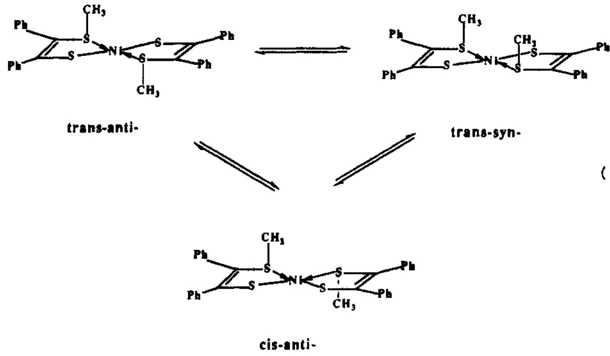
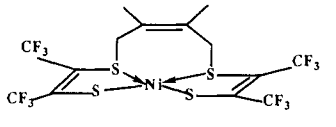
lengths of 2.380 (9) Å are longer than those in **1B**, and the C–S bond lengths of 1.792 (4) Å are normal for C–S single bonds. The S1–Ni–S2 bond angles are 83.87 and 96.13°, respectively, indicating a distorted square-planar structure.

Variable-Temperature ^{1}H NMR Measurements. In the ^{1}H NMR spectrum of **1B** in $CDCl_3$ at 50 °C, the signal of the methyl group protons appears as a single peak at 2.38 ppm. On cooling, the signal broadens, develops a shoulder, and at −50 °C splits into three signals at 2.28, 1.36, and 2.46 ppm with relative intensities of 7:1:11. This indicates the presence of dynamic equilibria involving three isomers. The two major signals at 2.28 and 2.48 ppm coalesce at 20 °C and are assigned to the syn- and anti-trans isomers of **1B**, which are interconvertible by sulfur inversion (eq 6).



(6)

The third signal at 2.36 ppm, which remains observable up to 30 °C, is assigned to the cis-anti isomer of **1C**, generated by a backbone isomerization process (see Figure 4 and eq 5). The cis-anti isomer could not be isolated in the solid state. Furthermore, no signal attributable to the presence of the cis-syn isomer was obtained. Its formation either by sulfur inversion or backbone isomerization is apparently sterically unfavorable. This could be due to the shortness of the Ni–S bonds. In **5**, two molecules of *cis*-1,2-bis(methylthio)stilbene are present in a cis-syn arrangement, but in this case the Ni–S bonds are longer by 0.22 Å. A cis-syn arrangement of two C–S bonds is also present in the cycloaddition product of $NiS_4C_4(CF_3)_4$ with 2,3-dimethylbutadiene (**7**).[8] In this complex, the two types of Ni–S bonds



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have the lengths of 2.156 (7) and 2.183 (8) Å. Here the steric obstruction is offset primarily by the formation of a macrocycle. As the conformational stabilities of individual isomers of organodithiolene complexes are evidently difficult to predict, further studies with series of analogous complexes of different metals, e.g. of Ni(II), Pd(II), and Pt(II), are now in progress and will be reported in a forthcoming paper.

Acknowledgment. This work was supported by Grant CHE-84-14567 of the National Science Foundation.

Supplementary Material Available: For complexes *anti*-**1B**, *anti*-**1B**·CH_2Cl_2, and **5**, tables of equivalent positions, scattering factors, least-squares parameters, positional parameters, torsion angles, least-squares planes, thermal parameters, bond distances and bond angles, and crystallographic details (33 pages); listings of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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Pentacoordinate Fe(CO)$_3$ Complexes of Diphosphine Ligands with Bite Angles Greater Than 120°

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Received November 21, 1989

The reaction of (benzylideneacetone)tricarbonyliron and *trans*-1,2-bis((diphenylphosphino)methyl)cyclopropane (**1**) in toluene produced [*trans*-1,2-bis((diphenylphosphino)methyl)cyclopropane]tricarbonyliron (**3**) in 24% yield. Crystals of **3** are orthorhombic with space group *Pcba*, $a = 16.359$ (5) Å, $b = 16.711$ (5) Å, $c = 21.057$ (6) Å, $V = 5757$ (3) Å^3, and $Z = 8$. The X-ray crystal structure of **3** reveals a trigonal-bipyramidal geometry about the iron atom with diequatorial chelation by diphosphine **1** (P–Fe–P = 123.9 (1)°). The reaction of (benzylideneacetone)tricarbonyliron with 2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl (**2**) formed [2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl]tricarbonyliron (**5**) in 7% yield. Crystals of **5**·CH_2Cl_2 are monoclinic with space group $P2_1/n$, $a = 12.863$ (3) Å, $b = 15.173$ (3) Å, $c = 18.753$ (4) Å, $\beta = 95.51$ (3)°, $V = 3643.1$ (13) Å^3, and $Z = 4$. The X-ray structure of **5** exhibits a distorted-square-pyramidal geometry with an apical carbonyl ligand. The P–Fe–P angle is 152.0 (1)°; the basal carbonyls form a OC–Fe–CO angle of 141.8 (4)°.

