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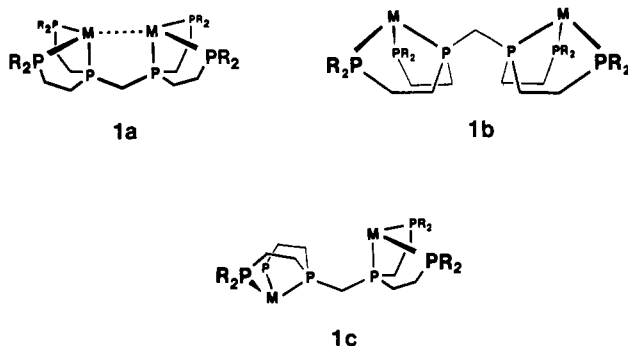
**Synthesis and Structural Characterization of
mer,mer-Cr₂Cl₆(eHTP) (eHTP =
(Et₂PCH₂CH₂)₂PCH₂P(CH₂CH₂PEt₂)₂). A New Binuclear
Coordination Mode for eHTP**

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The ligand system (Et₂PCH₂CH₂)₂PCH₂P(CH₂CH₂PEt₂)₂, abbreviated eHTP (for ethyl-substituted hexakis(tertiary phosphine)), has a central bis(phosphino)methane linkage that prefers bridging two metal centers, while the (dialkylphosphino)ethyl arms favor chelation to the two metal atoms. The ligand can be best viewed as a combination of two tridentate bischelating phosphine units. We have designed this phosphine to be a powerful binucleating ligand, and so far, every time we have added 2 equiv of a simple mononuclear metal halide, we have obtained bimetallic systems. An important consideration that is allowing us to develop the chemistry of eHTP is that it can be prepared in large quantities via a high-yield synthetic route that is amenable to modifications to produce a number of variations in the basic structure of the polyphosphine ligand to fine tune both steric and electronic effects.¹

eHTP was designed to form closed-mode dimer complexes of the general type **1a**, but it has been found that open-mode complexes of types **1b** and **1c** can also be produced. We have crys-



tallographically characterized conformations **1b** and **1c** in the complexes Co₂(CO)₈(eHTP)²⁺ and Ni₂Cl₂(eHTP)²⁺, and we have strong spectroscopic evidence for the closed-mode form **1a**.¹⁻³ The "W-shaped" configuration **1b** is unprecedented for a bis(phosphino)methane linkage and results from the unique combination of bridging and chelating moieties. It is quite clear that eHTP represents a remarkably versatile ligand, which could adopt a variety of other types of structures, either mono- or bimetallic. We, therefore, wish to report another novel and rather unexpected type of binuclear eHTP configuration for the Cr(III) dimer Cr₂Cl₆(eHTP).

Experimental Section

All manipulations were carried out under inert atmosphere (N₂ or Ar) by using standard Schlenk or glovebox techniques unless stated otherwise. Solvents were distilled under inert atmosphere from the following drying agents: toluene (sodium) and CH₂Cl₂ (CaH₂). CrCl₃, sodium, and potassium (Alfa Division of Morton Thiokol) were used as received without further purification. eHTP was prepared according to published procedures.¹ ¹H and ³¹P NMR spectra were run on a Varian XL-300 spectrometer, IR spectra were run on a Perkin-Elmer 283B spectrometer, magnetic susceptibilities were done on a Varian XL-300 NMR by using the Evans method,⁴ electronic spectra were run on a Cary 219 spectrophotometer, and the elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

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Table I. Crystallographic Data for Cr₂Cl₆(eHTP) (**2**)

Crystal Parameters	
formula: Cr ₂ Cl ₆ P ₆ C ₂₅ H ₅₈	fw = 861.3
cryst system: orthorhombic	space group: <i>Pbca</i>
<i>a</i> = 17.542 (5) Å	α = 90.00°
<i>b</i> = 14.516 (4) Å	β = 90.00°
<i>c</i> = 32.249 (8) Å	γ = 90.00°
<i>V</i> = 8212 (7) Å ³	<i>Z</i> = 8
<i>d</i> _{calcd} = 1.39 g/mL	μ (Mo K α) = 11.59 cm ⁻¹
temp = 22 °C	cryst size = 0.48 × 0.41 × 0.24 mm
cryst color: purple-red	

