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Direct Syntheses of 1-Phenylphosphetane and 1-Phenylphosphirane. Crystal and Molecular Structures of Neutral and Cationic Cyclotrimerization Precursor Complexes

David C. R. Hockless, Yew Beng Kang, Mark A. McDonald, Michael Pabel,
Anthony C. Willis, and S. Bruce Wild*

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory 0200, Australia

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Dilithium phenylphosphide reacts with 1,3-dichloropropane or 1,2-dichloroethane to give 1-phenylphosphetane (**1**) or 1-phenylphosphirane (**2**), respectively, both of which can be isolated by distillation in vacuo. The phosphetane rapidly polymerizes when neat but is stable in benzene wherefrom the polymer can be selectively and quantitatively separated from **1** by the addition of *trans*-dichlorobis(diethyl sulfide)palladium(II). Four-membered **1** has a remarkably low-field ^{31}P NMR chemical shift (13.9 ppm), and **2**, a remarkably high-field shift (−236 ppm). The crystal and molecular structures of the potential cyclotrimerization precursor complexes *fac*-[Mo(CO)$_3$(**1**)$_3$] (**7**), *fac*-[Mo(CO)$_3$(**2**)$_3$] (**8**), and [(η^5-C$_5$H$_5$)Fe(**2**)$_3$]PF$_6$ (**9**) have been determined. Both molybdenum complexes have C_3 symmetry in the solid state, and the iron complex has C_1 symmetry. An interesting feature of the three structures is that the phenyl groups of the small phosphorus heterocycles in each case are arranged in groups of three syn or anti to the auxiliary ligands.

Introduction

Strained three- and four-membered phosphorus heterocycles are potential building blocks for macrocyclic poly(tertiary phosphines) by cyclooligomerization on metal templates. For such syntheses, which are known for the conversion of oxirane into crown ethers,[1] *P*-substituted phosphiranes and phosphetanes are required with minimal substitution in the rings to facilitate oligomerization and to reduce the number of product diastereomers. Two ideal molecules for attempted cyclooligomerization under metal template conditions are 1-phenylphosphetane (**1**) and 1-phenylphosphirane (**2**). Hitherto, however, there is no reported synthesis of free **1** and the literature synthesis of **2** produces an equivalent of phenylphosphine as by-product,[2] which is difficult to remove without decomposition of the otherwise stable heterocycle. In a previous work, we reported the synthesis of **1** in the complex (R^*,R^*)-(±)-[(η^5-C$_5$H$_5$){1,2-C$_6$H$_4$(PMePh)$_2$}Fe(**1**)]PF$_6$·0.5CH$_2$Cl$_2$.[3] At the time no coordination complex of **2** was known. In the meantime, however, we have prepared (R^*,R^*)-(±)-[(η^5-C$_5$H$_5$){1,2-C$_6$H$_4$(PMePh)$_2$}Fe(**2**)]PF$_6$[3,4] and other workers have reported the synthesis of [W(CO)$_5$(**2**)].[5] 1-Methyl-1-phenylphosphiranium triflate has also been isolated and structurally characterized.[6] A number of dimethyl- to pentamethyl-substituted 1-phenylphosphetanes have been isolated following reductions of the corresponding highly substituted phosphine oxides,[7] and 3-*tert*-butyl-1-phenylphosphetane has been prepared by heteroatom transfer between a 3-*tert*-butyltitanacyclobutane and dichlorophenylphosphine.[8] On the other hand, 2-methyl-1-*tert*-butylphosphirane was prepared in low yield by a direct synthesis involving dilithium *tert*-butylphosphide and 1,2-dichloropropane.[9] We now report that both **1** and **2** can be prepared by direct syntheses between dilithium phenylphosphide and the respective dichloroalkane and that the distilled products can be used to prepare potential cyclotrimerization precursor complexes. A preliminary account of part of this work has been published.[10]

Results and Discussion

(a) Direct Synthesis of 1-Phenylphosphetane (1) and 1-Phenylphosphirane (2). Treatment of a suspension of dilithium phenylphosphide, which was prepared from phenylphosphine and 2.2 equiv of *n*-butyllithium in tetrahydrofuran (THF), with 1,3-dichloropropane at −78 °C, followed by stirring of the reaction mixture at room temperature for 18 h, gave a ca. 1:3 mixture of **1** and poly[(phenylphosphino)propane] (**3**)[11] (Scheme 1). (It had been noted previously that this

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[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1996.