Introduction

We have recently become interested in the synthesis of transition-metal complexes of chelating diphosphines with large P–M–P bite angles of greater than 120°. Diphosphines with bite angles near 90° are very common and have been useful in studying metal complexes with phosphines locked into cis positions in octahedral and square-planar complexes. Venanzi, Shaw, and Takeuchi have developed unusual chelating diphosphines capable of spanning trans sites.[2] However, few chelating diphosphines with a preferred bite angle near 120° have been available for studying metal complexes with phosphines locked into diequatorial sites in trigonal bipyramids. Such 120° chelating diphosphines are particularly interesting in relation to intermediates in rho-

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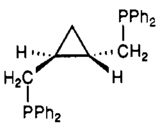
Table I. Selected Bond Lengths (Å) and Angles (deg) for [*trans*-1,2-Bis((diphenylphosphino)methyl)cyclopropane]$Fe(CO)_3$ (3)

	Bond Distances		
Fe–C(1)	1.764 (6)	Fe–C(2)	1.750 (6)
Fe–C(3)	1.774 (5)	Fe–P(1)	2.211 (1)
Fe–P(2)	2.220 (1)		
	Bond Angles		
P(1)–Fe–P(2)	123.9 (1)	P(1)–Fe–C(1)	86.5 (2)
P(1)–Fe–C(2)	117.9 (2)	P(1)–Fe–C(3)	87.6 (2)
P(2)–Fe–C(1)	87.2 (2)	P(2)–Fe–C(2)	118.1 (2)
P(2)–Fe–C(3)	89.9 (2)	C(1)–Fe–C(2)	94.5 (3)
C(1)–Fe–C(3)	170.4 (2)	C(2)–Fe–C(3)	94.9 (2)

dium-catalyzed hydroformylations.[3]

In trying to select diphosphine ligands with a preferred bite angle greater than 120°, we have employed molecular mechanics calculations to predict the "natural bite angle" of the chelate.[4] We have defined the natural bite angle (β_n) as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles. This definition is independent of electronic preference in the bite angle imposed by the metal center and is solely based on steric considerations. We have found the natural bite angle by minimizing the strain energy of the (diphosphine)M fragment with a zero force constant for P–M–P binding. The additional strain energy required to lock the system at arbitrary bite angles was also calculated, and potential energy diagrams were constructed to predict the flexibility of the chelate systems.

Two diphosphines that were calculated to have large natural bite angles were the cyclopropyldiphosphine **1** (t-BDCP)[5] (β_n = 110.9°) and **2**[6] (BISBI) (β_n = 128.6°). To test the utility of these bite angle calculations, we have synthesized and determined the X-ray crystal structures of iron tricarbonyl complexes of these two chelates.



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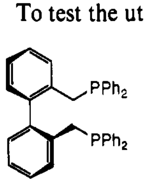

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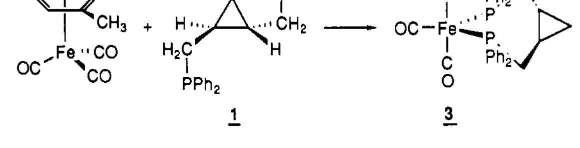
Results

Synthesis and Crystal Structure of a Diequatorial (Diphosphine)$Fe(CO)_3$ Complex. Molecular mechanics calculations on the iron cyclopropyldiphosphine fragment indicated a natural bite angle of 110.9° and a relatively flat potential well with excess strain energy of only 1.5 kcal for distortion to 120° (Figure 1).

Reaction of cyclopropyldiphosphine **1** with (benzylideneacetone)tricarbonyliron[7] in toluene at room temperature led to the isolation of [*trans*-1,2-bis((diphenylphosphino)methyl)cyclopropane]tricarbonyliron **3** as a yellow solid in 24% isolated yield.



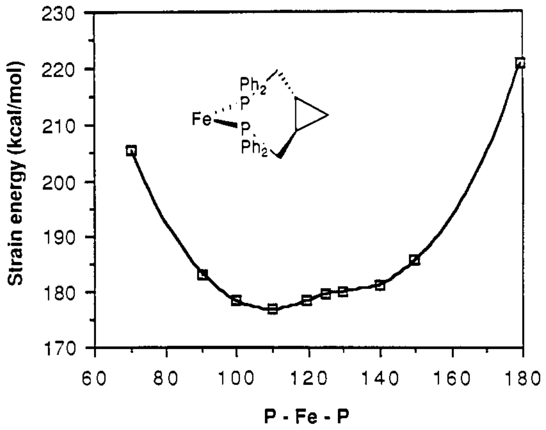


Figure 1. Potential energy diagram for Fe(t-BDCP).

Single crystals of compound **3** were grown from a methylene chloride–hexane solution. The X-ray crystal structure of **3** (Figure 2, Table I) reveals approximately trigonal-bipyramidal geometry at Fe with coordination of the diphosphine ligand at diequatorial sites. The P–Fe–P bite angle of 123.9 (1)° from X-ray analysis is larger than the calculated natural bite angle of 110.9°. However, only a small energy increase of 2.7 kcal was calculated for a bite angle of 124°. The P–Fe–P angle is slightly larger than the 120° equatorial angle of an ideal trigonal bipyramid. This distortion is accompanied by a bending of the axial carbonyls (C–Fe–C = 170.4 (2)°) toward the phosphine ligands. These slight distortions are toward a square-pyramidal geometry. Dunitz has pointed out that for PX_5 and MX_5 complexes opening of the equatorial angle of a trigonal bipyramid is associated with a closing of the axial angle.[8]

Complex **3** is the first structurally characterized $Fe(CO)_3$ complex in which a chelating ligand occupies diequatorial sites. Ligand **1** is apparently a selective chelating phosphine for coordination to diequatorial positions. Chelate **1** coordinates with a bite angle of near 120° in the presence of available coordination sites with P–Fe–P angles of 90 and 180°.

