

($\eta^5\text{-C}_5\text{H}_5$)₂Nb(CO)($\mu\text{-H}$)Fe₃(CO)₁₁ (**4b**): 30% yield (not analyzed).

Reaction of ($\eta^5\text{-C}_5\text{H}_4\text{CMe}_3$)₂M(CO)H (M = Ta, Nb) with Fe₃(CO)₁₂. The reaction was conducted as described above. After the mixture was stirred for 4 h, the infrared spectrum of the toluene mixture showed complete conversion of **2'a** (or **2'b**). The solvent was then removed, and the crude material was chromatographed on silica gel at low temperature (-30 °C) with toluene as eluant. Complex **4'a** (or **4'b**) eluted first and was obtained as a red solid in ca. 30% yield by removal of the solvent. Recrystallization from toluene-heptane provided pure samples.

($\eta^5\text{-C}_5\text{H}_4\text{CMe}_3$)₂Ta(CO)($\mu\text{-H}$)Fe₃(CO)₁₁ (**4'a**): dark red crystals; mp 105-107 °C; mass fragments, successive loss of CO from *m/e* 704 (M - 8CO, 2), 536 (M - 2Fe - 10CO, 20), 423 (Cp'₂Ta, 85), 422 (Cp'₂Ta-H, 100). Anal. Calcd for C₃₀H₂₇O₁₂Fe₃Ta: C, 38.82; H, 2.93; Fe, 18.05. Found: C, 39.41; H, 3.05; Fe, 17.78.

($\eta^5\text{-C}_5\text{H}_4\text{CMe}_3$)₂Nb(CO)($\mu\text{-H}$)Fe₃(CO)₁₁ (**4'b**): dark red crystals; mp 120 °C; mass fragments, successive loss of CO from *m/e* 812 (M - CO, 3) and from 797 (812 - CH₃, 3), 363 (Cp'₂NbCO, 30), 335 (Cp'₂Nb, 63), 334 (Cp'₂Nb - H, 78). Anal. Calcd for C₃₀H₂₇O₁₂Fe₃Nb: C, 42.89; H, 3.24; Fe, 19.95. Found: C, 43.50; H, 3.51; Fe, 19.4.

Reaction of ($\eta^5\text{-C}_5\text{H}_4\text{CMe}_3$)₂MH₃ (M = Ta, Nb) with an excess of Fe₂(CO)₉. Fe₂(CO)₉ (3 mmol) was added to a stirred solution of ($\eta^5\text{-C}_5\text{H}_4\text{CMe}_3$)₂MH₃ (1 mmol) in toluene (50 mL). After 10 h, the reaction mixture was evaporated to leave a dark brown solid. Chromatography on silica gel (at -30 °C) with toluene as eluant followed. The first material to elute was [$\eta^5\text{-C}_5\text{H}_4\text{CMe}_3$]

C₅H₄CMe₃Fe(CO)₂]₂ identified by comparison of its spectroscopic data with an authentic sample synthesized from C₅H₅CMe₃ and Fe(CO)₅. Recrystallization from toluene and heptane provided a pure sample. [($\eta^5\text{-C}_5\text{H}_4\text{CMe}_3$)Fe(CO)₂]₂: air-stable dark violet crystals; mp 162 °C; NMR (C₆D₆) δ 4.51 (t, 2 H), 3.87 (t, 2 H), 1.24 (s, 9 H); IR (toluene) 1990, 1944, 1777 cm⁻¹; mass fragments, *m/e* 466 (M, 35), 438 (M - CO, 18), 410 (M - 2CO, 23), 382 (M - 3CO, 38), 354 (M - 4CO, 8), 338 (M - 4CO - CH₃, 91), 205 (Cp'Fe(CO), 86), 177 (Cp'Fe, 100). Anal. Calcd for C₂₂H₂₆FeO₄: C, 56.58; H, 5.62; Fe, 23.96. Found: C, 56.75; H, 5.66; Fe, 24.59. This first fraction was followed by the previously described complex **4'a** (or **4'b**).

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Registry No. **1a**, 12117-02-1; **1'a**, 84749-48-4; **1b**, 11105-67-2; **1'b**, 84749-49-5; **2a**, 11105-69-4; **2'a**, 84749-50-8; **2b**, 11105-68-3; **2'b**, 84749-51-9; **3a**, 95765-90-5; **3'a**, 95765-91-6; **3b**, 67108-78-5; **3'b**, 95765-92-7; **4a**, 95765-93-8; **4'a**, 95765-94-9; **4b**, 95784-29-5; **4'b**, 95765-95-0; [Cp₂Ta(CO)(THF)]Fe₃(CO)₁₀($\mu\text{-H}$)($\mu\text{-CO}$), 95765-98-3; [Cp₂Nb(CO)(THF)]Fe₃(CO)₁₀($\mu\text{-H}$)($\mu\text{-CO}$), 95765-99-4; [Cp'₂Ta(CO)(THF)]Fe₃(CO)₁₀($\mu\text{-H}$)($\mu\text{-CO}$), 95766-01-1; [Cp'₂Nb(CO)(THF)]Fe₃(CO)₁₀($\mu\text{-H}$)($\mu\text{-CO}$), 95766-03-3; [Cp'Fe(CO)₂]₂, 95765-96-1; Fe₂(CO)₉, 15321-51-4; Fe₃(CO)₁₂, 17685-52-8; Fe(CO)₅, 13463-40-6; [Fe₃(CO)₁₀($\mu\text{-H}$)($\mu\text{-CO}$)], 55188-22-2; [HFe(CO)₄]⁻, 18716-80-8; C₅H₅CMe₃, 35059-40-6.

