Crystal and molecular structure of bis(.mu.-iodo)bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II), a product of the cyclopalladation for trans-[(o-tol)3P]2PdI2

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Crystal and Molecular Structure of Bis(μ-iodo)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), a Product of the Cyclopalladation for *trans*-$[(o\text{-tol})_3\text{P}]_2\text{PdI}_2$

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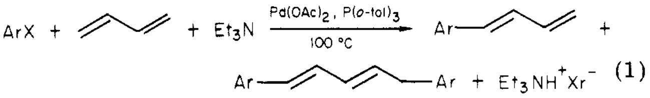
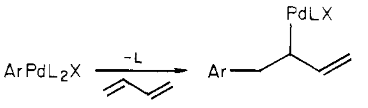
During the initial stages of arylation reactions of polyenes with aryl halides catalyzed by a mixture of Pd(OAc)_2, $\text{P}(o\text{-tol})_3$, and Et_3N (tol = tolyl), an orange, crystalline, catalytically inactive Pd(II) complex separates from the reaction solution. The complex has been identified by X-ray diffraction methods as $[(\mu\text{-I})\overline{\text{PdP}(o\text{-tol})_2\text{-}o\text{-C}_6\text{H}_4\text{CH}_2}]_2$: monoclinic, $P2_1/n$, a = 9.451 (3) Å, b = 10.864 (2) Å, c = 19.307 (6) Å, β = 92.22 (2)°, V = 1956.8 (13) Å^3, and Z = 2 (an inversion center resides within the Pd_2I_2 rhombus). The Pd(II) complex results from the internal cyclopalladation of one of the *o*-Me groups of the phosphine ligand in the precursor *trans*-$[\text{P}(o\text{-tol})_3]_2\text{PdI}_2$. The Pd_2I_2 rhombus is strictly planar, and the geometry about Pd is nearly square planar. Bond distances and angles, in general, conform to expectations based on limited precedent. One of the methyl hydrogen atoms is positioned in an axial site that may indicate the mode of C–H activation that precedes cyclometalation.

Introduction

The combination of palladium(II) acetate, tri-*o*-tolylphosphine and triethylamine is an effective catalyst for the mono- and diarylation of conjugated polyenes,[1,2] e.g., eq 1. Yields of mono- and diarylated products in the range of 60–80% are obtained when electron-withdrawing substituents are present in the aryl group.



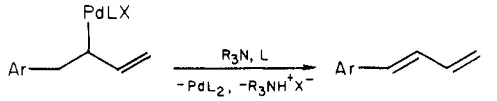
(1)



(2a)

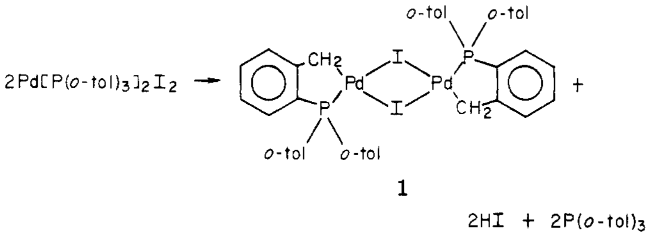
(in equilibrium with Π-allylic palladium intermediates)

Heck et al.[2] have suggested a mechanism involving the initial formation of PdL_2 (L = tri-*o*-tolylphosphine) followed by oxidative addition of ArX to form ArPdL_2X. Then



(2b)

A consistent feature of these arylation reactions is the early formation of an orange, crystalline compound that in its pure form is catalytically inactive.[3] Continued heating causes the crystalline material to redissolve and the arylation to then proceed normally. A sample of orange solid was provided to us by Prof. R. Heck, and we have determined by X-ray crystallography that, in the case when X = I, the compound formed is an iodine-bridged, dimeric, internally cyclopalladated complex, viz., *trans*-bis(μ-iodo)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), 1.