Data Collection and Structure Refinement

diffractometer: Nicolet P3	radiation: Mo K α
monochromator: graph. cryst	scan method: ω
scan speed: variable, 2-29°/min	data limits: 3° < 2 θ < 45°
octants collod: <i>h, k, l</i>	Friedel pairs collod: no
no. of reflns collod = 5930	no. of unique data ($F_o^2 > 3\sigma(F_o^2)$) = 2529
weighting scheme: non-Poisson	exptl instability factor, <i>P</i> = 0.06 ^a
no. of params refined = 352	data/parameter ratio = 7.2
<i>R</i> ^b = 0.048	<i>R</i> _w ^c = 0.051
quality of fit indicator ^d = 1.28	largest final Fourier pk = 0.33 e/Å ³
largest final shift/esd = 0.2	abs cor: yes

^a Experimental instability factor for downweighting intense reflections in the non-Poisson weighting scheme, $w = 3F_o^2[\sigma^2(I) + (PF_o^2)^2]^{-1}$. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. ^d Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

Cr₂Cl₆(eHTP) (2**).** A solution of CrCl₃·3THF (0.748 g, 2 mmol) in 50 mL of CH₂Cl₂ is added dropwise to a solution of eHTP (0.544 g, 1.00 mmol) in 75 mL of CH₂Cl₂. The solution becomes dark purple as the addition continues, and the mixture is stirred for 5 h after the addition is completed and then rotoevaporated to dryness. The resulting material is chromatographed on an alumina column with CH₂Cl₂ as an eluant. A purplish red material is the only material to move on the column under these conditions. Large rod-shaped crystals can be obtained readily by evaporation of a solution of CH₂Cl₂ and toluene to give a recrystallized yield of 55%. **2** is a paramagnetic, air-stable material.

Anal. Calcd for C₂₅H₅₈Cl₆Cr₂P₆: C, 34.9; H, 6.8; P, 21.6. Found: C, 34.9; H, 6.5; P, 21.1. IR (KBr): 2960 (m, C-H), 2940 (m, C-H), 2905 (m, C-H), 2880 (m, C-H), 1455 (m, CH), 1415 (m, CH), 1380 (m, CH), 1045 (m, P-Et), 1035 (m, P-Et). Effective magnetic moment (72 mg/mL, CH₂Cl₂): 3.9 μ_B /Cr atom (293 K). Electronic spectrum (CH₂Cl₂) [ν_{max} , cm⁻¹ (ϵ /Cr atom, L mol⁻¹ cm⁻¹): 26 600 (ca. 2000); 21 750 (330); 18 800 (300); 14 500 (70).

X-ray Crystallographic Procedure. Crystal and data collection information is summarized in Table I. A 1.2-mm collimator was used, producing a beam with an approximately 1-mm uniform diameter. Fifteen reflections from a rotation photograph were computer centered, and the resulting setting angles were used in the autoindexing program, in conjunction with axial photographs, to select the best unit cell. Final cell constants were based on 15 reflections collected in a 2 θ range of 25-35°. Structure solving was done on a microVAX II computing system with the Enraf-Nonius Structure Determination Package of crystallographic programs.

A crystal of **2** was mounted with epoxy at the end of a glass fiber. Three standard reflections measured every 100 data points showed only small, random variations in intensity. Data reduction included corrections for background, Lorentz, and polarization effects. An empirical absorption correction using the program DIFABS was also performed.⁵ The structure was solved in the space group *Pbca* (uniquely determined from systematic absences). The structure was solved by using a combination of direct methods (MULTAN) and Patterson map techniques, which gave the chromium and roughly half of the phosphorus and chlorine atom positions. Full-matrix least-squares refinement followed by difference Fourier maps located the remaining non-hydrogen atom positions. Anisotropic refinement of the non-hydrogen atoms gave final

