Inorg. Chem. **1987**, *26*, 374-377

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

$HCr[(Me_2PCH_2)_3CMe]_2{}^+BEt_4{}^-$: The First Synthesis of a Cationic Hydride Complex from $HBEt_3{}^-$

Eric Thaler, Kirsten Folting, John C. Huffman, and Kenneth G. Caulton*

Received August 19, 1986

Reaction of $CrCl_3$(tripod) (tripod = $MeC(CH_2PMe_2)_3$) with $LiHBEt_3$ in THF yields $HCr(tripod)_2{}^+$, isolated as its $BEt_4{}^-$ salt; $LiDBEt_3$ gives $DCr(tripod)_2{}^+$. The compound has been characterized by infrared and ^1H and ^{31}P NMR spectroscopies, by elemental analysis, and by single-crystal X-ray diffraction. While the infrared spectrum shows an absorption for a terminal hydride, both NMR-active nuclei show evidence for rapid intramolecular migration of the hydride. Three equivalent sites are equally occupied by the hydride in the solid state, which leads to the observed disorder in the unit cell. The cation is deprotonated in THF solution by *n*-BuLi or $LiHBEt_3$ to yield $Cr(tripod)_2$. Crystal data (−159 °C) for the hydride: space group $P\bar{4}2_1c$ with a = 14.059 (5) Å, c = 19.190 (6) Å, and Z = 4.

Introduction

We have a continuing interest in the synthesis of hydride complexes of the first transition series,[1,2] based in part on the belief that these will be more kinetically labile than their heavier analogues, which sometimes require elevated temperatures[3] or photolysis[4] to induce reactivity.

Polyhydride complexes of chromium are limited to $CrH_2[P(OMe)_3]_5$ (from H_2)[5] and $CrH_4(Me_2PC_2H_4PMe_2)_2$ (from $CrCl_2(Me_2PC_2H_4PMe_2)_2$ and BuLi).[6] We felt that an appropriate strategy for synthesis of a chromium phosphine polyhydride was to limit the number of phosphine ligands (L) to three per chromium, thus making L_3CrH_4 or L_3CrH_6 likely products. In addition, since we have found heavier analogues to react (eq 1) by

$$WH_6P_3 \rightarrow WH_4P_4 + ? \qquad (1)$$

partial decomposition (liberating phosphine), followed by displacement of H_2 by that phosphine, we set out to inhibit phosphine loss by use of the new, compact, and very basic threefold symmetric phosphine $MeC(CH_2PMe_2)_3$ ("tripod").[7] The results reported here reveal the unprecedented production of a *cationic* hydride complex from $LiHBEt_3$; this cation exhibits an intramolecular rearrangement that is readily explained by the molecular structure reported here and also is revealing with regard to the H^+ vs. H^- behavior of one first-transition-series hydride complex.

Experimental Section

General Procedures. All operations were performed under a nitrogen atmosphere, by using standard Schlenk techniques for air- and moisture-sensitive materials. $LiHBEt_3$ and $LiDBEt_3$ (in THF) and *n*-BuLi (in hexanes) were purchased from Aldrich Chemical Co. Tetrahydrofuran and pentane were dried and distilled prior to use from solutions containing sodium/potassium benzophenone ketyl. $CrCl_3\{CH_3C[CH_2P(CH_3)_2]_3\}$ was prepared by the action of $CH_3C[CH_2P(CH_3)_2]_3$ on anhydrous $CrCl_3$ in the presence of a catalytic amount of Zn dust in THF. $Cr\{CH_3C[CH_2P(CH_3)_2]_3\}_2$ was prepared by the method of Jones et al.[8]