Solid-State Conformations of Compounds (Arene)L₂MP(C₆H₅)₃ and (Arene)LL'MP(C₆H₅)₃

Henri Brunner* and Benedikt Hammer

Institut für Anorganische Chemie der Universität Regensburg, D-8400 Regensburg, Germany

Carl Krüger and Klaus Angermund

Max-Planck-Institut für Kohlenforschung, Postfach 011325, D-4330 Mülheim a.d. Ruhr, Germany

Ivan Bernal

Department of Chemistry, University of Houston, Houston, Texas 77004

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The solid-state structure of the ethane-type molecule Cp(CO)₂MnP(C₆H₅)₃ reveals a deviation from the staggered conformation, which can be described by an average torsion angle of 37.7° about the Mn-P bond. This deviation is caused by the propeller structure of the triphenylphosphine ligand. It brings the gauche phenyl, face exposed to Cp, closer to the Cp ring and the gauche phenyl, edge exposed to Cp, further away from the Cp ring. Additional adjustments of the phenyl rings by rotation of the P-C_{ipso} bonds further diminish the nonbonding interactions of the Cp ring with the neighboring phenyl ortho C-H bonds. Analyses of the structures of another 11 compounds of the type (arene)L₂MP(C₆H₅)₃ and 17 compounds of the type (arene)LL'MP(C₆H₅)₃, found by a search in the Cambridge Structural Database, demonstrate that their solid-state conformations are primarily determined by similar intramolecular effects and only insignificantly influenced by crystal packing forces.

Introduction

In the Rh-catalyzed enantioselective hydrogenation of olefins, using chelating bis(phosphines) of the type diop, prophos, chiraphos, BPPFA, BPPM, and norphos, the two phenyl rings at the P atoms are differentiated with respect to axial/equatorial arrangement and face/edge exposure.¹⁻⁶

This differentiation, caused by the puckering of the chelate ring, is thought to be the primary mechanism for chirality transfer from the asymmetric centers in the chelate backbone to the Rh coordination sites, active in the enantioselective catalysis.⁴⁻⁶ In this paper an alternate phenyl

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Table I. Torsional Angles α_1 , α_2 , α_3 , and α_3' , Rotation α , Individual Propeller Angles τ_1 , τ_2 , and τ_3 , and Average Propeller Angle τ (deg), As Defined in Figure 2, for Compounds 1-11

no.	compound	α_1	α_2	α_3	α_3'	α	τ_1	τ_2	τ_3	τ	space group	ref
1	$C_5H_5(CO)_2MnP(C_6H_5)_3$	39.0	157.4	276.6	-83.4	37.7	50.0	60.0	23.1	44.4	$P\bar{1}$	8
2	$C_5H_5(CO)_2FeP(C_6H_5)_3^+$	46.2	166.3	283.5	-76.5	45.4	55.4	76.6	17.5	47.8	$P\bar{1}$	15
3	$C_5H_5(CH_2)_4CoP(C_6H_5)_3$	50.4	171.0	290.3	-69.7	50.6	51.5	83.9	-1.0	44.8	$P2_1/n$	16
4	$C_5H_5[C(C_6F_5)]_4CoP(C_6H_5)_3$	29.8	151.4	275.4	-84.6	27.8	62.5	34.2	39.4	45.4	$P\bar{1}$	17
5	$C_5H_5(\text{norbornadiene})RuP(C_6H_5)_3^+$	37.7	157.6	279.1	-80.9	38.1	53.5	85.8	4.5	47.9	$P2_1/n$	18
6	$[C_5(CH_3)_5](CH_2)_4RhP(C_6H_5)_3$	45.0	165.8	285.7	-74.3	45.5	54.9	83.1	5.5	47.8	$P2_1/n$	19
7	$[C_5(CH_3)_5](CH_2)_4IrP(C_6H_5)_3$	45.3	164.7	285.7	-74.3	45.2	55.0	83.2	4.8	47.6	$P2_1/n$	16, 19
8	$[C_5(CH_3)_5](NO)_2RhP(C_6H_5)_3$	32.1	154.4	273.5	-86.5	33.3	69.3	51.4	7.8	42.8	$P2_1/n$	20
9	$[C_5(CH_3)_4C_2H_5]Cl_2CoP(C_6H_5)_3$	48.6	166.2	286.9	-73.1	47.2	70.7	33.2	-12.7	30.4	$P2_1/n$	21
10	$[C_5(C_2H_5)_6](CO)_2CrP(C_6H_5)_3$	48.5	166.0	282.6	-77.4	45.7	64.0	51.8	-7.8	36.0	$P\bar{1}$	22, 23
11	$C_6H_5COOCH_3(CO)_2CrP(C_6H_5)_3$	23.7	144.9	262.4	-97.6	23.7	63.4	52.6	15.2	43.7	$P112_1/n$	24