1

Cyclopalladation reactions have been recently reviewed.[4] A consistent theme is the ability of sterically congested phosphines to facilitate internal metalation.[5,6] In keeping with this, Tolman[7] has computed a ligand cone angle (σ) of 194 (6)° for $(o\text{-tol})_3\text{P}$; a crystallographically determined value of σ is 198°.[8] The thermodynamic effects promoting cyclometalation have also been discussed.[8] Both $(t\text{-Bu})(o\text{-tol})_2\text{P}$[9–11] and $(t\text{-Bu})_2(o\text{-tol})\text{P}$[11] have been shown to undergo cyclopalladation and cycloplatination involving the aryl alkyl group. But no previous report of $(o\text{-tol})_3\text{P}$ undergoing cyclopalladation could be found, and specifically it has been reported[12] that *trans*-$[(o\text{-tol})_3\text{P}]_2\text{PtI}_2$ did not cycloplatinate, which the authors attributed to such overcongestion that the ligands could not properly orient themselves for metalation to occur. Interestingly, the same authors report a *facile* metalation of $(\text{mes})_3\text{P}$ (mes = mesityl) on palladium to form a Cl-bridged dimer analogous to 1.[13] Tri-*o*-tolylphosphine has been reported to undergo side chain metalation on a Rh complex.[14] The

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Table I. Crystal and Data Collection Parameters for $C_{42}H_{40}Pd_2I_2$, 1

compound	$C_{42}H_{40}Pd_2I_2$
formula weight	991.19
crystal system	monoclinic
space group	$P2_1/n$ [$P2_1/c$; cell 2]
a, Å	9.451 (3)
b, Å	10.864 (2)
c, Å	19.307 (6)
β, deg	92.22 (2)
V, Å^3	1956.8 (13)
Z	2
μ, cm^{-1}	25.78 (Mo Kα)
ρ(calcd), g cm^{-3}	1.68
diffractometer	Nicolet R3 (graphite monochrometer)
cryst size, color	0.27 × 0.36 × 0.54, pale orange
temp, °C	23
scan speed, deg min^{-1}	variable 3-12
scan range	$4° \leqslant 2\theta \leqslant 45°$ ($\pm h,k,l$)
unique reflns	2579 (2933 collected)
unique reflns ($3\sigma(F_o)$)	2160
standards	3/97 (no decay obsd)
R_F, R_{wF}, %	3.34, 3.36
GOF	0.998
highest peak, final diff map, e Å^{-3}	0.49

same authors failed to detect metalation reactions with a number of $Pd^{II}(o\text{-tol})_3P$ complexes.[14]

The only previous structural characterization of a product of alkyl side chain metalation involving either Pd or Pt is that for the thermal reaction of $[(o\text{-tol})_2(t\text{-Bu})P]_2Pd(\text{acetate})_2$ that forms an acetate-bridged dimer analogous to 1.[9]

Experimental Section

Crystals of 1 were kindly provided by Prof. R. Heck. A well-formed bricklike specimen was affixed to a fine glass fiber with epoxy cement with the long dimension parallel to the fiber. The crystal parameters provided in Table I were obtained from the angular settings of 25 reflections in Friedel-related sets ($22° \leq 2\theta \leq 30°$). Systematic absences uniquely defined the space group. The intensity data were corrected for Lp effects and for absorption using an empirical, ψ-scan technique. The structure was solved by direct methods, SOLV–SHELXTL (version 3.0); the positions of the I, Pd, and P atoms were used in a subsequent difference Fourier synthesis to locate the remaining non-hydrogen atoms and the hydrogen atoms on C(27). The model used in the final blocked-cascade, least-squares refinement included anisotropic thermal parameters for all non-hydrogen atoms, isotropic refinement of the hydrogen atoms on C(27), and the remaining hydrogen atoms incorporated as fixed, isotropic contributions in idealized positions, d(C–H) = 0.96 Å. The mean shift/esd ratio for the last cycle was 0.028, and 218 parameters were refined by using 2160 reflections ($F_o \geq 3\sigma(F_o)$). The final difference map revealed only a diffuse background, highest peak 0.49 e Å^{-3} located within the Pd_2I_2 rhombus. A table of final atomic coordinates is presented in Table II.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å × 10^3) for $C_{42}H_{40}Pd_2I_2$, 1