$[HCr(tripod)_2]BEt_4$. In a typical preparation, $LiHBEt_3$ (3 mL, 1 M, 3 mmol) was added, by means of a syringe, to a slurry of $CrCl_3$(tripod) (0.5 g, 1.22 mmol) in THF at room temperature. Upon addition of $LiHBEt_3$, the blue slurry became a brown solution. Stirring was continued for 15 min to ensure completion of the reaction. The solution was then filtered through a medium-porosity frit to remove Cr metal. The volume of the solution was then reduced to 10 mL, and solid $NaBEt_4$ (Alfa, 0.18 g, 1.2 mmol)[9] was added at room temperature. The solution was then cooled to −20 °C for 48 h to yield amber crystals of $[HCr(tripod)_2]BEt_4$. ^1H NMR: δ 1.535 ($P-CH_2$), 1.490 ($P-(CH_3)_2$), 1.096 ($C-CH_3$), 0.650 (m, $B-CH_2-CH_3$), −0.112 (m, $B-CH_2$), −7.166 (septet, Cr–H, J_{PH} = 64.2 Hz). $^{31}P\{H\}$ NMR: δ 22.98 (s). The ^1H and ^{31}P NMR spectra are unchanged at −80 °C. IR (Nujol mull): ν(Cr–H) 1895 cm^{-1}. Anal. Calcd for $C_{30}H_{75}P_6BCr$: C, 52.60; H, 11.09. Found: C, 51.75; H, 10.71.

Table I. Crystal Data for $\{CrH[MeC(CH_2PMe_2)_3]_2\}BEt_4$

empirical formula	$BC_{30}H_{75}P_6Cr$
color	red at room temp; yellow-green at −159 °C
crystal dimens, mm	0.20 × 0.20 × 0.20
space group	$P\bar{4}2_1c$
cell dimens (at −159 °C; 38 reflcns), Å	a = 14.059 (5), b = 14.059 (5), c = 19.190 (6)
molecules/cell	4
vol, Å^3	3792.91
calcd density, g/cm^3	1.197
wavelength, Å	0.71069
mol wt	683.56
linear abs coeff, cm^{-1}	5.62
no. of unique intensities	1416
no. with $F > 0.0$	1375
no. with $F > 3.0\sigma(F)$	1279
final residuals ($F > 3\sigma(F)$)	
$R(F)$	0.0330
$R_w(F)$	0.0337
goodness of fit for last cycle	0.756
max Δ/σ for last cycle	0.05

Deprotonation of $[HCr(tripod)_2]BEt_4$. Crystalline $[HCr(tripod)_2]BEt_4$ (0.25 g, 0.37 mmol) was placed in THF (15 mL). The solution was stirred until all the material had dissolved, leaving an amber solution, to which was added, by means of a syringe, *n*-BuLi (0.24 mL, 1.55 M, 0.37 mmol) or $LiHBEt_3$ (0.37 mL, 1 M 0.37 mmol). Upon addition, the solution became bright yellow. The solvent was then removed in vacuo, the residual yellow oil was taken up in pentane, and the mixture was filtered, yielding a bright yellow solution. Upon reduction of the volume of the pentane solution to 5 mL and cooling to −20 °C overnight, a bright yellow powder, $Cr(tripod)_2$, was isolated. ^1H NMR (C_6D_6): δ 1.328 (s, $P-(CH_3)_2$), 1.244 (s, $P-CH_2$), 0.998 (s, $C-CH_3$). ^{31}P NMR: δ 30.62 (s). Mass spectrum (fast atom bombardment): $(M + 1)/e$ 557, M^+/e 556. The NMR chemical shift values reported here contradict those reported by Jones[8] but are consistent with the values obtained from an authentic sample of $Cr(tripod)_2$, which we have synthesized by the method of Jones.[8]

Protonation of $Cr(tripod)_2$. $Cr(tripod)_2$ (1.5 g, 2.7 mmol) was placed in THF (10 mL). This yielded a bright yellow solution, which was cooled to −70 °C with dry ice and EtOH. To this solution was then added $HBF_4 \cdot Et_2O$ (0.2 mL, 1.5 mmol) by means of a 100-μL syringe. Material immediately precipitated from the solution leaving a colorless solution that at −70 °C showed no ^{31}P signal. This solution, at 25 °C, again gave no ^{31}P signal. Extracting the precipitate with CH_3CN gave a red solution

---

(1) Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 7774.

(2) Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 6163.

(3) Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006.

(4) Trimarchi, M. C. L.; Green, M. A.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 514.

(5) Van-Cattledge, F. A.; Ittel, S. D.; Jesson, J. P. *Organometallics* **1985**, *4*, 18.

(6) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Patt, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954.

(7) Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 590.

(8) Arif, A. M.; Hefner, J. G.; Jones, R. A.; Whittlesley, B. R. *Inorg. Chem.* **1986**, *25*, 1080.