Table II. Torsional Angles α_1 , α_2 , α_3 , and α_3' , Rotation α , Individual Propeller Angles τ_1 , τ_2 , and τ_3 , Average Propeller Angle τ (deg), As Defined in Figure 2, for Compounds 12-28

no.	compound	α_1	α_2	α_3	α_3'	α	τ_1	τ_2	τ_3	τ	space group	ref
12	$C_5H_5(CO)(C_6H_5)FeP(C_6H_5)_3$	58.2	178.5	301.7	-58.3	59.5	32.6	58.4	56.3	49.1	$P2_1/n$	25
13	$C_5H_5(CO)(CH_2CO_2\text{menthyl})FeP(C_6H_5)_3$	40.8	162.0	279.5	-80.5	40.8	52.2	44.0	14.9	37.0	$P1$	26
	^a	43.2	160.5	283.2	-76.7	42.3	55.1	46.9	12.1	38.0	$P2_1$	
14	$C_5H_5(CO)(SO_2-i-Bu)FeP(C_6H_5)_3$	38.4	162.9	278.9	-81.1	40.1	49.8	-23.2	65.2	30.6	$P2_12_12_1$	27
15	$C_5H_5[\eta^3-CF_2C(CF_3)CC(CF_3)]FeP(C_6H_5)_3$	28.9	149.7	273.2	-86.8	30.6	76.5	37.4	9.0	41.0	$P2_1/c$	28
16	$C_5H_5(CO)[C(PPh_3)CH_2]FeP(C_6H_5)_3^+$	43.6	166.4	284.4	-75.6	44.8	21.9	55.9	60.8	46.2	$P\bar{1}$	29
17	$C_5H_5[CPhC(CO_2Me)CH(CO_2Me)CH(CO_2Me)]CoP(C_6H_5)_3$	36.5	157.6	279.6	-80.4	37.9	62.1	46.8	33.6	47.5	$P\bar{1}$	30
18	$C_5H_5[P(OMe)_2][NCC(CN)C(CN)_2]RuP(C_6H_5)_3$	33.1	155.4	275.3	-84.7	34.6	62.7	67.1	11.5	47.1	$C2/c$	31
19	$C_5H_5(CO)(CSC_6H_5)WP(C_6H_5)_3$	33.4	153.3	275.4	-84.6	34.0	72.5	35.8	13.4	40.6	$P2_1/c$	32
20	$C_5H_5(NO)(CHO)ReP(C_6H_5)_3$	33.7	154.4	271.9	-88.1	33.3	46.7	66.7	29.3	47.6	$P2_1/c$	33
21	$C_5H_5(I)[C(CH_3)SCH_3]IrP(C_6H_5)_3^+$	39.0	160.6	281.1	-78.9	40.2	72.0	45.0	13.5	43.5	$Pbc2_1$	34
22	$\eta^4-CH_3C_6H_4(CO)(NO)MnP(C_6H_5)_3$	37.5	158.4	277.1	-82.9	37.7	79.1	28.1	-0.3	35.6	$Pbca$	35
23	$[C_5H_3(CH_3)(C_6H_5)](CO)(I)FeP(C_6H_5)_3$	32.1	151.4	273.8	-86.2	32.4	62.6	45.1	14.8	40.8	$P2_1/n$	36
24	$[C_5H_3(CH_3)(C_6H_5)](CO)(COCH_3)FeP(C_6H_5)_3$	34.5	155.4	270.6	-89.4	33.5	59.6	62.7	4.3	42.2	$P\bar{1}$	36
25	$(C_5H_4\text{menthyl})(CO)(Cl)RuP(C_6H_5)_3$	54.0	175.1	294.6	-65.4	54.6	40.9	1.8	79.5	40.7	$P2_12_12_1$	37
26	$(C_{10}H_9O)(CO)(CS)CrP(C_6H_5)_3$	48.5	165.5	283.0	-77.0	45.7	44.8	84.2	12.3	47.1	$P2_12_12_1$	38
27	$C_5H_5(CO)Mn[P(C_6H_5)_3]_2$	53.2	171.6	296.3	-63.7	53.7	55.8	89.7	4.3	49.9	$P\bar{1}$	39
	^b	45.5	171.9	288.6	-71.4	48.7	78.0	57.3	-2.2	44.4	$P\bar{1}$	
28	$C_5H_5(Cl)Ru[P(C_6H_5)_3]_2$	49.8	173.0	292.6	-67.4	51.8	72.5	52.5	-1.6	41.1	$P\bar{1}$	40
	^b	53.7	173.5	298.9	-61.1	55.4	67.7	69.5	2.6	46.6	$P\bar{1}$	

^a Two independent molecules in the unit cell. ^b Second $P(C_6H_5)_3$ ligand.

differentiation mechanism is established for triphenylphosphine derivatives of the type $(\text{arene})_2MP(C_6H_5)_3$.

The phenyl rings in triphenylphosphine and triphenylphosphine derivatives usually assume a propeller-like conformation.⁷ Pseudotetrahedral (triphenylphosphine)metal complexes are ethane-type compounds which are predicted to adopt a staggered conformation with respect to the M-P bond. In this paper we present a conformational analysis of $Cp(CO)_2MnP(C_6H_5)_3$ ($Cp = \eta^5-C_5H_5$) based on single-crystal X-ray data⁸ which shows that the propeller structure of $P(C_6H_5)_3$ distorts the ideal staggered ethane conformation. Subsequently, this conformational analysis is extended to account for the solid-state structures of other ethane-like triphenylphosphine complexes of the type $(\text{arene})_2MP(C_6H_5)_3$ and $(\text{arene})-LL'MP(C_6H_5)_3$ found by a computer search in the Cambridge Structural Database.