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Scheme 1

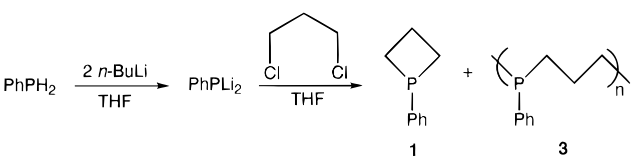
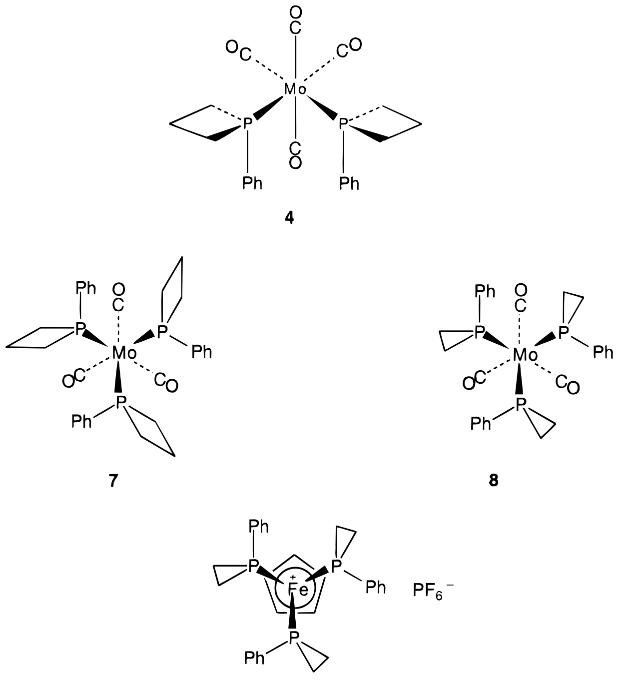


Chart 1



reaction gave **3** only, having δ_P −27 ppm.[8]) Removal of solvent, followed by extraction of the residue with petroleum ether (bp 40−60 °C) and subsequent distillation, gave **1** as a colorless oil, bp 63 °C (0.05 mmHg). Yield based on 1,3-dichloropropane: 13%. Pure **1** rearranges rapidly into **3**, but the rate of polymerization is reduced substantially by quickly diluting the distillate with benzene, whereupon a solution of ca. 4:1 **1**:**3** of considerable stability is obtained. The ^{31}P NMR spectrum of the mixture in benzene-d_6 contains a sharp singlet at 13.9 ppm for the phosphetane and a singlet at −27.2 ppm for the poly[(phenylphosphino)]propane. This material was used for the synthesis of the tricarbonylmolybdenum(0) cyclotrimerization precursor complex, although it was found subsequently that the polymer can be selectively and quantitatively precipitated from the ca. 4:1 **1**:**3** mixture in benzene by treatment with a small quantity of *trans*-[PdCl$_2$(SEt$_2$)$_2$] in the same solvent. The polymer-free solution of **1** in benzene was used for the quantitative preparation of *cis*-tetracarbonylbis(1-phenylphosphetane)molybdenum(0) (**4**) (see Chart 1) from the corresponding η^4-norbornadiene complex by titration with **1** and monitoring of the reaction by ^{31}P{^{1}H} NMR spectroscopy.