(9) This solid should be handled with rigorous exclusion of oxygen and moisture.

0020-1669/87/1326-0374$01.50/0

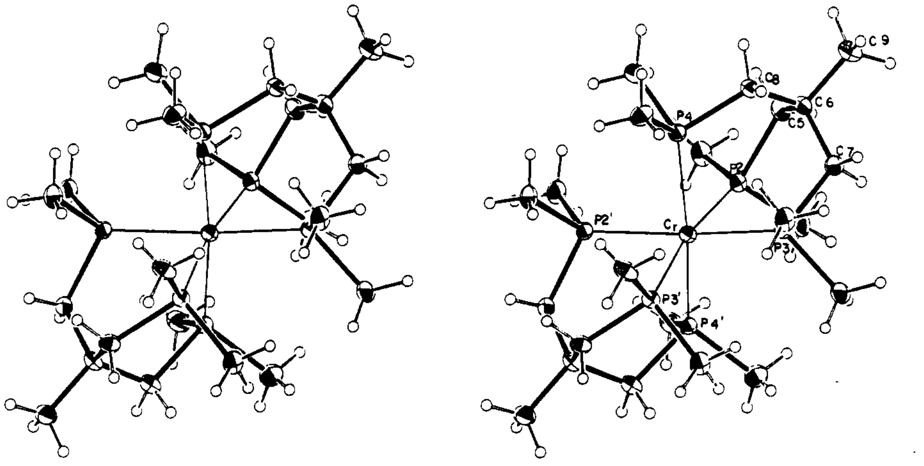


Figure 1. Stereo ORTEP drawing of the refined atoms located in $HCr[(Me_2PCH_2)_3CMe]_2^+$. The undetected hydride ligand is proposed to lie with equal probability between ligands P2 and P2′, between P3 and P4′, and between P4 and P3′.

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for Non-Hydrogen Atoms in $CrH(tripod)_2BEt_4$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Cr(1)	0^b	5000^b	7418 (1)	12
P(2)	1130 (1)	4346 (1)	6640 (1)	12
P(3)	1114 (1)	4621 (1)	8282 (1)	13
P(4)	941 (1)	6372 (1)	7274 (1)	14
C(5)	2364 (4)	4831 (4)	6693 (3)	15
C(6)	2659 (4)	5251 (4)	7405 (3)	15
C(7)	2383 (4)	4591 (5)	8007 (3)	16
C(8)	2221 (4)	6235 (4)	7503 (3)	16
C(9)	3755 (4)	5362 (4)	7400 (3)	20
C(10)	1419 (5)	3082 (4)	6751 (4)	20
C(11)	1028 (4)	4337 (5)	5678 (3)	20
C(12)	1110 (4)	3483 (5)	8762 (3)	19
C(13)	1239 (5)	5429 (4)	9044 (3)	18
C(14)	706 (5)	7482 (4)	7750 (3)	22
C(15)	1091 (5)	6892 (5)	6396 (4)	23
B(16)	10000^b	0^b	5000^b	20
C(17)	10710 (5)	−630 (5)	4494 (3)	23
C(18)	11435 (6)	−1255 (6)	4859 (4)	36
B(19)	0^b	0^b	0^b	18
C(20)	−815 (5)	−466 (5)	508 (3)	22
C(21)	−1644 (5)	−989 (6)	165 (4)	34

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609. [b] These parameters are fixed by symmetry.

that exhibited a $^{31}P\{^1H\}$ NMR singlet at δ −5.97, consistent with $CH_3C[CH_2P(CH_3)_2H]_3^{3+}$, the red color being due to a paramagnetic chromium complex exhibiting no ^{31}P or ^1H NMR.

$CH_3C[CH_2P(CH_3)_2H]_3^{3+}$. Tripod (0.05 mL) was placed into an NMR tube containing CH_3CN; then excess $HBF_4 \cdot Et_2O$ was added to the tube. $^{31}P\{^1H\}$ NMR: δ −5.9 (s).

Crystallography. A suitable small crystal of $[CrH(tripod)_2]BEt_4$ grown by cooling in THF was selected, transferred to the goniostat, and cooled to −159 °C. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited tetragonal symmetry and extinctions corresponding to the space group $P\bar{4}2_1c$. Details of data collection and processing, following our typical procedure,[10] are shown in Table I.