Solid-State Conformation of $Cp(CO)_2MnP(C_6H_5)_3$

Figure 1 shows the Newman projection along the Mn-P bond for a hypothetical staggered conformation of $Cp(CO)_2MnP(C_6H_5)_3$ with Cen = Cp centroid directed upwards. In this hypothetical staggered conformation the P-C_{ipso} bond to phenyl Ph₂ is exactly trans to the Cp centroid ($\alpha_2 = 180^\circ$). The P-C_{ipso} bonds to the other two phenyls Ph₁ and Ph₃ form the gauche angles $\alpha_1 = 60^\circ$ and

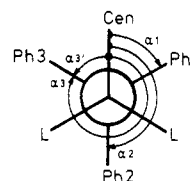


Figure 1. Newman projection of $CenL_2MP(C_6H_5)_3$ along the M-P bond. Staggered conformation: $\alpha_1 = 60^\circ$, $\alpha_2 = 180^\circ$, $\alpha_3 = 300^\circ$, and $\alpha_3' = -60^\circ$.

$\alpha_3 = 300^\circ$ ($\alpha_3' = -60^\circ$) with respect to Cen, the Cp centroid. The torsional angles α_1 , α_2 , and α_3 for $Cp(CO)_2MnP(C_6H_5)_3$, 1, and for compounds 2-11 (Table I) are measured from the arene centroid. For the following discussion it is not relevant that the CenML angles are usually larger than the LML angle.⁹ The staggered conformation in Figure 1 is attained starting from the eclipsed conformation by a formal rotation around the M-P bond of $+60^\circ$ (clockwise) or -60° (counterclockwise). The conformations in Figure 2 are obtained from the eclipsed conformation by a rotation α , clockwise for $0^\circ < \alpha < 60^\circ$ (case A) and counterclockwise for $-60^\circ < \alpha < 0^\circ$ (case B). The deviation from the ideal staggered conformation in Figure 1 is caused by the propeller arrangement of the three phenyl rings in the $P(C_6H_5)_3$ ligand.

$Cp(CO)_2MnP(C_6H_5)_3$, 1, and most of the compounds 2-28 crystallize in centrosymmetric space groups (Tables I and II). Therefore it is a matter of chance the data of

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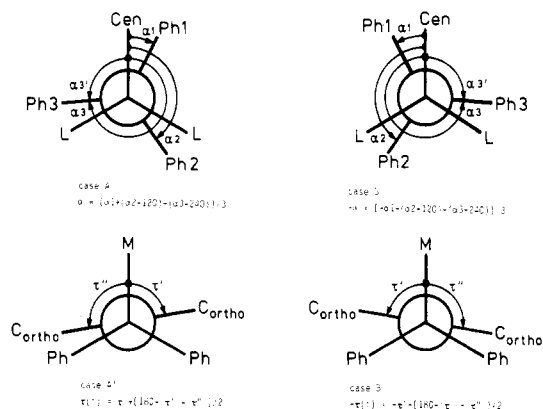


Figure 2. Newman projection of $\text{CpL}_2\text{MP}(\text{C}_6\text{H}_5)_3$ along the M-P bond: case A, clockwise rotation ($\alpha < 60^\circ$); case B, counter-clockwise rotation ($\alpha < -60^\circ$) with respect to the eclipsed conformation. Newman projection along the P-C_{ipso} bond of the P-Ph(*i*) moiety. Individual propeller angle $\tau(i)$, corrected for nonplanarity of the phenyl substituent: case A' ($\tau(i) > 0$) and case B' ($\tau(i) < 0$).

which enantiomer have been incorporated into the Cambridge Structural Database. In the following discussion the signs of all the angles of cases B have been inverted so that all the problems are dealt with the same chirality.

In $\text{Cp}(\text{CO})_2\text{MnP}(\text{C}_6\text{H}_5)_3$ the phenyl ring Ph1 approaches closer to Cp (see Figure 3), making the small gauche angle $\alpha_1 = 39^\circ$. Ph1 is then "face exposed" toward Cp because the phenyl and Cp planes are almost perpendicular to each other. The other gauche phenyl Ph3 is further away from the Cp, making the large gauche angle $\alpha_3' = -83.4^\circ$, as defined in Figure 2. Ph3 is therefore "edge exposed" toward Cp because it orients its ortho C-H bond toward the Cp ring (see Figure 3). It is this increased Cp/ortho C-H interaction which is responsible for the large gauche angle

α_3' of the edge-exposed phenyl. The face/edge exposure of phenyls Ph1 and Ph3 causes the trans phenyl Ph2 to deviate from the ideal trans angle $\alpha_2 = \pm 180^\circ$ to give the real trans angle $\alpha_2 = 157.4^\circ$. These interactions lead to a formal clockwise rotation of the $\text{P}(\text{C}_6\text{H}_5)_3$ ligand around the Mn-P bond by $\alpha = 37.7^\circ$ with respect to the eclipsed conformation.

In Figure 2, the Newman projection A' along the P-C bonds to the ipso-carbon atoms of $\text{P}(\text{C}_6\text{H}_5)_3$ phenyl rings is shown with the Mn-P bond directed upwards. The torsional angles M-P-C_{ipso}-C_{ortho} τ' and τ'' determine the arrangement of the phenyl blades in the triphenylphosphine propeller.⁷ As there are two such torsional angles to the two ortho C atoms, only the smaller one τ' ($|\tau'| < 90^\circ$) is used. When averaged according to Figure 2, this torsional angle is called propeller angle $\tau(i)$, its value being close to that of τ' . The propeller angles τ_1 , τ_2 , and τ_3 refer to the gauche and trans angles α_1 , α_2 , and α_3 for phenyls Ph1, Ph2, and Ph3 (Figure 2).