A similar reaction between dilithium phenylphosphide and 1,2-dichloroethane afforded **2** in 21% yield after distillation, bp 48 °C (1 mmHg), δ_P −236 ppm [lit.[2] bp 44−48 °C (1.5 mmHg), δ_P −234 ppm], together with 1,4-diphenyl-1,4-diphosphorinane (**5**)[12] and 1,2,3-triphenyl-1,2,3-triphospholane (**6**)[13] (Scheme 2). 1-Phenylphosphirane can be stored at 4 °C for 1 month without sign of polymerization.

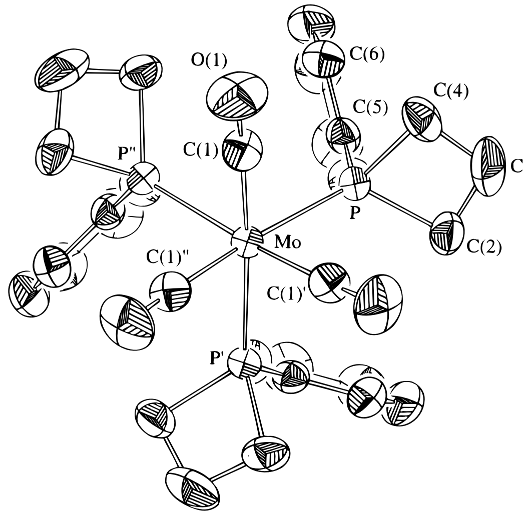
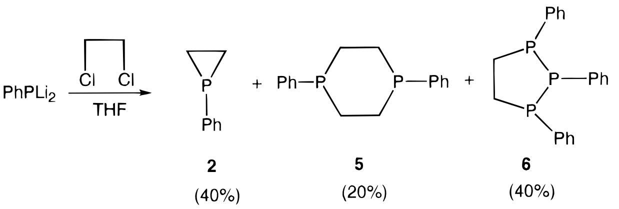


Figure 1. ORTEP view of **7** showing the atom-labeling scheme of selected non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels.

Scheme 2



It is noteworthy that the chemical shift values for the phosphorus nuclei in the heterocycles $\mathrm{Ph}\overline{\mathrm{P}-(\mathrm{CH}_2}\!)_n$ (quoted in ppm relative to 85% aqueous H$_3$PO$_4$) reach a maximum for the phosphetane (n = 3), *viz.* −236 (n = 2), 13.9 (n = 3), −15.3 (n = 4),[14] and −34.3 (n = 5).[14] We are intending to carry out *ab initio* calculations on some of the interesting features of these phosphorus heterocycles.

(b) Synthesis and X-ray Crystal Structures of Cyclotrimerization Precursor Complexes. Benzene solutions of **1** and **2** react with tricarbonyl(η^6-mesitylene)molybdenum(0) to give high yields of *fac*-[Mo(CO)$_3$(**1**)$_3$] (**7**) or *fac*-[Mo(CO)$_3$(**2**)$_3$] (**8**), respectively, both of which were isolated as colorless crystals suitable for X-ray crystallography. Complex [(η^5-C$_5$H$_5$)Fe(**2**)$_3$]PF$_6$ (**9**) was prepared from [(η^5-C$_5$H$_5$)Fe(η^6-C$_6$H$_5$CH$_3$)]PF$_6$ by irradiation in acetonitrile at −40 °C followed by the addition of **2**. Complexes **7**−**9** are the first compounds containing three three- or four-membered phosphorus heterocycles to be structurally characterized. In recent works, the structures of (R*,R*)-(±)-[(η^5-C$_5$H$_5$){1,2-C$_6$H$_4$(PMePh)$_2$}Fe(**2**)]PF$_6$[3,4] and [W(CO)$_5$(**2**)][5] have been reported. The molecular structures of **7**−**9** are given in Figures 1−3, respectively. Crystal data for the three complexes are provided in Table 1. Tables 2, 4, and 6 give positional parameters for the compounds

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Table 1. Crystallographic Data for 7−9