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Table II. Positional Parameters for Cr₂Cl₆(eHTP) (2)

atom	x	y	z	B, Å ²
Cr1	0.82957 (8)	-0.0021 (1)	0.08110 (4)	3.86 (3)
Cr2	1.10796 (8)	-0.2585 (1)	0.16461 (5)	4.23 (3)
Cl1	0.7328 (1)	0.1043 (2)	0.07729 (8)	5.60 (6)
Cl2	0.7655 (1)	-0.0943 (2)	0.12773 (7)	5.20 (6)
Cl3	0.9114 (1)	0.0738 (2)	0.03563 (8)	5.08 (6)
Cl4	1.1640 (2)	-0.3823 (2)	0.19677 (8)	6.27 (7)
Cl5	1.1697 (2)	-0.2750 (2)	0.10105 (8)	5.74 (7)
Cl6	1.0366 (2)	-0.2204 (2)	0.22178 (8)	6.58 (7)
P1	0.9253 (1)	-0.1283 (2)	0.07420 (8)	3.90 (6)
P2	0.7731 (2)	-0.0873 (2)	0.02277 (8)	4.67 (6)
P3	1.0110 (2)	-0.3650 (2)	0.1366 (1)	5.43 (7)
P4	1.0636 (1)	-0.1098 (2)	0.13293 (8)	3.91 (6)
P5	1.2133 (2)	-0.1595 (2)	0.18711 (9)	4.99 (7)
P6	0.8881 (2)	0.0913 (2)	0.13739 (8)	4.40 (6)
C'	1.0280 (5)	-0.1054 (6)	0.0800 (3)	4.2 (2)
C11	0.9161 (6)	-0.1679 (6)	0.0212 (3)	5.1 (3)
C12	0.8314 (6)	-0.1882 (6)	0.0118 (3)	5.7 (3)
C13	0.9115 (5)	-0.2317 (6)	0.1056 (3)	4.2 (2)
C14	0.9605 (6)	-0.3156 (6)	0.0929 (3)	5.2 (3)
C41	1.1495 (5)	-0.0401 (7)	0.1316 (3)	5.1 (2)
C42	1.1888 (5)	-0.0421 (7)	0.1733 (3)	5.8 (3)
C43	0.9969 (5)	-0.0383 (6)	0.1622 (3)	4.1 (2)
C44	0.9870 (5)	0.0618 (6)	0.1464 (3)	4.6 (2)
C21	0.7687 (6)	-0.0296 (7)	-0.0270 (3)	5.9 (3)
C22	0.7243 (7)	0.0569 (8)	-0.0294 (3)	8.1 (3)
C23	0.6753 (7)	-0.1255 (9)	0.0336 (3)	8.6 (3)
C24	0.6347 (9)	-0.171 (1)	0.0062 (5)	13.3 (5)
C31	0.9363 (6)	-0.4035 (7)	0.1694 (4)	7.5 (3)
C32	0.9602 (7)	-0.459 (1)	0.2076 (4)	11.1 (4)
C33	1.0559 (7)	-0.4705 (7)	0.1154 (4)	8.6 (4)
C34	1.0114 (9)	-0.5267 (9)	0.0872 (5)	11.4 (5)
C51	1.3046 (6)	-0.1737 (8)	0.1622 (4)	7.8 (3)
C52	1.3412 (7)	-0.265 (1)	0.1637 (6)	12.2 (5)
C53	1.2323 (8)	-0.160 (1)	0.2412 (4)	10.3 (4)
C54	1.298 (1)	-0.127 (2)	0.2572 (5)	18.3 (7)
C61	0.8889 (6)	0.2132 (7)	0.1248 (3)	5.6 (3)
C62	0.9219 (7)	0.2775 (7)	0.1571 (4)	8.1 (3)
C63	0.8461 (6)	0.0847 (7)	0.1883 (3)	5.6 (3)
C64	0.7640 (6)	0.1128 (8)	0.1913 (3)	7.0 (3)

^a Values for anisotropically refined atoms are given in the form of the isotropically equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

discrepancy indices shown in Table I. Positional parameters for the non-hydrogen atoms are listed in Table II. Because only about half of the hydrogen atoms could be located, the positions of all hydrogen atoms were calculated and included in the final structure factor calculations. The presence of unusually short C-C bonds and larger than normal thermal parameters indicated that there was a disorder problem with two of the ethyl groups, C23-C24 and C53-C54, on the eHTP ligand.

Tables of hydrogen positional parameters, anisotropic thermal parameters, all bond distances and angles, and observed and calculated structure factors are included in the supplementary material.