atom	x	y	z	U^a
Pd	4258 (1)	422 (1)	5864 (1)	35 (1)
I	4203 (1)	1402 (1)	4562 (1)	43 (1)
P	3145 (2)	1888 (2)	6415 (1)	36 (1)
C(11)	193 (7)	1458 (6)	5953 (4)	44 (3)
C(12)	−1183 (8)	1206 (7)	6084 (4)	58 (3)
C(13)	−1476 (8)	1092 (8)	6755 (4)	61 (3)
C(14)	−411 (8)	1234 (7)	7311 (5)	63 (3)
C(15)	987 (8)	1465 (7)	7205 (4)	51 (3)
C(16)	1297 (7)	1582 (6)	6527 (4)	40 (2)
C(17)	459 (8)	1588 (8)	5215 (4)	61 (3)
C(21)	4455 (7)	4055 (6)	6030 (3)	41 (2)
C(22)	4380 (9)	5268 (7)	5799 (4)	60 (3)
C(23)	3116 (9)	5922 (7)	5690 (5)	68 (3)
C(24)	1863 (10)	5388 (7)	5813 (5)	74 (4)
C(25)	1900 (8)	4186 (7)	6042 (4)	54 (3)
C(26)	3167 (7)	3494 (6)	6138 (3)	39 (2)
C(27)	5875 (7)	3429 (7)	6169 (4)	53 (3)
C(31)	4857 (7)	664 (7)	7403 (4)	45 (2)
C(32)	5849 (8)	494 (8)	8020 (4)	59 (3)
C(33)	6191 (9)	1447 (10)	8477 (4)	74 (4)
C(34)	5536 (9)	2577 (10)	8349 (4)	68 (3)
C(35)	4535 (7)	2766 (7)	7757 (4)	50 (3)
C(36)	4222 (7)	1811 (6)	7280 (3)	40 (2)
C(37)	4468 (8)	−325 (6)	6867 (4)	51 (3)
H(27a)	5984 (52)	2568 (49)	6134 (22)	54 (28)
H(27b)	6351 (43)	3461 (40)	6622 (21)	77 (27)
H(27c)	6477 (46)	3848 (42)	5940 (21)	99 (37)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (deg) and Angles (Å) for $C_{42}H_{40}Pd_2I_2$, 1

Bond Distances

Pd–I	2.723 (1)	P–C(16)	1.825 (7)
Pd–I′	2.665 (1)	P–C(26)	1.826 (7)
Pd···Pd	3.929 (1)	P–C(36)	1.813 (6)
Pd–P	2.266 (2)	C(31)–C(37)	1.496 (10)
Pd–C(37)	2.079 (7)	H(27a)–Pd	2.84 (3)

Bond Angles

Pd–I–Pd′	93.59 (6)	Pd–C(37)–C(31)	109.9 (5)
I–Pd–I′	86.41 (7)	Pd–P–C(36)	99.5 (2)
P–Pd–I	102.52 (8)	P–C(36)–C(31)	111.3 (5)
P–Pd–I′	170.08 (7)	C(37)–C(31)–C(36)	118.3 (6)
C(37)–Pd–I	175.7 (2)	C(16)–P–C(26)	105.4 (3)
C(37)–Pd–I′	91.2 (2)	C(16)–P–C(36)	106.8 (3)
P–Pd–C(37)	79.6 (2)	C(26)–P–C(36)	106.5 (3)

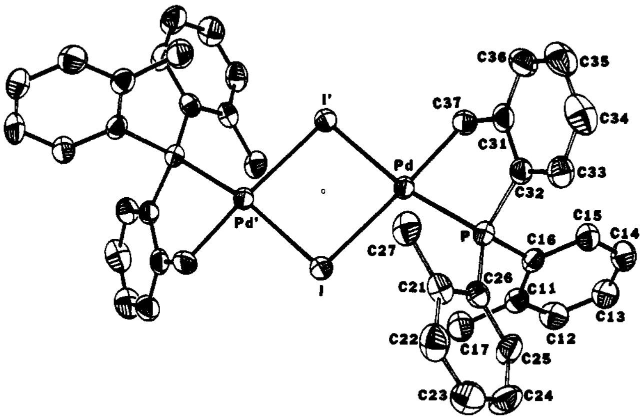

Figure 1. Molecular structure and labeling scheme for $[(\mu\text{-I})\overline{\text{PdP}(o\text{-tol})_2\text{-}o\text{-C}_6\text{H}_4\text{C}}\text{H}_2]_2$, 1. Hydrogen atoms have been deleted to improve clarity. A crystallographic inversion center is located in the center of the Pd_2I_2 rhombus.