The propeller angles for $\text{Cp}(\text{CO})_2\text{MnP}(\text{C}_6\text{H}_5)_3$ are $\tau_1 = 50.0^\circ$, $\tau_2 = 60.0^\circ$, and $\tau_3 = 23.1^\circ$ (Table I). The average of these three angles 44.4° is called the average propeller angle τ . The edge exposed phenyl Ph3 with the large gauche angle α_3' deviates from the average propeller angle by 21.3° , thereby diminishing the edge exposure of Ph3 and the steric hindrance of Cp/ortho C-H. The steric interaction of Cp/ortho C-H would be much larger if phenyl Ph3 were to retain the average propeller angle 44.4° . Generally, a phenyl which is edge exposed to a π -bonded arene ligand tends to decrease the average propeller angle $|\tau|$ and thus to reduce the Cp/ortho C-H interaction.

On the other hand, phenyl Ph1 which is face exposed to the Cp ligand increases its propeller angle τ_1 with respect to the average propeller angle τ by 6° . This increase allows better face exposure and thus Cp/Ph contact with

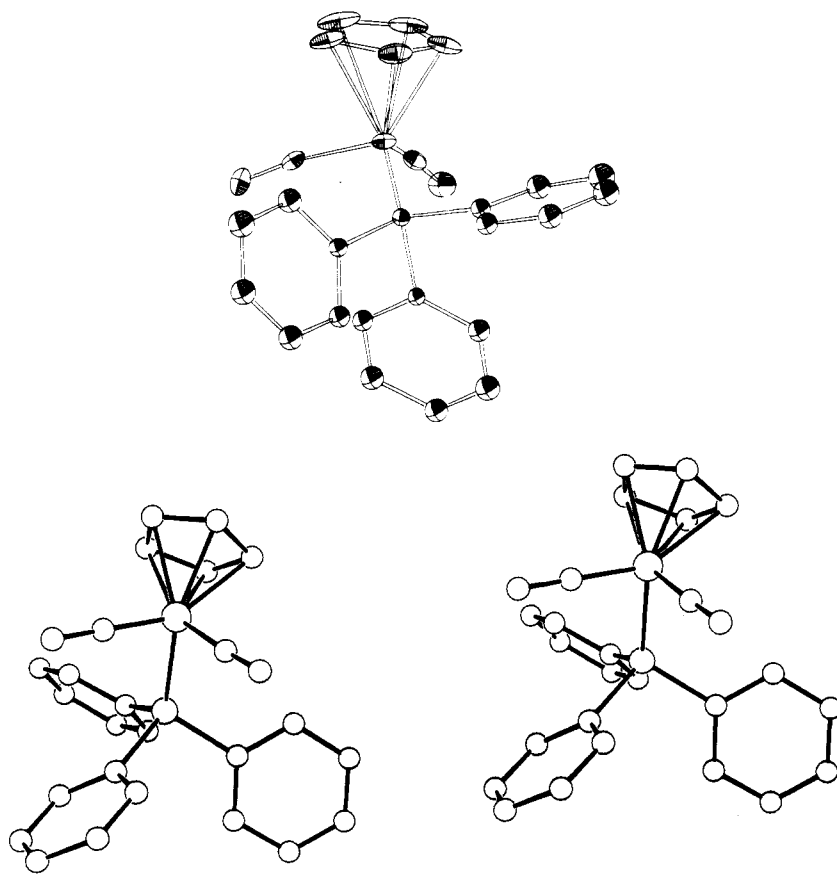


Figure 3. ORTEP drawing and stereoview of $\text{Cp}(\text{CO})_2\text{MnP}(\text{C}_6\text{H}_5)_3$ (case B).⁸