Results and Discussion

The reaction of 2 equiv of CrCl₃·3THF with eHTP produces the purplish red bimetallic complex Cr₂Cl₆(eHTP) (2) in 55% recrystallized yield. The magnetic susceptibility in acetonitrile solution at room temperature gave an effective magnetic moment of 3.9 μ_B/chromium atom, which corresponds to three unpaired electrons. This is in perfect agreement with that measured for mononuclear chromium(III) phosphine halide complexes.⁶ As expected for a paramagnetic Cr(III) complex, no ³¹P NMR could be observed, while the ¹H NMR is broadened to the point of supplying no structural information. The lack of any deviations in the magnetic susceptibility from that seen for mononuclear complexes, moreover, points to the presence of an open-mode eHTP configuration where the two Cr centers are well separated and magnetically isolated. On the basis of the structure of the Co₂(CO)₄(eHTP)²⁺ complex, we expected to find a similar

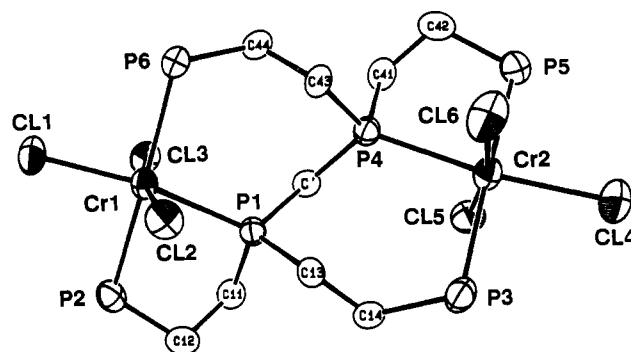


Figure 1. ORTEP plot of Cr₂Cl₆(eHTP) (2). Ethyl groups on the terminal phosphine groups are omitted for clarity. Thermal ellipsoids are shown at a 33% probability level.

Table III. Comparison of Selected Bond Distances (Å) and Angles (deg) for CrCl₃(tetraphos) and Cr₂Cl₆(eHTP)

	Cr ₂ Cl ₆ (eHTP) ^a	CrCl ₃ (tetraphos) ^b
Cr1-Cl1	2.298 (3), 2.294 (3)	2.306 (4)
Cr1-Cl2	2.306 (3), 2.297 (3)	2.292 (6)
Cr1-Cl3	2.330 (3), 2.331 (3)	2.320 (5)
Cr1-P1	2.496 (3), 2.512 (3)	2.399 (4)
Cr1-P2	2.460 (3), 2.469 (3)	2.466 (5)
Cr1-P6	2.487 (3), 2.451 (3)	2.489 (6)
P1-Cr1-P2	80.42 (9), 81.37 (9)	80.8 (2)
P1-Cr1-P6	100.80 (9), 100.12 (9)	81.0 (2)
P1-Cr1-Cl1	170.3 (1), 171.5 (1)	176.6 (2)
P1-Cr1-Cl2	87.71 (9), 87.16 (9)	88.8 (2)
P1-Cr1-Cl3	82.88 (9), 82.78 (9)	81.9 (2)
P2-Cr1-P6	176.8 (1), 174.1 (1)	160.5 (2)
P2-Cr1-Cl1	90.0 (1), 91.8 (1)	98.3 (2)
P2-Cr1-Cl2	90.59 (9), 88.3 (1)	93.2 (2)
P2-Cr1-Cl3	90.27 (9), 90.1 (1)	84.8 (2)
P6-Cr1-Cl1	88.74 (9), 88.3 (1)	99.4 (2)
P6-Cr1-Cl2	92.39 (9), 94.0 (1)	93.4 (2)
P6-Cr1-Cl3	86.97 (9), 86.2 (1)	85.8 (2)
P1-C'-P4	115.2 (4)	

^a The two values listed are for the essentially symmetric halves of the dimer, but only the numbering scheme for the Cr1 half is used. ^b Bond distances and angles for CrCl₃(tetraphos) are from ref 6. Numbering scheme is shown in Figure 1.

open-mode geometry involving octahedral Cr(III) centers with a facial set of three chloride and phosphine ligands.¹