The NMR and IR spectra of **3** gave information about its structure in solution. In the $^{13}C\{^1H\}$ NMR spectrum of **3** even at −85 °C, only one ^{13}CO resonance was seen as a triplet (J_{PC} = 16 Hz) at δ 224.6. This is consistent with a rapid fluxional process that interchanges axial and equatorial carbonyl groups. A broadened doublet (J = 28 Hz) in the $^{13}C\{^1H\}$ NMR spectrum at δ 36.4 was assigned to the methylene carbons bound to phosphorus. If the phosphorus atoms were strongly coupled, this resonance would appear as a virtual triplet; computer simulation of the spectrum suggests that $J_{PP'}$ must be less than 10 Hz for a doublet to be seen. This small J_{PP} is consistent with a P–M–P angle of 123°, since large J_{PP} values are usually seen only for trans phosphines. Three carbonyl bonds were seen in the IR spectrum of **3** in toluene at 1987 (w), 1910 (m), and 1883 (s) cm^{-1}; this is consistent with the distorted-trigonal-bipyramidal geometry found by X-ray analysis.

We were interested in determining whether **1** was sufficiently flexible to span cis coordination sites in an octahedral complex. Reaction of **1** with *cis*-$(piperidine)_2Mo(CO)_4$[9] in CH_2Cl_2 resulted in formation of a material **4**, which was shown to be a mixture of oligomers with *cis*-$L_2Mo(CO)_4$ units. The infrared spectrum of the oligomeric mixture **4** exhibited carbonyl bands at 2015 (w), 1917 (s), 1890 (s), and 1844 (w) cm^{-1}, consistent with cis-disubstituted $Mo(CO)_4$ units. The only resonance seen in the $^{31}P\{^1H\}$ NMR spectrum was a singlet at δ 34.3, consistent with a single phosphorus environment. The average solution molecular weight of the oligomeric mixture **4** was found to be 9706 ± 900 by isopiestic determination in CH_2Cl_2, consistent with an oligomeric structure with an average formula of $[Mo(CO)_4(\mathbf{1})]_{15}$. The

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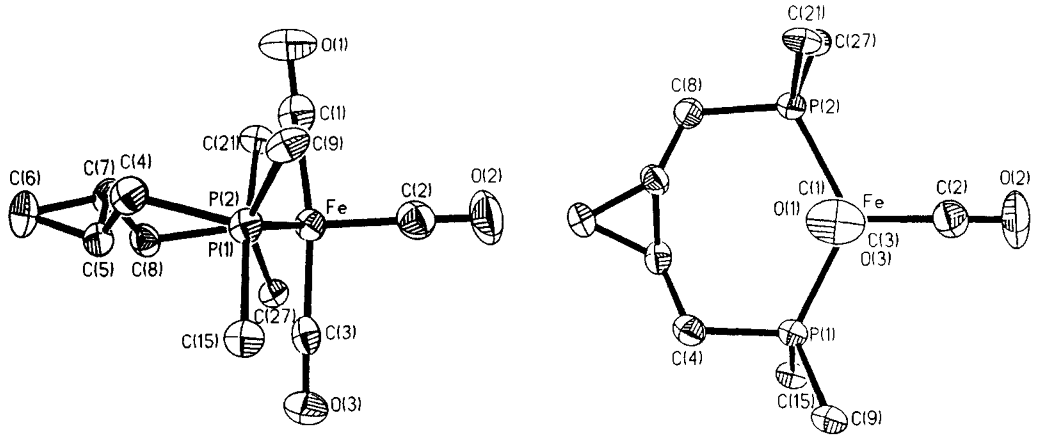


Figure 2. ORTEP diagrams of 3 emphasizing distortions from trigonal-bipyramidal geometry with 50% probability ellipsoids. Phenyl rings have been omitted for clarity.

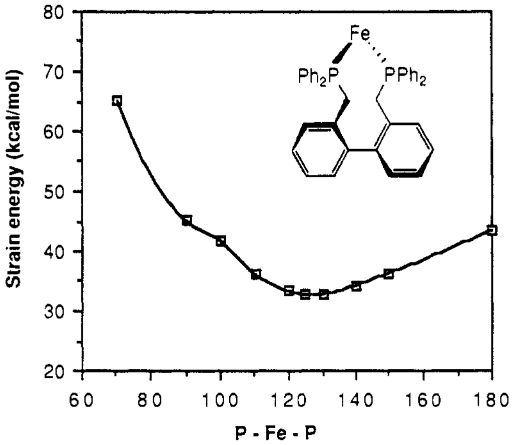


Figure 3. Potential energy diagram for Fe(BISBI).

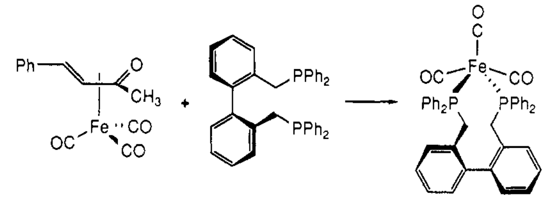
Table II. Selected Bond Lengths (Å) and Angles (deg) for [2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl]Fe(CO)$_3$ (**5**)

	Bond Distances		
Fe–C(39)	1.781 (9)	Fe–C(40)	1.789 (8)
Fe–C(41)	1.769 (8)	Fe–P(1)	2.195 (2)
Fe–P(2)	2.192 (2)		
	Bond Angles		
P(1)–Fe–P(2)	152.0 (1)	P(1)–Fe–C(39)	104.1 (2)
P(1)–Fe–C(40)	90.0 (2)	P(1)–Fe–C(41)	83.3 (2)
P(2)–Fe–C(39)	103.8 (2)	P(2)–Fe–C(40)	82.2 (2)
P(2)–Fe–C(41)	86.3 (2)	C(39)–Fe–C(40)	109.4 (3)
C(39)–Fe–C(41)	108.7 (3)	C(40)–Fe–C(41)	141.8 (4)

material **4** is therefore formulated as a mixture of oligomers in which ligand **1** bridges cis positions of Mo(CO)$_4$ units. The absence of ^{31}P NMR resonances upfield from H_3PO_4 in the region typical of uncoordinated tertiary phosphine ligands suggests a cyclic structure for the oligomers.