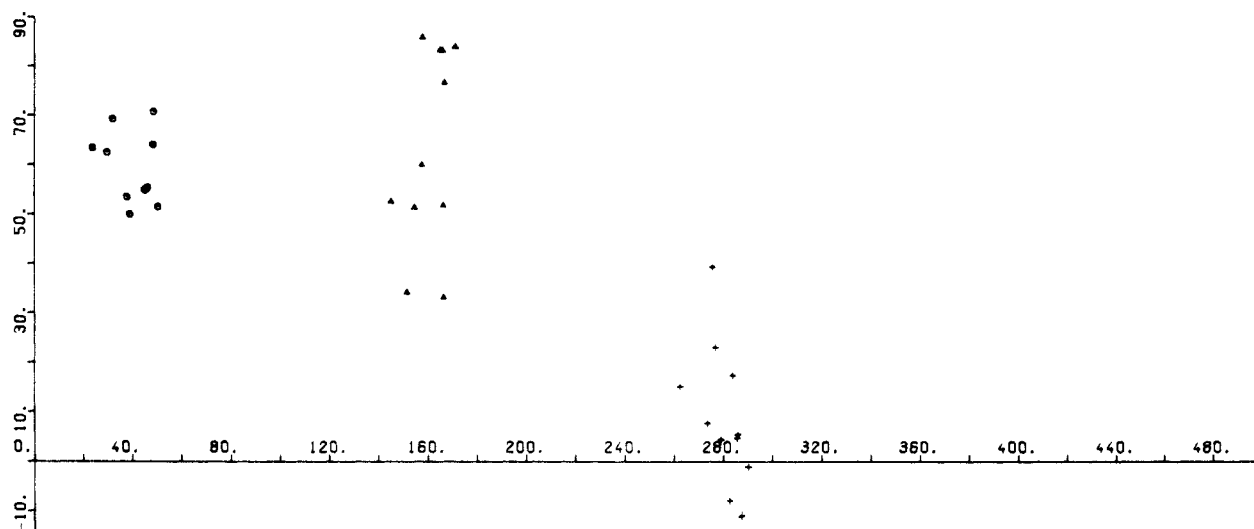


Figure 4. α/τ plot for compounds 1-11. Average values: $\alpha_1 = 40.6$, $\alpha_2 = 160.6$, $\alpha_3 = 280.1$, $\tau_1 = 59.1$, $\tau_2 = 63.2$, and $\tau_3 = 8.8^\circ$.

reduced steric hindrance. Deviations from the average propeller angle should increase with decreasing gauche angles and allow closer Ph approach to the π -bonded Cp. Phenyl 2, trans to Cp, orients its ortho C-H unit exactly between the $\text{Mn}(\text{CO})_2$ group due to the given rotation α and its individual propeller angle $\tau_2 = 60^\circ$. To produce the same result for a larger rotation α , a smaller propeller angle $|\tau_2|$ would be required and vice versa.

The ORTEP plot and the stereoview of $\text{Cp}(\text{CO})_2\text{MnP}(\text{C}_6\text{H}_5)_3$ in Figure 3 clearly show the face exposure of phenyl Ph1 and the edge exposure of phenyl Ph3 toward the Cp ring. It is primarily the interaction of the Cp with the neighboring ortho C-H bond of the edge-exposed Ph3 which causes the rotation α and the differentiation into large and small gauche angles α_3' and α_1 .

Conformation of $\text{P}(\text{C}_6\text{H}_5)_3$ Bonded to C_{3v} Fragments

In $(\text{NO})_3\text{MnP}(\text{C}_6\text{H}_5)_3$ triphenylphosphine is bonded to a $(\text{NO})_3\text{Mn}$ fragment with C_{3v} symmetry.¹⁰ Angles $\alpha_1 = 5.3^\circ$, $\alpha_2 = 126.7^\circ$, and $\alpha_3 = 246.0^\circ$ ($\alpha_3' = -114.0^\circ$) show that $\text{P}(\text{C}_6\text{H}_5)_3$ is rotated by only $\alpha = 6^\circ$ from the eclipsed conformation with respect to the MnP bond. However, taking into account the propeller structure of $\text{P}(\text{C}_6\text{H}_5)_3$, an average propeller angle $\tau = 44.3^\circ$ locates the ortho hydrogen atoms of the phenyl groups exactly between the NO ligands, the combination of $\alpha = 6^\circ$ and $\tau = 44.3^\circ$ being an excellent choice for such an arrangement. It is noteworthy that the individual propeller angles for $(\text{NO})_3\text{MnP}(\text{C}_6\text{H}_5)_3$ ($\tau_1 = 42.9^\circ$, $\tau_2 = 45.3^\circ$, $\tau_3 = 49.1^\circ$) are remarkably constant with deviation from τ of less than 5° . There is no face or edge exposure of the phenyl rings in $(\text{NO})_3\text{MnP}(\text{C}_6\text{H}_5)_3$ as discussed for $\text{Cp}(\text{CO})_2\text{MnP}(\text{C}_6\text{H}_5)_3$. The pseudo- C_{3v} compounds $(\text{CO})_2(\text{NO})\text{CoP}(\text{C}_6\text{H}_5)_3$ ¹¹ and $(\text{NO})_2(\text{CO})\text{FeP}(\text{C}_6\text{H}_5)_3$ ¹² have α and τ values very similar to those in $(\text{NO})_3\text{MnP}(\text{C}_6\text{H}_5)_3$.

The three propeller angles for $\text{OP}(\text{C}_6\text{H}_5)_3$ are 24.7 , 59.3 , and 21.1° (average $\tau = 35.0^\circ$)¹³ and for the two independent molecules in the unit cell of $\text{SP}(\text{C}_6\text{H}_5)_3$ are 50.3 , 55.2 , and 10.6° (average $\tau = 38.7^\circ$) and 50.0 , 57.5 , and 12.2° (average $\tau = 39.9^\circ$).¹⁴ The average τ values of both are

close to the average propeller angles of $(\text{NO})_3\text{MnP}(\text{C}_6\text{H}_5)_3$, $\tau = 44.3^\circ$ (individual τ values given above), $(\text{CO})_2(\text{NO})\text{CoP}(\text{C}_6\text{H}_5)_3$, $\tau = 45.2^\circ$ ($\tau_1 = 50.7$, $\tau_2 = 40.4$, $\tau_3 = 44.5^\circ$), and $(\text{NO})_2(\text{CO})\text{FeP}(\text{C}_6\text{H}_5)_3$, $\tau = 45.5^\circ$ ($\tau_1 = 50.0$, $\tau_2 = 41.8$, $\tau_3 = 44.6^\circ$). However, the individual propeller angles of $\text{OP}(\text{C}_6\text{H}_5)_3$ and $\text{SP}(\text{C}_6\text{H}_5)_3$ deviate appreciably from the average τ value, whereas for the $\text{P}(\text{C}_6\text{H}_5)_3$ complexes of the fragments $(\text{NO})_3\text{Mn}$, $(\text{CO})_2(\text{NO})\text{Co}$, and $(\text{NO})_2(\text{CO})\text{Fe}$ they are almost constant (maximum deviation from τ , $\pm 5^\circ$). In molecules such as $\text{OP}(\text{C}_6\text{H}_5)_3$ and $\text{SP}(\text{C}_6\text{H}_5)_3$, where no large fragment bonded to P is able to cause directive interactions for the phenyl rings, individual propeller angles are probably due to packing effects. In the C_{3v} and pseudo- C_{3v} complexes, however, intramolecular nonbonding interaction of the L_3M fragment rather than packing forces control the propeller structure of the $\text{P}(\text{C}_6\text{H}_5)_3$ moiety.