	7	**8**	**9**
formula	$C_{30}H_{33}MoO_3P_3$	$C_{27}H_{27}MoO_3P_3$	$C_{29}H_{32}F_6FeP_4$
mol wt	630.46	588.37	674.30
cryst system	cubic	trigonal	orthorhombic
space group	$I\bar{4}3d$	$P\bar{3}$	*Pbca* (No. 61)
a, Å	22.966(2)	14.321(1)	20.797(6)
b, Å			13.608(6)
c, Å		7.506(1)	21.231(5)
V, Å^3	12 113(2)	1333.2(2)	6008(5)
Z	16	2	8
cryst dimens, mm	0.13 (radius) sphere	0.16 × 0.14 × 0.16	0.26 × 0.32 × 0.28
d_{calcd}, g cm^{-3}	1.382	1.465	1.491
μ, cm^{-1}	6.2	7.0	66.05
X-ray radiation[a]	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Cu Kα (λ = 1.541 78 Å)
diffractometer	Philips PW1100/20	Philips PW1100/20	Rigaku AFC6R
T, °C	20(1)	20(1)	−60(1)
no. of unique data	1377	2242	4993
no. of data used[b]	1075	1831	1945
no. of variables	112	132	234
R^c	0.028	0.024	0.070
$R_w{}^c$	0.032	0.031	0.075
GOF[c]	1.02	1.05	2.20
F(000)	5184	600	2768

[a] Graphite monochromator. [b] $I > 3\sigma(I)$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2\}^{1/2}$; GOF $= \{\sum w(|F_o| - |F_c|)^2/(N_{reflcns} - N_{var})\}^{1/2}$.

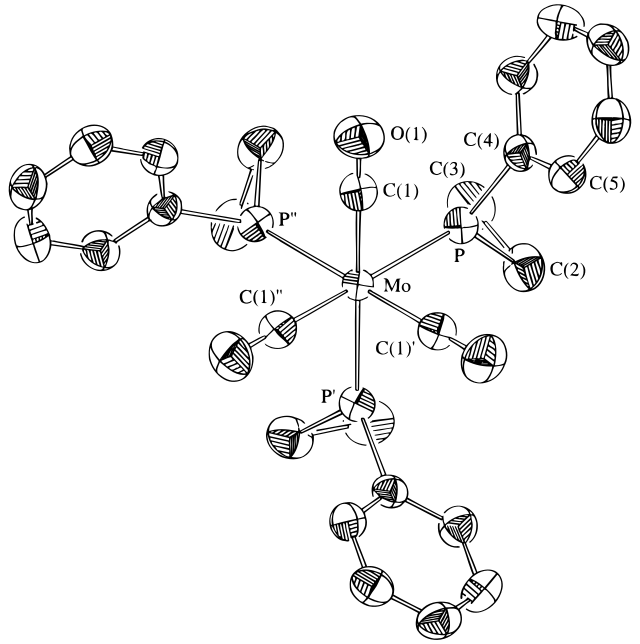

Figure 2. ORTEP view of **8** showing the atom-labeling scheme of selected non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels.

employing the atom-labeling schemes given in Figures 1−3. The most important bond distances and angles for **7**−**9** are listed in Tables 3, 5, and 7, respectively. The two molybdenum complexes have C_3 symmetry in the solid state. The thermal ellipsoid for the central carbon C(3) of each phosphetane ring in **7** is elongated in the direction perpendicular to the C(2), P, C(4) plane, consistent with conformational disorder over two or more sites. Calculations on phosphetane ($HPCH_2CH_2CH_2$) indicated a similarity in energies between two conformers of C_s symmetry, with a pucker angle of 155.63° and a barrier to ring flipping of 5.81 kJ mol^{-1}.[15] The precision of the data for the phosphetane ligands in **7** is greater than that obtained for the corresponding