Synthesis and Crystal Structure of a Square-Pyramidal (Diphosphine)Fe(CO)$_3$ Complex. The ligand 2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl (**2**, BISBI) has been reported by Eastman Kodak to give very high selectivity in rhodium-catalyzed propene hydroformylation at moderate temperatures and pressures.[6] Hydroformylation of propene in the presence of BISBI at 125 °C resulted in a normal:iso ratio of product butyraldehydes of 25:1. The Fe(CO)$_3$ adduct of BISBI was calculated to have a natural bite angle of 128.6° and a relatively flat potential energy surface (Figure 3).

The reaction of BISBI with (benzylideneacetone)tricarbonyliron in toluene produced (BISBI)Fe(CO)$_3$ (**5**) as a yellow, crystalline solid in 7% yield.



2 5

The molecular structure of **5** was determined by X-ray crystallographic analysis (Figure 4, Table II). **5** is best described as a square pyramid with a carbonyl ligand in the apical position. The chelating diphosphine spans trans positions in the base of the

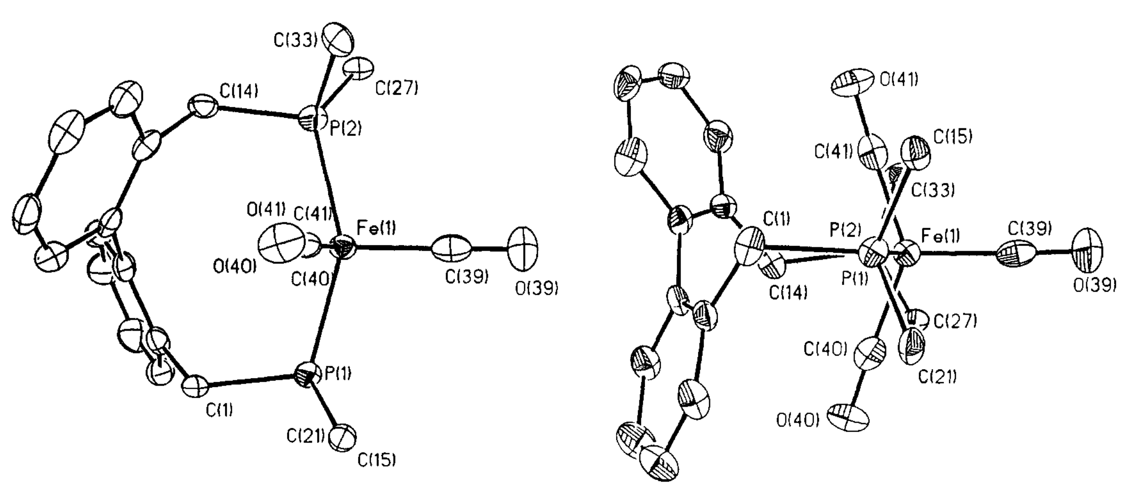


Figure 4. ORTEP diagrams of **5** emphasizing distortions from trigonal-bipyramidal geometry with 50% probability ellipsoids. Phenyl rings have been omitted for clarity.

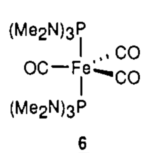
square pyramid, and two carbonyl groups occupy another set of trans positions in the base. The P–Fe–P bite angle of the coordinated BISBI ligand is 152.0 (1)°, which is substantially larger than the calculated natural bite angle of 128.6°. However, the potential energy surface for **5** is broad and the calculated excess strain energy for a P–Fe–P bite angle of 152° is only 3.5 kcal above the minimum. The two basal CO ligands have a C–Fe–C bond angle of 141.8 (4)°. The iron atom sits 0.555 (8) Å above the mean plane defined by the atoms bound in basal positions. The difference between the P–Fe–P and C–Fe–C basal angles indicates a distortion from ideal square-pyramidal geometry. Indeed, **5** can also be viewed as a severely distorted trigonal bipyramid in which equatorial phosphorus atoms bend away from one another to 152° and axial carbonyls bend toward the phosphines. Thinking of **5** as a severely distorted trigonal bipyramid allows comparison with the slightly distorted trigonal-bipyramidal structure of **3**.

Complex **5** is the first square-pyramidal (disphosphine)Fe(CO)$_3$ complex in which the phosphorus atoms occupy trans positions in the base. The bite angle of **2** in this complex is unusually large.

The $^{13}C\{^1H\}$ NMR spectrum of **5** even at −80 °C had only a single ^{13}CO triplet (J_{PC} = 29 Hz) at δ 215.1. The equivalence of the carbonyls is consistent with a rapid fluxional process that interchanges apical and basal CO ligands. The methylene carbons bonded to phosphorus gave rise to a four-line AA′XX′ multiplet at δ 35.3 (J_{PC} = 28 Hz, $J_{PP'}$ = 100 Hz). The large $J_{PP'}$ is consistent with the large P–Fe–P angle of 152° seen by X-ray analysis. The carbonyl region of the infrared spectrum of **5** has a weak band at 1970 cm^{-1} and a lower energy, broad asymmetric band at 1882 cm^{-1}, which is probably due to two overlapping carbonyl bands.