The X-ray structure of 2, however, reveals a very different and rather unexpected eHTP coordination mode shown in Figure 1. The chromium atoms are in a distorted octahedral environment (selected bond distances and angles listed in Table III) with a meridional set of three chloride and phosphine ligands. In order to attain this *mer* geometry, the eHTP ligand adopts a coordination mode in which the phosphine atoms P2-P1-P3, instead of acting as an independent group bischelating to one Cr atom, span the two chromium centers to give a P1-P2 chelate to one metal atom while P3 bridges to the other Cr center. This gives rise to fused five- and seven-membered ring systems for the Cr₂(eHTP) moiety. The Cr-Cr separation of 6.7000 (3) Å is in good accord with the magnetic susceptibility data which indicated that the two chromium centers do not interact magnetically and, hence, are well separated. In spite of the very different eHTP conformation, the M-M distance is essentially the same as that seen for the cobalt dimer system,¹ 6.697(1) Å. This distance (ca. 6.7 Å) probably represents a rough maximum separation for two metal centers chelated by eHTP. There is an approximate 2-fold rotation axis passing through the central methylene group, and the bond distances and angles about each chromium center are quite similar. Therefore, we will generally refer to only half of the complex when discussing bond distances and angles.

Our initial thought was that eHTP was adopting this unusual configuration since it could not form a symmetrical square-planar coordination geometry using P2-P1-P3 on half of the ligand because of the strain of having two transoidally fused five-mem-

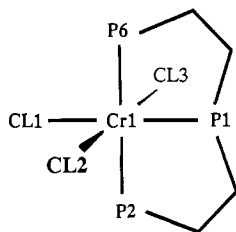
(6) Gray, L. R.; Hale, A. L.; Levason, W.; McCullough, F. P.; Webster, M. J. *Chem. Soc., Dalton Trans.* 1984, 47.

bered ring systems. Complexes that have tridentate phosphine ligands with planar, *mer*-type coordination geometries are, however, known,⁷ and we have shown that eHTP can adopt this geometry in square-planar Ni(II) and Pt(II) complexes.^{2,8} The key factor in understanding why the observed eHTP conformation is seen in **2** lies in the long Cr–P bond distances and their effect on the coordination geometry of eHTP.

The Cr–P bond distances in **2** are quite long compared to those seen for lower valent M–P bonds: Cr1–P1 = 2.496 (3) Å, Cr1–P2 = 2.460 (3) Å, and Cr1–P6 = 2.487 (3) Å. The result is that there are distortions from octahedral geometry about the chromium atoms that range from small to significant with the largest angular variance being about 10° from ideal (e.g., P1–Cr1–P2 = 80.42 (9)°). The small P1–Cr1–P2 angle is expected for a five-atom chelate ring with fairly long Cr–P bond distances. Pt₂Cl₂(eHTP)²⁺, for example, with the shorter internal Pt–P bond distances of 2.197 (4) Å and Pt–P distances of 2.302 (5) and 2.323 (5) Å for the transoidal outer phosphine groups, has cisoidal P–M–P angles of 85.3 (2) and 86.9 (2)°.⁸ The increased Cr–P bond distances in **2** cause the P1–Cr–P2 chelate angle to drop down to about 81°. If the eHTP ligand were to adopt a geometry similar to that seen for the nickel and platinum systems with two fused five-membered rings in a trans orientation, the distortions from octahedral geometry would be quite a bit greater than those seen for the observed complex, which has the five- and seven-membered ring systems.

One unusual feature of eHTP that has intrigued us is the flexibility of the central methylene bridge, which can accommodate some of the sterically demanding structures we have observed. Previous eHTP dimer complexes have had P–CH₂–P bridge angles ranging from 120.9 (2)° for [Ni₂Cl₂(eHTP)²⁺][Cl⁻]₂ to the extraordinarily large value of 129.8 (9)° for Pt₂Cl₂(eHTP)²⁺.^{2,8} The methylene bridge angle seen for Cr₂Cl₆(eHTP), on the other hand, has a relatively "normal" value of 115.2 (4)°, which is a typical angular value seen for R₂PCH₂PR₂ type linkages.⁹

There are only two other reported structures on CrX₃P₃ systems to which we can make comparisons, namely, CrCl₃(tetraphos) (tetraphos = P(CH₂CH₂PPh₂)₃), prepared by Levason and co-workers,⁶ and CrCl₃(tripod) (tripod = MeC(CH₂PMe₂)₃), which has been prepared by Jones and co-workers.^{10,11} Jones' tripod complex has facial geometry, while Levason's CrCl₃(tetraphos) complex has a meridional arrangement of phosphine and chloride ligands. Although tetraphos is formally a tetradentate ligand, only three of the phosphine groups are coordinated to the chromium atom, leaving a dangling phosphine functionality. Although the local coordination geometry about the chromium atoms in our Cr₂Cl₆(eHTP) complex is similar to that found for CrCl₃(tetraphos)



there are significant differences that are tied into the strain of having transoidally fused five-membered rings in the tetraphos

complex. Table III shows a comparison of selected bond distances and angles for our eHTP dimer and the mononuclear tetraphos system. It can be seen that for certain bond angles there are noticeably larger deviations from octahedral geometry in the tetraphos complex than in **2**.