The structure was solved by a combination of direct methods and Fourier techniques. The unit cell contains four Cr atoms at the site d (0, $^1/_2$, z), with point symmetry of 2. The unit cell also contains four $B(C_2H_5)_4^-$ anions, two each at the sites b and a; these sites have $\bar{4}$ point symmetry. All hydrogen atoms except that on Cr were located after initial refinement. The least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The results of the structure determination are shown in Tables II and III and Figures 1 and 2. Additional data are available as supplementary material.

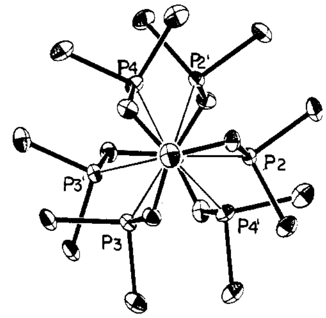


Figure 2. ORTEP drawing of the non-hydrogen atoms of $HCr[(Me_2PCH_2)_3CMe]_2^+$ viewed down the Cr–C6 (quaternary carbon) line. The crystallographic C_2 axis bisects the P3–Cr–P3′ angle.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[CrH(tripod)_2]BEt_4$[a]

Cr(1)–P(2)	2.3654 (17)	P(4)–C(14)	1.839 (6)
Cr(1)–P(3)	2.3426 (17)	P(4)–C(15)	1.849 (7)
Cr(1)–P(4)	2.3557 (16)	C(5)–C(6)	1.545 (8)
P(2)–C(5)	1.867 (6)	C(6)–C(7)	1.532 (8)
P(2)–C(10)	1.836 (6)	C(6)–C(8)	1.525 (8)
P(2)–C(11)	1.852 (6)	C(6)–C(9)	1.549 (8)
P(3)–C(7)	1.860 (6)	C(17)–C(18)	1.518 (11)
P(3)–C(12)	1.846 (6)	C(17)–B(16)	1.650 (6)
P(3)–C(13)	1.861 (6)	C(20)–C(21)	1.528 (10)
P(4)–C(8)	1.862 (5)	C(20)–B(19)	1.641 (6)
P(2)–Cr(1)–P(3)	84.79 (6)	C(12)–P(3)–C(13)	97.9 (3)
P(2)–Cr(1)–P(4)	82.36 (5)	Cr(1)–P(4)–C(8)	115.49 (20)
P(3)–Cr(1)–P(4)	83.89 (5)	Cr(1)–P(4)–C(14)	122.40 (29)
P(2)–Cr(1)–P(2)′	101.74 (8)	Cr(1)–P(4)–C(15)	119.64 24)
P(3)–Cr(1)–P(3)′	89.89 (8)	C(8)–P(4)–C(14)	98.3 (3)
P(4)–Cr(1)–P(4)′	166.54 (9)	C(18)–P(4)–C(15)	98.4 (3)
P(3)–Cr(1)–P(4)′	105.77 (8)	C(14)–P(4)–C(15)	97.9 (3)
P(2)–Cr(1)–P(4)′	89.12 (8)	P(2)–C(5)–C(6)	115.9 (4)
P(3)–Cr(1)–P(2)′	169.77 (9)	C(5)–C(6)–C(7)	111.5 (5)
Cr(1)–P(2)–C(5)	116.59 (18)	C(5)–C(6)–C(8)	110.3 (5)
Cr(1)–P(2)–C(10)	116.87 (22)	C(5)–C(6)–C(9)	107.4 (5)
Cr(1)–P(2)–C(11)	125.48 (22)	C(7)–C(6)–C(8)	110.8 (5)
C(5)–P(2)–C(10)	98.1 (3)	C(7)–C(6)–C(9)	108.5 (5)
C(5)–P(2)–C(11)	97.4 (3)	C(8)–C(6)–C(9)	108.1 (5)
C(10)–P(2)–C(11)	97.2 (3)	P(3)–C(7)–C(6)	116.3 (4)
Cr(1)–P(3)–C(7)	116.45 (19)	P(4)–C(8)–C(6)	117.0 (4)
Cr(1)–P(3)–C(12)	123.23 (21)	C(18)–C(17)–B(16)	116.4 (5)
Cr(1)–P(3)–C(13)	118.70 (21)	C(21)–C(20)–B(19)	117.9 (5)
C(7)–P(3)–C(12)	97.2 (3)	C(17)–B(16)–C(17)′	110.28 (23)
C(7)–P(3)–C(13)	98.5 (3)	C(20)–B(19)–C(20)′	110.67 (22)

[a] Phosphorus atoms marked by a prime are related to their unprimed atom by a C_2 axis. Carbon atoms C(17)′ and C(20)′ are related to C(17) and C(20) by a S_4 axis.