Discussion

We have synthesized and structurally characterized two (diphosphine)Fe(CO)$_3$ complexes with large chelate bite angles. Complex **3** contains a trigonal-bipyramidal iron center, which is chelated by diphosphine **1** in an unusual diequatorial manner. The crystal structures of [(Me$_2$N)$_3$P]$_2$Fe(CO)$_3$[10] (**6**) and [P(OCH$_2$)$_3$P]$_2$Fe(CO)$_3$[11] (**7**) indicate that (R$_3$P)$_2$Fe(CO)$_3$ complexes of monodentate phosphines prefer to adopt trigonal-bipyramidal structures in whcih the phosphine ligands occupy trans axial positions. The constraints of a chelating ligand can impose other geometries, as seen in (DIPHOS)Fe(CO)$_3$[12] (**9**) and (DPPM)-Fe(CO)$_3$[13] (**8**), which adopt distorted geometries intermediate between trigonal bipyramidal and square pyramidal due to the small bite angles of these chelates.



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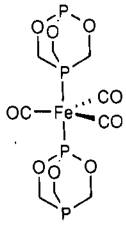

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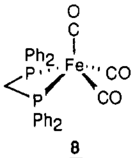

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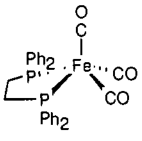

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The crystal structure of **5** reveals a distorted-square-pyramidal geometry due to the 152.1 (2)° P–Fe–P bite angle of the BISBI chelate. Complex **5** has the largest P–Fe–P bite angle reported for a (diphosphine)Fe(CO)$_3$ complex. The observed P–Fe–P angle of 152.0 (2)° is larger than the natural bite angle of 128.6° calculated by molecular mechanics. The potential energy diagram for BISBI predicts that these bite angles differ in energy by only 3.5 kcal/mol, and therefore the BISBI ligand is somewhat flexible.

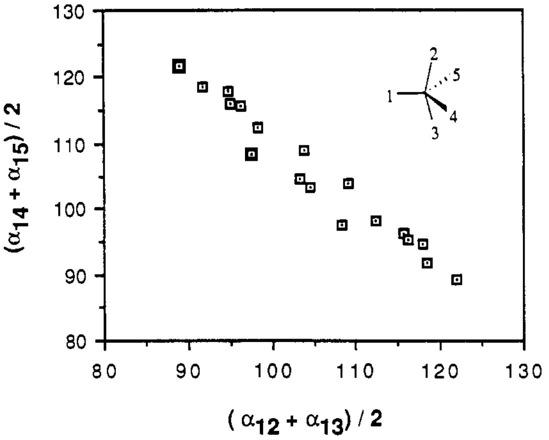

Figure 5. Distribution of $(\alpha_{12} + \alpha_{13})/2$ vs $(\alpha_{14} + \alpha_{15})/2$ angles for Fe(CO)$_3$ complexes of chelating diphosphines.

Table III. Crystallographic Data for [*trans*-1,2-Bis((diphenylphosphino)methyl)cyclopropane]Fe(CO)$_3$ (**3**) and [2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl]Fe(CO)$_3$·CH$_2$Cl$_2$ (**5**)

	3	**5**
chem formula	$C_{32}H_{28}O_3P_2Fe$	$C_{42}H_{34}O_3P_2Cl_2Fe$
fw	578.3	775.4
a, Å	16.539 (5)	12.863 (3)
b, Å	16.711 (5)	15.173 (3)
c, Å	21.057 (6)	18.753 (4)
β, deg		95.51 (3)
V, Å^3	5757 (3)	3643
Z	8	4
space group	*Pbca*	$P2_1/n$
T, °C	−150	−100
λ, Å	0.71072	0.71072
ρ_{calcd}, g·cm^{-3}	1.335	1.414
μ, cm^{-1}	6.61	6.85
transm coeff		0.7315–0.7378
$R(F_o)$	0.039	0.057
$R_w(F_o)$	0.040	0.043

In trigonal-bipyramidal compounds, an opening of the equatorial angle occurs in conjunction with closing of the axial angle, resulting in formation of an isomeric square-pyramidal compound. Continuation of the bending motion results in an isomerized trigonal bipyramid in which the axial ligands and two of the equatorial ligands exchange positions. The structure-correlation method has been applied to isomerization of pentacoordinate complexes and suggests that the Berry pseudorotation[14] is a low-energy coordinate for ligand exchange.[8]

Figure 5 shows a compilation of seven (R$_3$P)$_2$Fe(CO)$_3$ complexes from the Cambridge Structural Database (version 1989) along with data from complexes **3** and **5**. A range of structures from nearly ideal trigonal-bipyramidal to square-pyramidal geometries is included. Opening of the equatorial angle results in a decrease of the axial angle until a square-pyramidal structure is obtained. Compounds near the center of Figure 5 are therefore more accurately described as distorted square pyramids, and complexes near the end of the plot have close to ideal trigonal-bipyramidal geometry. Two structures in Figure 5 are very nearly square pyramidal. The Fe(CO)$_3$ complexes of 1,1-bis(diphenylphosphino)ethene[15] (**10**) and of BISBI both have nearly equivalent equatorial and axial angles, as expected for square-