Results and Discussion

The title compound crystallizes as discrete molecules of a bis(μ-iodo)-bridged internally cyclopalladated complex. The molecular structure and labeling scheme are provided in Figure 1, and a molecular stereoview is provided in Figure 2. The packing of molecules in the unit cell as shown in Figure 3 reveals that significant intermolecular interactions of Pd and I are prevented by the bulk of the phosphine ligand. Atomic coordinates are provided in Table II, and selected bond distances and angles are given in Table III. Molecules of 1 are situated about a crystallographically imposed inversion center that requires strict planarity on the Pd_2I_2 rhombus (see Figure 4). Several bis(allyl)bis(μ-halo)dipalladium(II) complex structures have been reported, and they are about equally divided among examples with a planar Pd_2X_2 core[15,16] and

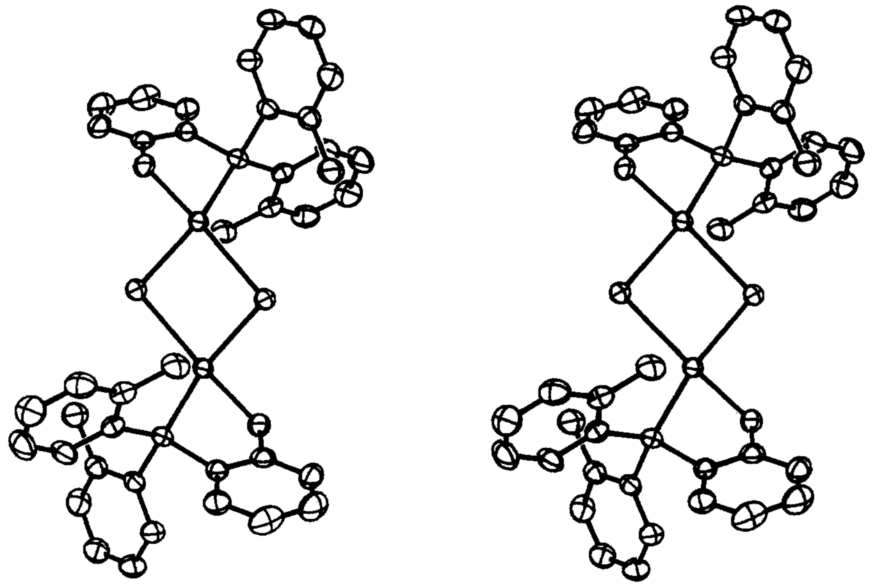

Figure 2. Stereoview of $[(\mu\text{-I})\overline{\text{PdP}(o\text{-tol})_2\text{-}o\text{-C}_6\text{H}_4\text{C}}\text{H}_2]_2$, 1.