Compounds of the Type $(\text{Arene})\text{L}_2\text{MP}(\text{C}_6\text{H}_5)_3$

The cation $[\text{Cp}(\text{CO})_2\text{FeP}(\text{C}_6\text{H}_5)_3]^+$, **2**,¹⁵ is isoelectronic

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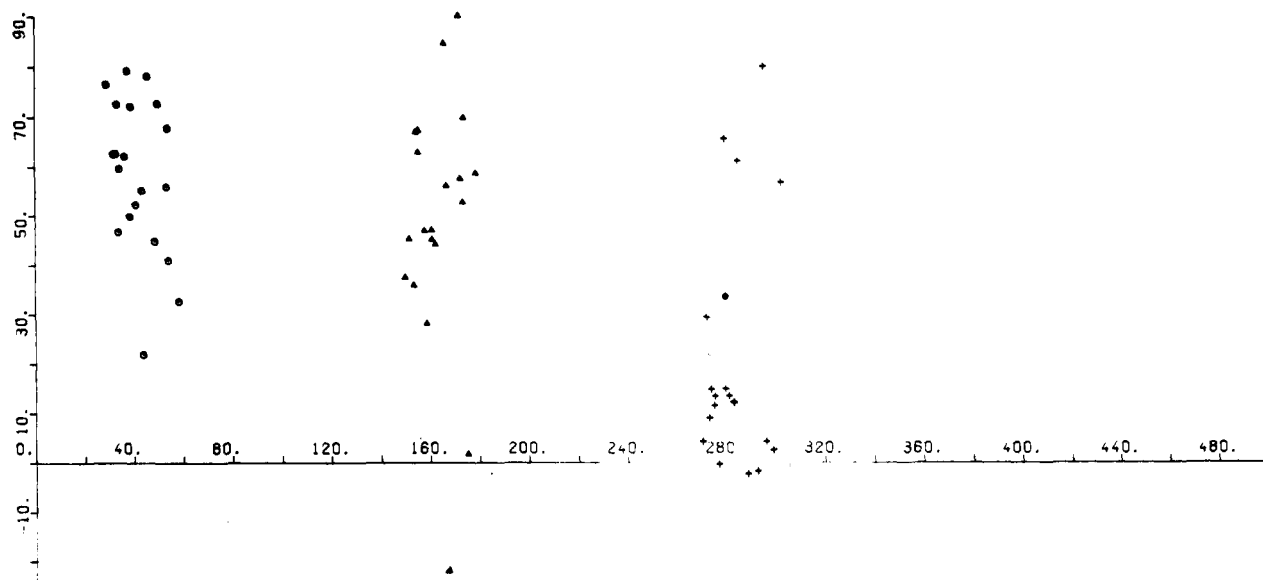


Figure 5. α/τ plot for compounds 12–28. Average values: $\alpha_1 = 41.9$, $\alpha_2 = 162.9$, $\alpha_3 = 283.0$, $\tau_1 = 58.3$, $\tau_2 = 48.6$, and $\tau_3 = 21.7^\circ$.

with $Cp(CO)_2MnP(C_6H_5)_3$, 1^8 Its rotation by $\alpha = 45.4^\circ$ and its average propeller angle of $\tau = 47.8^\circ$ are slightly larger than the corresponding values in 1. Table I shows that the individual propeller angles for both compounds are also very similar. For compound 2, the face-exposed phenyl ring deviates by 7.6° and the edge-exposed phenyl ring deviates by 30.3° from the average propeller angle in the direction expected to minimize Cp/ortho CH interactions.

The cyclopentadienyl and pentamethylcyclopentadienyl derivatives 3–9 (L = substituted or unsubstituted metallocycles, norbornadiene, or two monodentate ligands like NO_3 and Cl) show rotations in the range between 50 and 27° . With the exception of 9 which has the lowest value (30.4°) in Table I all the absolute values of the average propeller angles τ are somewhat above 40° .⁷ The propeller angles for the face-exposed phenyls of compounds 3–9 are slightly higher, and those for the edge exposed phenyls are markedly lower, than the average propeller angles. For compounds 3 and 9 this effect even leads to a change in the propeller sense for the edge-exposed phenyl 3, indicated by the change in sign given in Table I.

The rotations and the average and individual propeller angles of compounds 10 and 11, which contain six-membered arenes, fit well into the overall pattern.

Figure 4 shows a plot α/τ which on the abscissa contains the angles α_1 (face-exposed phenyl), α_2 (trans phenyl), and α_3 (edge-exposed phenyl). The average values of α_1 , α_2 , and α_3 given in Figure 4 correspond to a rotation of the

$P(C_6H_5)_3$ ligand by 42.0° with respect to the eclipsed conformation.