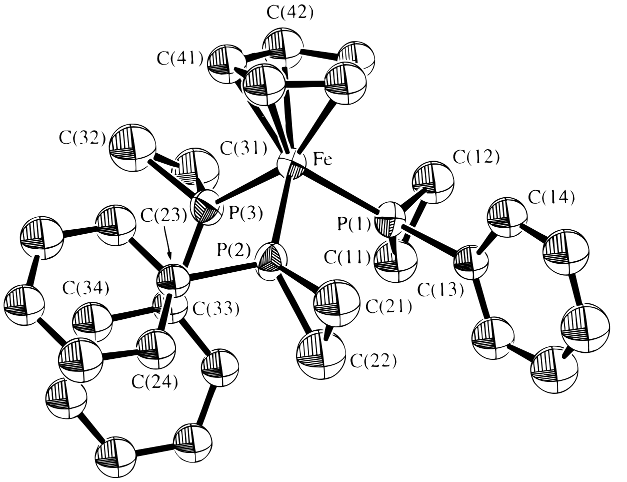

Figure 3. ORTEP view of cation of **9** showing the atom-labeling scheme of selected non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters[a] for Non-Hydrogen Atoms in 7

	x/a	y/b	z/c	U_{eq},[a] Å^2
Mo	0.40202(1)	0.40202(1)	0.40202(1)	0.03257(8)
P	0.38098(5)	0.50827(5)	0.41340(5)	0.0371(3)
C(1)	0.3938(2)	0.4103(2)	0.3169(2)	0.051(2)
O	0.3897(2)	0.4133(2)	0.2670(2)	0.092(2)
C(2)	0.3211(2)	0.5339(2)	0.4609(2)	0.059(2)
C(3)	0.2957(3)	0.5678(4)	0.4124(4)	0.120(4)
C(4)	0.3301(2)	0.5433(2)	0.3612(2)	0.059(2)
C(5)	0.4372(2)	0.5638(2)	0.4238(2)	0.041(1)
C(6)	0.4652(2)	0.5888(2)	0.3768(2)	0.051(2)
C(7)	0.5099(3)	0.6286(2)	0.3855(3)	0.067(2)
C(8)	0.5266(2)	0.6433(3)	0.4409(3)	0.076(2)
C(9)	0.4998(3)	0.6191(3)	0.4877(2)	0.072(2)
C(10)	0.4551(2)	0.5789(2)	0.4796(2)	0.055(2)

[a] $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

ligand in the related iron(II) complex.[3] X-ray crystal structure determinations have been performed also on the complexes *cis*-dichlorobis(3-*tert*-butyl-1-phenylphosphetane)platinum(II)[8] and tricarbonylbis(*trans*-2,2,3,4,4-pentamethyl-1-phenylphosphetane)iron(0).[16] An inter-

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Table 3. Selected Bond Distances and Angles for 7

Distances (Å)			
Mo−P	2.501(1)	C(3)−C(4)	1.526(10)
Mo−C(1)	1.974(4)	C(5)−C(6)	1.382(6)
P−C(2)	1.851(5)	C(5)−C(10)	1.390(6)
P−C(4)	1.857(5)	C(6)−C(7)	1.388(7)
P−C(5)	1.831(4)	C(7)−C(8)	1.370(9)
C(1)−O	1.152(6)	C(8)−C(9)	1.357(9)
C(2)−C(3)	1.480(10)	C(9)−C(10)	1.393(8)
Angles (deg)			
P−Mo−C(1)	89.49(15)	P−C(2)−C(3)	91.0(4)
P−Mo−P′	96.12(4)	C(2)−C(3)−C(4)	100.4(5)
P−M−C(1)′	83.81(13)	P−C(4)−C(3)	89.3(4)
P−Mo−C(1)″	174.36(15)	P−C(5)−C(6)	121.1(3)
C(1)−Mo−C(1)′	90.54(19)	P−C(5)−C(10)	120.1(3)
Mo−P−C(2)	120.98(16)	C(6)−C(5)−C(10)	118.6(4)
Mo−P−C(4)	118.49(17)	C(5)−C(6)−C(7)	120.3(5)
Mo−P−C(5)	123.83(14)	C(6)−C(7)−C(8)	120.2(5)
C(2)−P−C(4)	77.1(2)	C(7)−C(8)−C(9)	120.5(6)
C(2)−P−C(5)	103.1(2)	C(8)−C(9)−C(10)	120.0(5)
C(4)−P−C(5)	103.1(2)	C(5)−C(10)−C(9)	120.4(5)
Mo−C(1)−O	177.8(5)		

[a] Primes (′) indicate atoms generated by the symmetry operation (*z*, *x*, *y*); double primes (″) indicate atoms generated by the symmetry operation (*y*, *z*, *x*).