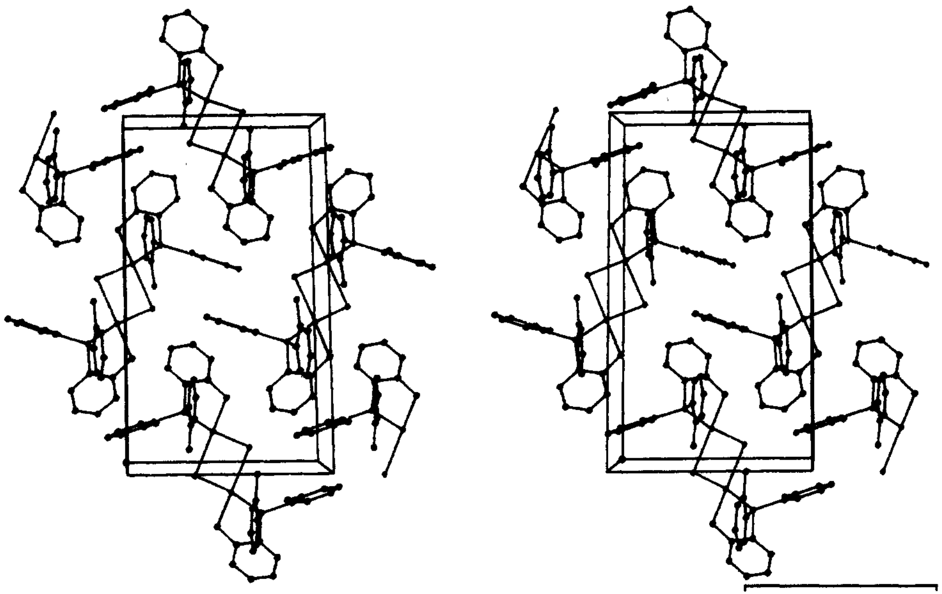

Figure 3. Stereoview of the unit cell packing diagram as viewed along the *a* axis for $[(\mu\text{-I})\overline{\text{PdP}(o\text{-tol})_2\text{-}o\text{-C}_6\text{H}_4\text{C}}\text{H}_2]_2$, 1.

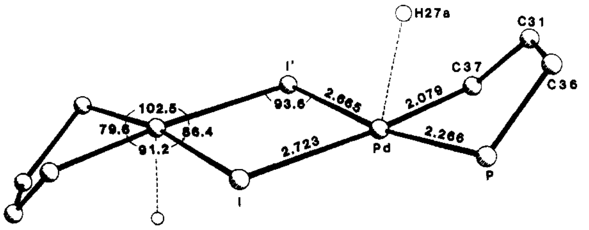

Figure 4. The central Pd_2I_2 rhombus and Pd coordination geometry for $[(\mu\text{-I})\overline{\text{PdP}(o\text{-tol})_2\text{-}o\text{-C}_6\text{H}_4\text{C}}\text{H}_2]_2$, 1.

those with a X···X hinged dihedral angle of 135–150°.[17,18]

The Pd···Pd distance in 1, 3.929 (1) Å, precludes meaningful metal–metal bonding. The Pd–I distances, 2.665 (1) (trans to P) and 2.723 (1) Å (trans to C(37)), are both longer than found in two polymorphs of binary PdI_2: α-PdI_2, 2.60 Å; β-PdI_2, 2.61 (2) and 2.62 (2) Å.[19] In both polymorphs the iodines are bridging. In $C_3H_5Pd_2(PPh_3)_2I{\cdot}C_6H_6$,[20] one I atom bridges two bonded Pd atoms with Pd–I = 2.650 (4) Å. The two Pd–I distances in 1 differ significantly, but since both alkyl groups and phosphines are comparable in their trans influence, the primary cause for the elongation of the Pd–I distance trans to C(37) may be due largely to the steric consequences of the positioning of the methyl groups $C(17)H_3$ and $C(27)H_3$ on this side of the molecule.

The range of Pd–P distances seen in square-planar Pd(II) complexes is 2.22–2.35 Å.[21] The Pd–P distance in 1, 2.266 (2) Å, is comparable to that found in $[o\text{-}(C_6H_5)_2PC_6H_4S]PdI_2$, 2.250 (2) Å, in which the Pd–P bond is also trans to I.[21]

For all bis(μ-halo)dipalladium(II) complexes with a planar Pd_2X_2 rhombus found in the literature,[15,16,19,21,22]

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the X–Pd–X bond angle is slightly acute, 86–89°, and the Pd–X–Pd bond angle slightly obtuse, 91–94°; the corresponding angles in 1 are within these ranges. The coordination geometry about Pd(II) is clearly square planar: the maximum deviation (0.008 Å) from perfect planarity is slight and occurs at C(37). The interplanar angle relating the central rhombus to the Pd coordination plane is 2.4°. The five-membered chelate ring is folded along the P···C(37) vector at a dihedral angle of 40.6°.