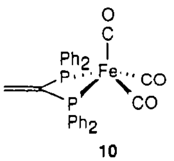

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Table IV. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^4$) for **3**

	x	*y*	*z*	*U*(eq)[a]
Fe	−78 (1)	1470 (1)	1202 (1)	25 (1)
C(1)	903 (4)	1250 (3)	901 (3)	37 (2)
O(1)	1544 (2)	1096 (2)	709 (2)	56 (2)
C(2)	−596 (3)	927 (3)	616 (3)	41 (2)
O(2)	−943 (3)	565 (3)	237 (2)	69 (2)
C(3)	−976 (3)	1755 (3)	1617 (2)	28 (2)
O(3)	−1569 (2)	1925 (2)	1882 (2)	42 (1)
C(4)	1109 (3)	1340 (3)	2527 (2)	31 (2)
C(5)	922 (3)	2218 (3)	2530 (2)	29 (2)
C(6)	1526 (3)	2868 (3)	2690 (2)	39 (2)
C(7)	1251 (3)	2751 (3)	2020 (2)	29 (2)
C(8)	663 (3)	3288 (3)	1681 (2)	30 (2)
P(1)	304 (1)	828 (1)	2071 (1)	26 (1)
C(9)	723 (3)	−182 (3)	1993 (2)	29 (2)
C(10)	1054 (3)	−567 (3)	2516 (3)	36 (2)
C(11)	1361 (3)	−1325 (3)	2472 (3)	44 (2)
C(12)	1346 (4)	−1724 (3)	1909 (3)	53 (2)
C(13)	1017 (4)	−1360 (3)	1380 (3)	60 (3)
C(14)	709 (3)	−589 (3)	1421 (3)	47 (2)
C(15)	−498 (3)	655 (3)	2661 (2)	30 (2)
C(16)	−1165 (3)	204 (3)	2483 (3)	43 (2)
C(17)	−1798 (3)	68 (4)	2909 (4)	63 (3)
C(18)	−1176 (5)	386 (4)	3505 (4)	72 (3)
C(19)	−1119 (5)	834 (4)	3676 (3)	66 (3)
C(20)	−477 (3)	971 (3)	3270 (3)	46 (2)
P(2)	197 (1)	2749 (1)	1014 (1)	27 (1)
C(21)	907 (3)	2927 (3)	364 (2)	30 (2)
C(22)	669 (4)	2670 (4)	−235 (3)	50 (2)
C(23)	1154 (5)	2792 (4)	−754 (3)	70 (3)
C(24)	1892 (5)	3159 (5)	−690 (3)	77 (3)
C(25)	2151 (4)	3404 (4)	−103 (3)	61 (3)
C(26)	1666 (3)	3288 (3)	426 (3)	44 (2)
C(27)	−625 (3)	3425 (3)	773 (2)	28 (2)
C(28)	−487 (3)	4248 (3)	739 (3)	37 (2)
C(29)	−1097 (4)	4759 (4)	554 (3)	49 (2)
C(30)	−1852 (4)	4470 (4)	398 (3)	50 (2)
C(31)	−1989 (3)	3671 (4)	413 (3)	49 (2)
C(32)	−1384 (3)	3148 (3)	599 (3)	41 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **5**

	x	*y*	*z*	*U*(eq)[a]	occ
Fe(1)	2498 (1)	2555 (1)	861 (1)	196 (3)	
P(1)	872 (1)	2098 (1)	716 (1)	208 (6)	
P(2)	4181 (1)	2344 (1)	843 (1)	210 (6)	
C(1)	796 (4)	929 (4)	437 (4)	238 (24)	
C(2)	1455 (4)	326 (4)	931 (3)	212 (24)	
C(3)	1062 (5)	36 (4)	1548 (4)	296 (26)	
C(4)	1637 (5)	−481 (5)	2048 (4)	392 (29)	
C(5)	2639 (5)	−724 (5)	1920 (4)	406 (30)	
C(6)	3036 (5)	−463 (5)	1301 (4)	290 (26)	
C(7)	2468 (5)	62 (4)	797 (4)	223 (23)	
C(8)	2940 (4)	272 (4)	123 (4)	221 (23)	
C(9)	2457 (5)	−65 (5)	−521 (4)	315 (27)	
C(10)	2868 (5)	68 (5)	−1163 (4)	318 (27)	
C(11)	3756 (5)	561 (5)	−1186 (4)	299 (27)	
C(12)	4243 (5)	890 (5)	−561 (4)	303 (27)	
C(13)	3866 (4)	765 (4)	96 (4)	211 (23)	
C(14)	4461 (4)	1157 (4)	749 (4)	234 (24)	
C(15)	45 (4)	2648 (5)	5 (4)	206 (23)	
C(16)	−408 (4)	2233 (5)	−604 (4)	302 (26)	
C(17)	−986 (5)	2705 (5)	−1133 (4)	342 (29)	
C(18)	−1123 (4)	3585 (5)	−1069 (4)	321 (29)	
C(19)	−684 (5)	3998 (5)	−456 (4)	359 (29)	
C(20)	−100 (5)	3544 (5)	64 (4)	299 (27)	
C(21)	38 (4)	2166 (4)	1456 (4)	231 (24)	
C(22)	458 (5)	2366 (5)	2142 (4)	319 (26)	
C(23)	−176 (5)	2399 (6)	2703 (4)	397 (28)	
C(24)	−1233 (5)	2241 (5)	2574 (5)	466 (33)	
C(25)	−1659 (5)	2064 (5)	1889 (5)	436 (32)	
C(26)	−1030 (4)	2022 (5)	1336 (4)	318 (26)	
C(27)	5002 (4)	2668 (5)	1647 (4)	217 (23)	
C(28)	5355 (5)	2091 (5)	2193 (4)	301 (26)	
C(29)	5947 (4)	2400 (6)	2801 (4)	348 (29)	
C(30)	6193 (5)	3281 (6)	2864 (4)	372 (30)	
C(31)	5846 (5)	3852 (5)	2335 (4)	342 (28)	
C(32)	5255 (4)	3550 (5)	1730 (4)	295 (27)	
C(33)	4895 (5)	2884 (5)	182 (4)	246 (25)	
C(34)	4483 (5)	3579 (5)	−213 (4)	339 (28)	
C(35)	5073 (6)	4043 (6)	−665 (4)	486 (33)	
C(36)	6096 (6)	3806 (6)	−721 (5)	545 (37)	
C(37)	6519 (5)	3115 (6)	−338 (5)	493 (34)	
C(38)	5937 (5)	2659 (6)	116 (4)	398 (28)	
C(39)	2397 (4)	3690 (6)	1084 (4)	283 (28)	
O(39)	2333 (4)	4432 (4)	1202 (3)	466 (22)	
C(40)	2710 (4)	1920 (5)	1666 (4)	266 (27)	
O(40)	2886 (3)	1542 (3)	2193 (3)	344 (19)	
C(41)	2416 (4)	2453 (5)	−82 (4)	250 (24)	
O(41)	2365 (3)	2415 (4)	−701 (3)	365 (18)	
Cl(1)	9741 (4)	4724 (4)	1954 (3)	492 (14)	0.55
Cl(2)	9452 (6)	4624 (5)	1849 (4)	739 (26)	0.45
Cl(3)	7574 (8)	5331 (7)	1328 (7)	550 (24)	0.35
Cl(4)	7867 (10)	5285 (10)	1070 (9)	769 (42)	0.25
Cl(5)	7630 (10)	5374 (10)	1652 (8)	836 (51)	0.25
Cl(6)	7438 (18)	5025 (15)	990 (15)	849 (74)	0.15
C(42)	8384 (7)	4380 (7)	1528 (6)	823 (32)	1.00