The average propeller angle τ for compounds 1–11 in Table I is 43.5° .⁷ Figure 4 shows the deviation of the individual τ values characteristic of the three groups of phenyls from the average propeller angle. The α_1 values cluster around 59.1° . They differ from the average by 17.5° and indicate an increased face exposure. The α_3 values cluster around 8.8° . They differ from the average by 34.7° in the opposite direction and thus indicate a decreased edge exposure. Both deviations tend to decrease the arene/ortho C–H interaction. The individual τ values of the trans phenyls (α_2) span a wide range probably due to the different nature of ligands L in the compounds (arene) $L_2MP(C_6H_5)_3$ (Figure 4).

Compounds of the Type (Arene) $LL'MP(C_6H_5)_3$

Compounds 12–24 include unsubstituted and substituted cyclopentadienyl compounds (Table II). L and L' are different one-, two-, or three-electron ligands such as CO, CS, NO, phenyl, alkyl, formyl, acetyl, halogen, carbene, carbyne, SO_2R , PR_3 , nitrile, other carbon ligands, or carbocyclic chelates. The rotations α of all these compounds are between 30 and 45° , except for 12 and 25 which are close to the staggered conformation. All the average propeller angles are in the range 30 – 50° . There is a clear differentiation between the individual propeller angles of face-exposed phenyls 1 vs. edge-exposed phenyls 3, with only four exceptions. Due to the small rotations α , the assignment of face-exposed and edge-exposed character to the gauche phenyls in 12 (practically staggered) and 25 (almost staggered) becomes arbitrary. Thus, only compounds 14 and 16 remain as real exceptions in which τ_3 of the edge-exposed phenyl 3 is higher than the average propeller angle. In the case of 16, the propeller angle τ_1 of the face-exposed phenyl 1 is smaller than the average propeller angle. The deviations found for 14 and 16 may be attributed to the excessively bulky nature of ligands L or L'.

Compound 13 has two independent molecules in the unit cell both of which fit well into the overall picture. The same is true for the η^4 -methylcyclopentadienyl derivative 26 and for the tetralone complex 27, included for comparison. Although both sets of phenyls for compounds 27 and 28 have rotations of 50 – 55° , the individual and average propeller angles are in perfect accord with the conforma-

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tional analysis proposed and the values given in Table II.

The α/τ plot for compounds 12–28 (Figure 5) is similar to that in Figure 4. These compounds exhibit an average rotation of $\alpha = 42.6^\circ$ and an average propeller angle of $\tau = 42.8^\circ$.⁷ The individual deviations of the τ angles for the face-exposed phenyls ($\alpha 1$) and the edge-exposed phenyls ($\alpha 3$) are obvious, especially by comparison with the average τ angles of the different groups of phenyls given in the caption of Figure 5. The situation is analogous to Figure 4 except for the four cases (12, 14, 16, and 25) discussed above, which have the smallest τ angles for $\alpha 1$ and the highest τ angles for $\alpha 3$.

Tables I and II show that a positive rotation α of the triphenylphosphine correlates with a positive propeller angle. Thus, in Figure 2 torsional angles A/A' are correlated.

Conclusions

The trends noted in the data of Tables I and II demonstrate that the conformations of three-legged piano stool compounds of the type (arene) $L_2MP(C_6H_5)_3$ and (arene) $LL'MP(C_6H_5)_3$ are determined primarily by intramolecular effects and not by packing forces.

Triphenylphosphine adopts a compact propeller arrangement which minimizes intramolecular repulsions between the phenyl rings.

The three phenyl substituents of $P(C_6H_5)_3$ and the fragments (arene) L_2M or (arene) $LL'M$ prefer a staggered arrangement with regard to the M–P bond similar to ethane-type molecules.

The propeller structure of the $P(C_6H_5)_3$ moiety causes a distortion from the ideal staggered conformation. The distortion arises from the interaction of the two phenyl blades of the propeller with the arene ligand which leads to a rotation about the M–P bond with respect to the staggered conformation so that the face-exposed phenyl adopts the small gauche angle $\alpha 1$ and the edge-exposed phenyl adopts the large gauche angle $\alpha 3'$ with regard to the arene centroid. By additional rotations about the $P-C_{ipso}$ bonds, the face-exposed phenyl becomes more face exposed and the edge-exposed phenyl less edge exposed.

Both adjustments diminish the arene/ortho C–H interaction.

A similar conformational analysis has already been presented for a limited number of compounds of the type (arene) $LL'MP(C_6H_5)_2NRCH(CH_3)(C_6H_5)$.⁴¹ In these compounds the amino substituent prefers the gauche position and not the trans position with respect to the arene centroid, if there are no intramolecular hydrogen bonds.^{42,43} However, the amino substituent always adopts the large gauche angle making the gauche phenyl a face-exposed one in agreement with the present discussion.

Experimental Section

A search in the Cambridge Data File⁴⁴ using the program CSSR⁴⁵ for structures of the type (arene) $L_2MP(C_6H_5)_3$ and (arene) $LL'MP(C_6H_5)_3$ (M = transition metal) was carried out in October 1983. From the extracted atomic coordinates and cell parameters the center of the arene C_{en} was calculated, and with use of the program XANADU⁴⁶ the torsional angles τ' and τ'' were determined. (Parameters were not available for seven of the 35 compounds found.) Three compounds^{10–12} with C_{3v} or pseudo- C_{3v} symmetry at the metal and $XP(C_6H_5)_3$ with X = O and S had been included from the literature and were handled likewise.

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