The closest non-hydrogen contact between the cation and the anions is 3.87 Å. There was no evidence for hydride electron density within

---

(10) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

reasonable bonding distance to chromium in a final difference map. Carbon–hydrogen distances range from 0.80 (5) to 1.02 (5) Å in the cation and from 0.88 (10) to 1.05 (7) Å in the anion. The tetraethylborate anion exhibits no unusual features.

Results

Synthesis and Characterization. Reaction of $CrCl_3$(tripod) with $LiHBEt_3$ (1:2.5 mole ratio) in THF yields a single metal complex whose ^1H NMR spectrum shows a hydride ligand coupled to *six* phosphorus nuclei. Filtration of the solution, addition of $NaBEt_4$,[11] concentration, and cooling yield a solid with ^{31}P and ^1H NMR spectra that duplicate those of the reaction solution. The ^1H and ^{31}P NMR spectra show only one chemical shift each for the CH_3–C, CH_2, P–CH_3, and phosphorus nuclei. The *H*–Cr–*P* coupling constant is quite large (64.2 Hz), and a hydride-coupled ^{31}P NMR spectrum shows a doublet characteristic of monohydride complex. It was established that the hydride ligand originates from the borohydride by repeating the synthesis with $LiDBEt_3$. The isolated product shows a $^{31}P\{^1H\}$ NMR triplet (intensity 1:1:1) with J(P–D) = 9.7 Hz and a ^2H NMR multiplet (−7.14 ppm, J(P–D) = 9.8 Hz). Proton NMR resonances for the BEt_4^- anion are unexceptional. Integration of the tripod, BEt_4^-, and hydride proton resonances yields a measured mole ratio of 2.0:1.0:1.0. The infrared spectrum of the solid shows a weak stretching absorption at 1895 cm^{-1}, suggestive of a terminal location. This band is absent in the deuteride analogue. The NMR data suggest a fluxional molecule. Consequently, we undertook an X-ray structure determination in the hope of securing a clear determination of the location of the hydride.

Solid-State Structure of [HCr(tripod)$_2$]BEt$_4$. The solid is composed of equal numbers of $HCr(tripod)_2^+$ and BEt_4^- ions. The BEt_4^- anion is ordered and reveals no unusual features, although this appears to be the first determination of its structure. The cation lies on a crystallographic two fold rotation axis that relates the two tripod ligands and bisects the angle P(3)–Cr–P(3)′ (Figure 1). The actual symmetry of the cation is higher , with a virtual C_3 axis along Cr–C(6)–C(9), with three C_2 axes perpendicular to this (Figure 2). The Cr–P distances, while they differ by as much as 9.5σ (difference), 0.023 Å, nevertheless appear to be *chemically* equivalent. Angles P–Cr–P within a tripod ligand are all close to 84°. The cage unit $Cr(PC)_3CMe$ does *not* have three vertical mirror planes in the solid state due to a twist or skewing of the CH_2 groups. As a result, viewed down the idealized C_3 axis of the cation (Figure 2), Cr–P bonds do not precisely eclipse CH_2–CMe bonds. A skewing of this sort is typical for tripodal ligands.