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

pyramidal geometry. That a range of structures in the $(PR_3)_2Fe(CO)_3$ series exists along the trigonal-bipyramid–square-pyramid coordinate suggests that this coordinate is of low energy.

Compounds **3** and **5** show fluxional behavior by ^{13}C NMR spectroscopy at temperatures as low at −80 °C. A Berry pseudorotation with a phosphorus atom as the pivot is presumably responsible for the interchange of carbonyl ligands. These diphosphines can apparently span the apical and basal sites of square pyramids. The bond angles for such a geometry are typically in the range of 100 ± 10°.

Conclusion

We have synthesized $Fe(CO)_3$ complexes of two chelating ligands with unusually wide bite angles. The cyclopropyldiphosphine **1** forms a diequatorial $Fe(CO)_3$ complex **3** with a P–Fe–P bite angle of 123.9 (1)°. The BISBI ligand forms a square-pyramidal $Fe(CO)_3$ complex **5** with the largest reported P–Fe–P bite angle of 152.0 (1)°. The complexes lie along the Berry pseudorotation coordinate for interconversion of two trigonal bipyramids via a square pyramid.

Experimental Section

General Procedures. ^1H NMR spectra were measured on a Bruker AM500 spectrometer. $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM500 spectrometer operating at 125.76 MHz. $^{31}P\{^1H\}$ NMR spectra were obtained on an AM500 instrument (202.46 MHz) and were referenced to external H_3PO_4. Infrared spectra were measured on a Mattson Polaris (FT) spectrometer. Mass spectra were determined on a Kratos MS-80. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN). Molecular mechanics calculations were performed on a Evans & Sutherland PS300 graphics terminal as described elsewhere.[4]

Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard high-vacuum and Schlenk techniques. Toluene and hexane were distilled prior to use from purple solutions of sodium and benzophenone. CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2.

[*trans*-1,2-Bis((diphenylphosphino)methyl)cyclopropane]tricarbonyliron (3). A solution of (benzylideneacetone)tricarbonyliron[7] (0.31 g, 1.1 mmol) and *trans*-1,2-bis((diphenylphosphino)methyl)cyclopropane[5] (715 mg, 1.63 mmol) in 20 mL of toluene was stirred under nitrogen for 4 h. Solvent was evaporated under vacuum. The resulting dark orange solid was purified by chromatography (silica gel, toluene) and recrystallized from CH_2Cl_2–hexane to give **3** (152 mg, 24%) as a yellow powder. Crystals suitable for X-ray diffraction were grown by diffusion of hexanes into a dichloromethane solution of **3** at room temperature: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 57.6 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ 224.5 (t, J_{PC} = 16 Hz, CO), 139.6 (virtual t, peak separation 18 Hz, ipso), 132.9, 132.4, 130.1, 129.8, 128.2, 36.4 (d, J_{PC} = 28 Hz, CH_2P), 20.4 (s, CH), 14.4 (s, CH_2); IR (toluene) 1987 (w), 1910 (m), 1883 (s) cm^{-1}.

Reaction of *trans*-1,2-Bis((diphenylphosphino)methyl)cyclopropane with *cis*-(Piperidine)$_2$Mo(CO)$_4$. A solution of **1** (0.31 g, 0.71 mmol) and *cis*-(piperidine)$_2$Mo(CO)$_4$[9] (0.25 g, 0.66 mmol) in 20 mL of CH_2Cl_2 was stirred for 1.5 h. Solvent was evaporated under vacuum. The resulting oil was dissolved in 10 mL of Et_2O, and the mixture was filtered. Solvent was evaporated under vacuum to yield the oligomeric mixture **4** (366 mg) as a light yellow solid: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 34.3 (s); IR (CH_2Cl_2) 2015 (m), 1917 (sh), 1890 (s), 1844 (m) cm^{-1}.