As indicated in the Introduction, steric congestion in the precursor is a prerequisite for cyclopalladation. The effect of this congestion is to force the placement of a C–H bond in an axial coordination site where activation can occur. Empirical evidence has been cited for the repulsive nature of distal, axial CH···Pd interactions;[23] this conclusion has very recently been supported for d^8 square-planar coordination by a theoretical study of C–H bond activation.[24] Therefore, in the absence of steric constraint, axial CH···Pd interactions are avoided. The structure of 1 provides evidence for the axial placement of one of the C(27) bonded hydrogen atoms at 2.84 (3) Å and 89 (2)° to the Pd(II) coordination plane. (In one form of $(Me_2PhP)_2PdI_2$, two phenyl hydrogen atoms are similarly positioned at 2.84 and 2.85 Å.[25]) Additionally, all structurally characterized products of cyclopalladation reactions of *o*-alkylphenyl substituents show the formation of five-membered chelate rings[9,11,13,26] In the cyclopalladation of $P(t\text{-Bu})_2(o\text{-EtC}_6H_4)$, the α side chain carbon is preferentially metalated.[27] The unique preference for five-membered ring formation provides strong circumstantial evidence for a specific steric constraint in cyclopalladation reactions.

Acknowledgment. The National Science Foundation provided funds supporting the purchase of the diffractometer. Crystals of 1 were kindly supplied by Prof. R. Heck.

Registry No. 1, 89510-88-3.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic temperature factors, hydrogen atom coordinates, and observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Coordinated Homoatomic Polyorganophosphorus Catenates. The Crystal Structure and Molecular Geometry of $Fe_2(CO)_6(PCH_3)_4$ and $Fe_2(CO)_6(PC_6H_5)_4$

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The crystal structure and molecular geometry of $Fe_2(CO)_6(PCH_3)_4$ (I) and $Fe_2(CO)_6(PC_6H_5)_4$ (II) have been determined. I: $P2_1/c$, monoclinic, a = 7.906 (4) Å, b = 17.139 (6) Å, c = 13.849 (6) Å, β = 101.41 (3)°, V = 1839.5 (12) Å^3, Z = 4, R_F = 6.4%. II: $P2_1/c$, monoclinic, a = 16.988 (6) Å, b = 11.492 (2) Å, c = 16.336 (4) Å, β = 101.09 (2)°, V = 3129.5 (16) Å^3, Z = 4, R_F = 3.6%. Both I and II possess similar distorted tetragonal-pyramidal metal atom coordination geometries joined along a basal edge formed by the mutually bridging termini of tetraphosphorus atom catenates. The structure of I is crystallographically isomorphous with its arsenic analogue. Both I and II possess single Fe–Fe bonds [I, 2.634 (2) Å; II, 2.633 (1) Å]. The only significant structural accommodation for the greater steric demands of phenyl vs. methyl substitution is the P–P–P–P dihedral angle [I, −10.5 (2)°; II, −23.6 (1)°]. The formally nonbonded phosphorus chain termini are separated by a distance only 0.5 Å longer than a normal P–P single bond [d(P···P): I, 2.715 (3) Å, II, 2.689 (1) Å]. The ${}^{31}P\{{}^1H\}$ NMR data for II reveals a rather large ${}^2J_{P-P}$, 125.4 Hz, possibly indicative of an attractive P···P interaction.

Introduction

Homoatomic polyorganophosphorus and arsenic rings, *cyclo*-$(RE)_n$, E = P or As, readily undergo ring-opening reactions when combined with metal carbonyls to yield a variety of coordinated homoatomic catenates.[1,2] One class of products is binuclear and contains a chain of RE units with usually four or five but occasionally as many as eight units. Each chain terminus bridges both metal atoms. Examples both with and without metal–metal bonds are known. If each chain terminus is considered a three-electron donor, then metal–metal bonds are expected for 14-electron metal groups, and no metal–metal bond for 15-electron groups. No exceptions to these expectations are known for this class of compound.

Of the compounds believed to possess this structure, only three have been structurally characterized: $[Fe(CO)_3]_2(AsCH_3)_4$, III,[3] $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(AsCH_3)_5$,[2] and $[Mo(CO)_3]_2(AsC_3H_7)_8$.[4] No polyorganophosphorus structures of this kind have been previously determined. West et al. originally reported the preparation of a series

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