We now analyze the stereochemical relationship of the two tripodal ligands about chromium, ignoring for the moment the presence of one hydride ligand on the metal. The six-coordinate $Cr(tripod)_2$ unit has two limiting structures of high symmetry, octahedral (more properly a regular trigonal antiprism), A, and trigonal prismatic, B. In these sketches, a triangle represents the three P atoms within one tripod. Form A has six equivalent edges linking apices of the two triangles drawn; there will be six identical cisoid interligand P–Cr–P angles. Form B will show only three identical cisoid angles. The pattern of interligand P–Cr–P′ angles exhibited by $HCr(tripod)_2^+$ identifies the actual structure as intermediate between A and B. The observed structure is a trigonal antiprism twisted toward a trigonal prism. If the twist angle is defined as the angle between ligands projected on a plane perpendicular to the idealized threefold axis (60° in A; 0° in B), these angles average 45 (three times) and 74° (three times) in $HCr(tripod)_2^+$. In terms of the actual (not projected) angles within the coordination sphere of this cation, these interligand angles for cis-phosphorus nuclei are 89.9, 89.1 (twice), 105.8, and 101.7° (twice); these are best compared to the corresponding angles in neutral $Cr(tripod)_2$, 96.4 and 96.7°. The transoid P–Cr–P angles in $HCr(tripod)_2^+$ are 166.5 and 169.8° (twice).

A

B

The nature of this torsional distortion from the precisely eclipsed regular trigonal-antiprismatic form adopted by $Cr(tripod)_2$ must of course be linked to the presence of an additional ligand, H, bound to chromium. However, the actual structure determined for the heavy atoms of $HCr(tripod)_2^+$ reveals *three* expanded cisoid P–Cr–P angles, instead of the *one* sufficient to accommodate the hydride ligand.

Since all carbon-bound hydrogens were located and refined, the diffraction intensities are expected to be of sufficient quality to also allow determination of the hydride position. Since this expectation is not realized, we conclude that an additional problem exists: disorder of the hydride position. With the postulate that the hydride is disordered among the three wider P–Cr–P angles, the description of the structure of $HCr(tripod)_2^+$ is complete. Such disorder is made plausible by a space-filling drawing (supplementary material), which shows that the hydride ligand is totally shielded by the hydrocarbon periphery of this compact and ovoid molecular ion, a feature that is also expected to influence chemical reactivity.

Reactivity. $HCr(tripod)_2^+$ is cleanly deprotonated in THF by either *n*-BuLi or $LiHBEt_3$ to yield $Cr(tripod)_2$, isolable as a bright yellow hydrocarbon-soluble solid. Numerous attempts to effect the reverse reaction, protonation of $Cr(tripod)_2$ with $HBF_4{\cdot}OEt_2$, failed, even when a deficiency of acid was employed in CH_2Cl_2 or THF at −70 °C. The only identifiable product was triply protonated free ligand: $MeC(CH_2PMe_2H)_3^{3+}$. The metal-containing product was a red solid that dissolved only in acetonitrile, and then showed no ^1H or ^{31}P NMR signals, suggestive of paramagnetism.

The hydride cation was recovered unchanged after 12 h at 25 °C in THF under 1 atm of either CO or CO_2.

Details of the Synthesis. Given the surprising production of a bis(tripod) complex from $CrCl_3$(tripod), we investigated the influence of reagent stoichiometry on yield. The yield of the "standard reaction" ($CrCl_3$(tripod):$LiHBEt_3$ = 1:2.5) approaches 100%, based on available tripod, and the unused chromium is found as an insoluble black solid upon filtration of the reaction solution. That the reaction is quantitative in tripod is also shown by the absence of a ^{31}P NMR resonance for free tripod in the reaction solution prior to workup. Curiously, however, addition of 1 mol of free tripod/mol of Cr does not increase the yield of $HCr(tripod)_2BEt_4$.

The reaction product is unequivocally a reduced form of chromium compared to the trivalent reagent complex. Consistent with this, we observe gas evolution (presumably H_2) during the addition of the first mole of $LiBEt_3H$ per mole of chromium. The influence of the B:Cr mole ratio thus comes into question, since $LiHBEt_3$ is a reductant as well as a source of hydride ligands. As the B:Cr ratio exceeds 3:1, the cationic product is accompanied by increasing amounts of a second product, $Cr(tripod)_2$. $Cr(tripod)_2$ is an obvious deprotonation product of $HCr(tripod)_2^+$ (eq 2). This deprotonation has been verified with an isolated sample of the monohydride cation (see above). Mole ratios of B:Cr less than 2.5:1 have not been investigated because of our feeling (see eq 3) that such a ratio approximates the minimal need for one hydride ligand and 1 reducing equiv.