The largest variation occurs in the trans P2–Cr–P3 angle with a value of only 160.5 (2)° in the tetraphos complex versus an average value of 175.5° in **2**. Additionally, the cisoidal P–Cr–Cl angles in **2** are all much closer to 90° than those in the tetraphos system. If eHTP were to adopt the usual symmetrical chelating mode, the distortions from octahedral geometry would be even greater than those seen for the tetraphos complex, particularly if the central Cr–P1 bond distance remained 0.1 Å longer. This would give rise to increased ring strain and to compressed, more acute P–Cr–P coordination angles about the Cr center. The eHTP ligand however can, and does, avoid much of this by adopting the observed configuration, which the tetraphos ligand naturally cannot duplicate.

The longer Cr–P1 bond distance in **2** probably results from steric effects coupled with the fact that all the phosphine groups are alkylated and, hence, are very good donor groups. These two effects can work to make the lengthening of the Cr–P1 bond energetically acceptable from a steric demand viewpoint.¹² Levason's CrCl₃(tetraphos) complex, on the other hand, has phenylated outer phosphine groups, which are not as basic and there is a significant difference between Cr–P bond distances for the internal alkylphosphine (2.399 (4) Å) and outer diphenylphosphines (2.466 (5) and 2.489 (6) Å). It seems likely that the chromium center in the tetraphos complex is less willing to sacrifice a stronger bonding interaction with only one basic alkylphosphine group on steric grounds than that in our system, where all the phosphines are quite basic. Steric factors in the mononuclear CrCl₃(tetraphos) complex will also work to favor a shorter central Cr–P bond distance, as this tends to minimize the L–Cr–L angular distortions. In **2**, however, the steric factors tend to work in the opposite direction with the multibridging nature of the eHTP conformation working to increase the central Cr–P1 bond length. Jones' *fac*-CrCl₃(tripod) complex, which does have electron-rich phosphorus atoms but rather different steric features than the *mer* complexes **2** or CrCl₃(tetraphos), has Cr–P bond lengths that are relatively uniform and are in the same range as our complex (2.45–2.46 Å).¹⁰

The electronic absorption spectrum of **2** is similar to those of other chromium(III) phosphine complexes. The simplest analogous complex, CrCl₃[P(CH₃)₃]₃, was prepared by Karsch¹³ as brown-violet crystals; although neither its detailed structure nor its spectrum was reported, its color is very similar to that of **2**. A more extensive series of chromium(III) phosphine complexes has been studied by Levason and co-workers. They concluded that an appropriate spectrochemical series for Cr(III) is N > P > Cl. Phosphines are ordinarily considered to be stronger field ligands than amines; however, the unusually weak interaction between the soft phosphorus and hard Cr³⁺ center, as evidenced by the long Cr–P bond distances observed both in our system and in Levason's crystal structures,^{6,14} would explain the observed ordering of N > P.

The first two spin-allowed d–d absorption bands, ν_1 (⁴A_{2g} → ⁴T_{2g}) and ν_2 (⁴A_{2g} → ⁴T_{1g}(F)) (assuming octahedral geometry), appear at 17 010 and 24 270 cm⁻¹ in Cr(dmpe)₃³⁺ (dmpe = Me₂PCH₂CH₂PMe₂)¹⁵ and at 13 180 and 18 700 cm⁻¹ in CrCl₆³⁻,¹⁶ respectively. Corresponding bands in **2** are expected at intermediate positions; we therefore assign the band at 14 500 cm⁻¹ to ν_1 and the pair of bands at 18 800 and 21 750 cm⁻¹ to ν_2 , split

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by the lower symmetry CrCl_3P_3 environment.¹⁷ The third spin-allowed d-d absorption band ν_3 (${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$) is probably obscured by the intense chloride-to-metal charge-transfer transitions, which begin above $25\,000\text{ cm}^{-1}$.

