position between the iron atoms. However, whereas previous examples of the use of this technique allowed one to refine the position of the hydrogen atom using the low-angle data, in the present case the hydrogen atom could be refined only by using the full set of data. The anion, including the hydrogen, was refined by least squares and resulted in a final  $R$  factor of 0.081 ( $R_w = 0.089$ ).<sup>9</sup> The positional parameters of the phenyl hydrogens were not refined and their isotropic temperature factors were set arbitrarily to  $4.0$  Å<sup>2</sup>.

#### Discussion

The final atomic parameters of  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HFe}_2(\text{CO})_8]^-$  are given in Table I and the interatomic distances and angles for the anion and cation are given in Tables II and III, respectively. An ORTEP plot of the anion is presented in Figure 1. A listing of the observed and calculated structure factors is available as supplementary material.

As predicted from the spectroscopic studies,<sup>4</sup> the carbonyl hydride anion has a structure very similar to  $\text{Fe}_2(\text{CO})_9$ . The anion consists of two approximately octahedrally coordinated