The average molecular weight of the oligomeric mixture **4** was determined by the isopiestic method using a Signer-type apparatus.[16] **4** (0.0231 g) was placed in one leg of the apparatus. (DIPHOS)Mo(CO)$_4$[17] (0.0282 g, 0.0465 mmol) was added to the reference leg. CH_2Cl_2 was distilled into the apparatus, which was sealed under vacuum. Solvent levels equilibrated after 5 days at 25 °C, indicating the mole fractions of each solution were equivalent. The molecular weight of **4** was calculated to be 9706 ± 900.

(BISBI)Fe(CO)$_3$–CH$_2$Cl$_2$ (5). (Benzylideneacetone)tricarbonyliron (677 mg, 2.37 mmol) and 2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl, BISBI[6] (1.304 g, 2.37 mmol), were stirred in 30 mL of toluene for 18 h. The solution was evaporated under vacuum, and the residue was chromatographed (silica gel, toluene) to give **5** (108 mg, 7%) as a yellow powder. X-ray-quality crystals were grown by diffusion of hexanes into a dichloromethane solution of **5**. Elemental analysis and X-ray crystallography indicated that **5** crystallized with one CH_2Cl_2 molecule of crystallization: ^1H NMR (CD_2Cl_2) δ 7.9–6.8 (m, 28 H), 4.28 (m, 4 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 215.1 (t, J_{PC} = 29 Hz, CO), 143.6 (1,1′ C), 141.0 (virtual t, peak separation 20 Hz, ipso C_6H_5), 134.5 (virtual t, peak separation 18 Hz, 2,2′ C), 134.2 (para C_6H_5), 132.0 (3,3′ C), 131.7 (4,4′ C), 130.8 (ortho C_6H_5), 128.6 (meta C_6H_5), 127.2 and 127.0 (6,6′ C and 5,5′ C), 35.3, (4-line AA′XX′, J_{PC} = 28, $J_{PP'}$ = 100 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 72.6 (s); IR (CH_2Cl_2) 1970 (w), 1881 (s) cm^{-1}; HRMS calcd for M − 2CO ($C_{39}H_{32}P_2OFe$) 634.1277, found 634.1295. Anal. Calcd for $C_{42}H_{34}O_3Cl_2P_2Fe$: C, 65.56; H, 4.45; P, 8.97. Found: C, 65.63; H, 4.05; P. 8.55.

X-ray Crystallography. Diffraction data for both **3** and **5** were collected on a Nicolet P3f diffractometer. The 4371 measured data for **3** yielded 2304 independent, observed ($R > 6\sigma(F)$) data. A total of 6048 data were measured for **5**, producing 2847 independent, observed ($F > 4\sigma(F)$) data. Both structures were solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL PLUS[18] software package. Details of the crystal data, experimental conditions, and a summary of refinement details are given in Table III and in the supplementary material. Atomic coordinates and isotropic displacement parameters for **3** and **5** are presented in Tables IV and V.

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Supplementary Material Available: A full table of crystallographic data, figures with complete numbering schemes, and tables of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters (14 pages); observed and calculated structure factor amplitudes for **3** and **5** (30 pages). Ordering information is given on any current masthead page.

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Solid-State ^{95}Mo NMR Study of (Aryldiazenido)- and (Organohydrazido)polyoxomolybdates. Investigation of Model Compounds of Catalytic Molybdenum Environments

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The ^{95}Mo static powder and magic angle spinning NMR spectra of the central $\pm^1/_2$ transition of a number of (aryldiazenido)polyoxomolybdates, (organohydrazido)polyoxomolybdates, and unsubstituted polyoxomolybdates were obtained. The spectra clearly demonstrated the existence of octahedral and tetrahedral sites within these compounds by the contrast between the respective line widths and the dependence under MAS conditions of the resonances from these sites. Variation of ligand coordination was also seen to yield a visible chemical shift to the octahedral molybdenum sites in selected complexes. An interactive graphics curve-fitting program was used to estimate the quadrupolar coupling constants, asymmetry parameters of the electric field gradients, the three principal elements of the shielding tensor, and the Euler angles relating the quadrupole and chemical shielding principal axis systems for the molybdenum sites from the static powder spectra. Assignments of the line shape components was made to the different molybdenum sites present in these species. The method of assignment, based on degree of distortion at the site, was vindicated by MO calculations carried out on a simple $[MoO_6]^{6-}$ model species. These MO calculations demonstrate the increase in the magnitude of the electric field gradient (and hence the value of A_{∞}) was one distorts the octahedral environment by a combination of bond length and angular variations. The effectiveness of the ^{95}Mo NMR technique to obtain these data from Mo(VI) compounds was thus demonstrated and has laid a foundation from which future solid-state ^{95}Mo NMR studies of biological and catalytic molybdenum systems can benefit by comparison of the results obtained with those obtained for these model compounds.

Introduction

The use of liquid-state ^{95}Mo NMR spectroscopy has developed into a very active area of research in the past 7 years and has been the subject of review by Minelli et al.[1] This rapid development is due to the importance of molybdenum in organometallic and inorganic chemistry[2] as well as bioinorganic chemistry.[3-8] Liquid-state ^{95}Mo NMR spectroscopy has been applied to studies of molybdates in impregnation solutions of catalysts[9,10] as well as to characterizing many Mo(VI) and Mo(IV) species that are believed to model the active sites of molybdenum enzymes such as xanthine oxidase, xanthine dehydrogenase, sulfite oxidase,

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