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters[a] for Non-Hydrogen Atoms in 8

	x/*a*	*y*/*b*	*z*/*c*	U_{eq},[a] Å^2
Mo	$^{1}/_{3}$	$^{2}/_{3}$	0.28868(3)	0.03337(9)
P	0.30934(4)	0.51021(4)	0.47011(6)	0.0387(2)
C(1)	0.2121(2)	0.5637(2)	0.1384(3)	0.0443(9)
O	0.1410(1)	0.5034(1)	0.0509(2)	0.0674(8)
C(2)	0.3970(2)	0.5013(2)	0.6377(3)	0.061(1)
C(3)	0.2893(2)	0.4801(2)	0.7073(3)	0.063(1)
C(4)	0.2453(2)	0.3789(1)	0.3622(3)	0.0387(8)
C(5)	0.2981(2)	0.3611(2)	0.2218(3)	0.0463(9)
C(6)	0.2504(2)	0.2633(2)	0.1335(3)	0.053(1)
C(7)	0.1489(2)	0.1830(2)	0.1833(3)	0.056(1)
C(8)	0.0953(2)	0.2002(2)	0.3169(3)	0.059(1)
C(9)	0.1425(2)	0.2975(2)	0.4074(3)	0.050(1)

[a] $U_{eq} = {}^{1}/_{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Table 5. Selected Bond Distances and Angles for 8

Distances (Å)			
Mo−P	2.4945(6)	C(4)−C(5)	1.393(3)
Mo−C(1)	1.975(2)	C(4)−C(9)	1.388(2)
P−C(2)	1.826(3)	C(5)−C(6)	1.382(3)
P−C(3)	1.821(2)	C(6)−C(7)	1.379(3)
P−C(4)	1.818(2)	C(7)−C(8)	1.358(4)
C(1)−O	1.155(2)	C(8)−C(9)	1.385(3)
C(2)−C(3)	1.508(5)		
Angles (deg)			
P−Mo−C(1)	88.07(7)	P−C(2)−C(3)	65.37(17)
P−Mo−P′	93.04(3)	P−C(3)−C(2)	65.77(15)
P−Mo−C(1)′	88.24(12)	P−C(4)−C(5)	119.17(13)
P−Mo−C(1)″	178.27(7)	P−C(4)−C(9)	122.33(18)
C(1)−Mo−C(1)′	90.63(11)	C(5)−C(4)−C(9)	118.38(18)
Mo−P−C(2)	130.39(8)	C(4)−C(5)−C(6)	120.67(18)
Mo−P−C(3)	132.96(12)	C(5)−C(6)−C(7)	119.73(25)
Mo−P−C(4)	117.22(7)	C(6)−C(7)−C(8)	120.27(22)
C(2)−P−C(3)	48.86(15)	C(7)−C(8)−C(9)	120.59(20)
C(2)−P−C(4)	104.08(13)	C(4)−C(9)−C(8)	120.33(23)
C(3)−P−C(4)	104.59(11)	Mo−C(1)−O	179.85(24)

[a] Primes (′) indicate atoms generated by the symmetry operation (1 − *y*, 1 + *x* − *y*, *z*); double primes (″) indicate atoms generated by the symmetry operation (−*x* + *y*, 1 − *x*, *z*).