$$HBEt_3^- + HCr(tripod)_2^+ \rightarrow H_2 + Cr(tripod)_2 + BEt_3 \qquad (2)$$

$$2H^- + \text{“}CrCl_3\text{”} \rightarrow \text{“}CrH^+\text{”} + 3Cl^- + {}^1/_2H_2 \qquad (3)$$

Discussion

The question still remains as to why and how tripod transfer occurs between metal centers to generate a bis(tripod) product. We have attempted to inhibit this by trapping any hypothetical (tripod)CrH_3 intermediate with H_2. However, the reaction product is unchanged when $CrCl_3$(tripod) reacts with $LiHBEt_3$ under 1 atm of H_2. One possibility is that a transient paramagnetic hydride (e.g. (tripod)CrH_3) dimerizes to achieve an 18-electron configu-

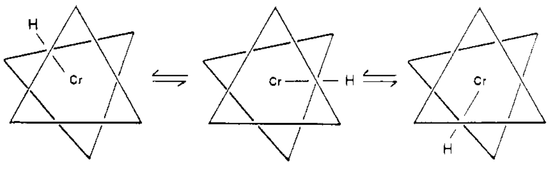
---

[11] Our first isolation of this salt occurred with BEt_4^- present as an impurity in an old sample of $LiHBEt_3$. In subsequent work, we precipitate product with $NaBEt_4$.

ration and that the $(tripod)_2Cr_2H_n$ species is instrumental in transfer of tripod. A second explanation is based on the possibiliity that the first reaction of $CrCl_3$(tripod) with $LiHBEt_3$ is reduction to Cr(II), as in "$CrCl_2$(tripod)". The work of the Jones group,[8] taken together with the kinetic lability of Cr(II) and the highly unsaturated character of "$CrCl_2$(tripod)", allows the conclusion that tripod transfer may occur at this stage of the reaction, yielding the known compound $CrCl_2(\eta^2\text{-tripod})_2$. From this point, a single Cl^-/H^- exchange, followed by Cl^- displacement by one pendant arm of tripod, could yield $HCr(tripod)_2^+$. The production of a cationic hydride from $LiHBEt_3$ thus might follow from the kinetic lability of Cr(II) halides.

The structure of $HCr(tripod)_2^+$ demands comparison to that of its conjugate base, $Cr(tripod)_2$.[8] Intraligand P–Cr–P angles are unchanged on protonation. The degrees of freedom exercised upon protonation are (1) a systematic lengthening of Cr–P distances by (on average) 0.068 Å, consistent with protonation being *oxidative* addition, and (2) a twisting away from the precisely staggered form in $Cr(tripod)_2$ *toward* (but stopping far short of) a trigonal-prismatic form. This latter motion creates three nearly equally attractive edges of the former octahedron (trigonal antiprism) for the proton, with two consequences. The first is a nuisance consequence, in that it leads to disorder in the crystalline solid. The second consequence is that the three nearly equienergetic edges are attractive sites for a hydrogen migration process (eq 4), which alone is sufficient to account for the hydrogen fluxionality required by both the ambient-temperature ^1H and ^{31}P NMR spectra.

While intramolecular migration of hydrogen in $HCr(tripod)_2^+$ is facile, our observations of the ^{31}P NMR of a mixture of the



(4)

conjugate acid/base pair $HCr(tripod)_2^+/Cr(tripod)_2$ show neither coalescence of the two resonances nor even line broadening of these resonances. The rate of intermolecular proton transfer is thus less than approximately 10 s^{-1}, if it occurs at all. Since the structural study reported here reveals only modest changes in CrP_6 skeletal geometry upon proton transfer, the slow proton transfer must be attributed to the steric bulk of the acid and base (Figure 3, supplementary materials). Previous work[12] has raised this point for $HMo(CO)_2(Ph_2PC_2H_4PPh_2)^+$ and has demonstrated catalysis of proton transfer by small anionic bases.

Acknowledgment. This work was supported by the National Science Foundation. We thank Scott Horn for skilled technical assistance.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters and Figure 3, showing stereo stick figures and space filling drawings (4 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

---

(12) Hanckel, J. M.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1983**, *105*, 6979.