An interesting question that arises is why the Cr(III) center forces the phosphine/chloride ligand set into a *mer* coordination geometry. The M-P bond distances in the related mononuclear complex *fac*- $\text{Mo}(\text{CO})_3(\text{triphos})$ (triphos = $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$), for example, are at least as large as those seen for *mer,mer*- $\text{Cr}_2\text{Cl}_6(\text{eHTP})$, showing that a facial coordination geometry for **2** would be geometrically feasible.¹⁸ According to Levason, a Cr(III) center has a relatively strong electronic preference for meridional coordination with halide and phosphine ligands.⁶ Only when tripodal tris(phosphine) ligands were used (e.g., $\text{MeC}(\text{CH}_2\text{CH}_2\text{PR}_2)_3$), which are sterically forced to bind in a facial manner, were nonmeridional coordination geometries observed.^{6,9} Surprisingly, Levason found that facial coordination was the preferred geometry for arsine ligands. The root cause of these electronic factors is not understood, and this represents a good case for molecular orbital calculations to shed further light on the matter.

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Supplementary Material Available: Tables of hydrogen positional parameters, full bond distances and angles, and anisotropic thermal parameters and a figure of the IR spectrum for $\text{Cr}_2\text{Cl}_6(\text{eHTP})$ (8 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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CO_2 Rotational Isomerism in Bis(ethylene)(carbon dioxide)molybdenum Complexes: A Theoretical Study

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The organometallic chemistry of carbon dioxide has recently been the subject of numerous experimental studies, some emphasis being put on the synthesis of organic products of commercial interest.¹ In that respect the synthesis, by Carmona et al.,² of acrylic acid derivatives from the reaction of CO_2 with ethylene complexes of molybdenum and tungsten is especially attractive. The complex *trans*- $\text{M}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_4$ ($\text{M} = \text{Mo}, \text{W}$) reacts with CO_2 to yield the dinuclear system $[\text{M}(\text{H}_2\text{CCHCOOH})(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]_2$, whose X-ray crystal structure indicates coupling of the ethylene and CO_2 ligands in the putative $\text{M}(\text{C}_2\text{H}_4)_2(\text{CO}_2)(\text{PMe}_3)_3$ intermediate. The knowledge of the structure of this intermediate is a prerequisite for understanding

Table I. Relative Energies (kcal/mol) and Orbital Populations for Various Rotamers of the *trans,mer*- $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{CO}_2)(\text{PH}_3)_3$ System

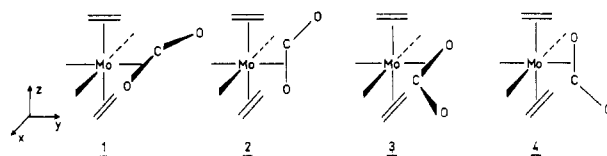
	1	2	3	4
rel energy	0	11.1	0	34.8
orbital pop.				
4s + 4d _e	1.38	1.29	1.38	1.25
4d _{xy}	1.02	1.86	1.02	1.86
4d _{xz}	1.51	1.50	1.51	1.45
4d _{yz}	1.56	0.84	1.56	1.04
net charge of Mo	+0.09	+0.10	+0.09	+0.13
net charge of CO_2	-0.51	-0.49	-0.51	-0.45

the coupling mechanism, which is presently unknown. From the X-ray crystal structures of the dinuclear product,² of the starting *trans*- $\text{M}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_4$ system,³ and of the *trans,mer*- $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{CO})(\text{PMe}_3)_3$ complex,³ one can reasonably infer that the phosphine ligands are in a meridional arrangement, leaving the two ethylene groups *trans* to each other (and staggered) and *cis* to the η^2 -coordinated CO_2 ligand. It is more difficult, however, to assess the rotational isomerism around the M-CO₂ bond, which is also important for delineating the productive channels of the coupling reaction.

We therefore undertook a theoretical analysis of this problem, and we report here the results of LCAO-MO-SCF ab initio calculations⁴ carried out on various conformers of the *trans,mer*- $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{CO}_2)(\text{PH}_3)_3$ model system. The relative stabilities of the rotamers are then analyzed in terms of molecular orbital interactions.

Results and Discussion

For the *trans,mer*- $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{CO}_2)(\text{PH}_3)_3$ system we consider four rotamers, which we denote **1-4** and which correspond to the



rotation of CO_2 around the axis going through the metal and the coordinated C-O bond.⁹ The corresponding relative energies of

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