Contribution from the Departments of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455, and University of California, Davis, California 95616

1,3-Bis(diphenylphosphino)propane-Bridged Complexes. X-ray Crystal and Molecular Structure of $Ir_2(CO)_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}_2$, Its Reactions with H_2 and O_2, and the Structure of $Ir_2(CO)_2Cl_2(O_2)\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}_2$

Hsien-Hau Wang,[1a] Louis H. Pignolet,*[1a] Philip E. Reedy, Jr.,[1b] Marilyn M. Olmstead,[1b]
and Alan L. Balch*[1b]

Received August 12, 1986

Yellow $Ir_2(CO)_2Cl_2(\mu\text{-dppp})_2\cdot 3CH_2Cl_2$ (**1**) [dppp is 1,3-bis(diphenylphosphino)propane] crystallized in the monoclinic space group $C2/c$ (No. 15), with $a = 19.626$ (3) Å, $b = 22.051$ (3) Å, $c = 15.135$ (8) Å, $\beta = 90.36$ (3)°, $V = 6550$ (5) Å^3, and $Z = 4$ at 298 K. Refinement yielded $R = 0.061$ and $R_w = 0.072$ for 3462 reflections with $F_o^2 \geq 2.5\sigma(F_o^2)$. The molecule consists of a 12-membered ring with *trans*-$IrP_2(CO)Cl$ units connected through the bridging dppp ligands. The planar Ir units are noninteracting, with the closest intramolecular approach being a 4.179 (4) Å Cl···Cl contact. Reaction of **1** with dioxygen at 1 atm with CH_2Cl_2 as solvent produced $Ir_2(CO)_2Cl_2(O_2)(\mu\text{-dppp})_2$ (**2**), while under 3 atm, $Ir_2(CO)_2Cl_2(O_2)_2(\mu\text{-dppp})_2$ was formed. Yellow $Ir_2(CO)_2Cl_2(O_2)(\mu\text{-dppp})_2$ crystallized in the monoclinic space group $P2_1/c$ (No. 14), with $a = 13.070$ (2) Å, $b = 20.474$ (7) Å, $c = 17.223$ (3) Å, $\beta = 90.75$ (1)°, $V = 5762$ (2), and $Z = 4$ at 130 K. Refinement yielded $R = 0.049$ and $R_w = 0.052$ for 5853 reflections with $I > 2\sigma(I)$. The complex consists of one planar $IrP_2(CO)Cl$ unit connected to a $IrP_2(CO)Cl(O_2)$ unit through two dppp bridges. The closest approach of the two coordination spheres of the iridium involves an intramolecular Cl···O contact of 3.91 (2) Å. Reaction of **1** with dihydrogen at 1 atm with CH_2Cl_2 as solvent produced a mixture of $Ir_2(CO)_2Cl_2(H)_2(\mu\text{-dppp})_2$ and $Ir_2(CO)_2Cl_2(H)_4(\mu\text{-dppp})_2$. In both of these complexes the hydrogen ligands are positioned in the region of space between the iridium atoms.

Introduction

There has been considerable exploration of the properties of binuclear transition-metal complexes with diphosphines as bridging ligands.[2,3] Most of these have concentrated on the use of small-bite ligands like bis(diphenylphosphino)methane,[3] which place the metal ions involved in close proximity and make direct metal···metal interactions and metal–metal bonding into major features of these compounds. Much less attention has been paid to the structural characterization and chemical behavior of complexes that provide for larger separations between the metal ions.[4]

---

(1) (a) University of Minnesota. (b) University of California.

(2) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; p 167.

(3) Puddephatt, R. *J. Chem. Soc. Rev.* **1983**, *12*, 99.

(4) (a) March, F. C.; Mason, R.; Thomas, K. M.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, 584. (b) Pryde, A.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1976**, 322. (c) Sanger, A. R. *J. Chem. Soc., Dalton, Trans.* **1977**, 120. (d) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971. (e) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59. (f) Faraone, F.; Bruno, G.; Tresoldi, G.; Faraone, G.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1981**, 1651. (g) Eisenberg, R.; Fisher, B. J. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 67. (h) Fisher, B. J.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 3216. (i) Brown, J. M.; Canning, L. R. *J. Chem. Soc., Chem. Commun.* **1983**, 460. (j) Alcock, N. W.; Judd, L.; Pringle, P. G. *Inorg. Chim. Acta* **1986**, *113*, L13.