Table 6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters[a] for Non-Hydrogen Atoms in 9

	x/*a*	*y*/*b*	*z*/*c*	U_{eq},[a] Å^2
Fe	0.07748(5)	0.75368(10)	0.08534(5)	2.82(2)
P(1)	0.14739(9)	0.7691(1)	0.16228(10)	3.04(5)
P(2)	0.1134(1)	0.6103(2)	0.05398(10)	3.32(5)
P(3)	0.1376(1)	0.8327(2)	0.01776(9)	3.21(5)
C(11)	0.2167(4)	0.8485(6)	0.1682(4)	4.8(2)
C(12)	0.1598(4)	0.8817(6)	0.2060(4)	4.5(2)
C(13)	0.1613(4)	0.6714(6)	0.2197(3)	3.1(2)
C(21)	0.1195(5)	0.4993(7)	0.0986(4)	5.6(2)
C(22)	0.1809(5)	0.5397(7)	0.0844(4)	6.2(3)
C(23)	0.1055(4)	0.5706(6)	−0.0288(3)	3.0(2)
C(31)	0.1523(5)	0.9646(7)	0.0180(4)	5.7(2)
C(32)	0.1089(5)	0.9290(7)	−0.0333(4)	5.6(2)
C(33)	0.2071(4)	0.7814(6)	−0.0218(4)	3.3(2)

[a] $U_{eq} = {}^{1}/_{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Table 7. Selected Bond Distances and Angles for 9

Distances (Å)			
Fe−P(1)	2.197(3)	P(2)−C(23)	1.85(1)
Fe−P(2)	2.193(4)	P(3)−C(31)	1.82(1)
Fe−P(3)	2.186(4)	P(3)−C(32)	1.80(1)
P(1)−C(11)	1.81(1)	P(3)−C(33)	1.81(1)
P(1)−C(12)	1.81(1)	C(11)−C(12)	1.50(2)
P(1)−C(13)	1.83(1)	C(21)−C(22)	1.42(2)
P(2)−C(21)	1.79(1)	C(31)−C(32)	1.50(2)
P(2)−C(22)	1.82(1)		
Angles (deg)			
P(1)−Fe−P(2)	94.9(1)	P(2)−C(21)−C(22)	67.9(8)
P(1)−Fe−P(3)	93.6(1)	P(2)−C(22)−C(21)	65.6(8)
P(2)−Fe−P(3)	92.5(1)	Fe−P(3)−C(31)	125.4(5)
Fe−P(1)−C(11)	129.6(4)	Fe−P(3)−C(32)	124.3(5)
Fe−P(1)−C(12)	123.8(4)	Fe−P(3)−C(33)	124.8(4)
Fe−P(1)−C(13)	122.1(4)	P(3)−C(31)−C(32)	65.0(8)
P(1)−C(11)−C(12)	65.7(7)	P(3)−C(32)−C(31)	66.2(8)
P(1)−C(12)−C(11)	65.3(7)	C(11)−P(1)−C(13)	105.3(6)
Fe−P(2)−C(21)	128.0(5)	C(21)−C(2)−C(23)	105.3(6)
Fe−P(2)−C(22)	128.7(5)	C(31)−C(3)−C(33)	104.3(6)
Fe−P(2)−C(23)	121.3(4)		

esting feature of the structures of **7** and **8** is that the phenyl groups of the 1-phenylphosphetane ligands in **7** are arranged anti to the carbonyl ligands, whereas in **8** the phenyl groups of the 1-phenylphosphirane ligands form a belt around the middle of the molecule syn to the carbonyls. In **9**, however, the phenyl groups of the 1-phenylphosphirane adopt anti dispositions with respect to the bulky cyclopentadienyl group, which is an indication of the importance auxiliary ligands could have on the attempted conversion of **1** and **2** into face-capping tridentates by cyclotrimerization on metal templates.

Conclusion

1-Phenylphosphetane (**1**) and 1-phenylphosphirane (**2**) have been synthesized directly from dilithium phenylphosphide and the appropriate terminal dichloroalkane in THF. The phosphetane polymerizes rapidly in the neat state but has considerable stability in benzene. The two heterocycles have extreme ^{31}P NMR chemical shifts, *viz.* 13.9 ppm for **1** and −236 ppm for **2** in benzene. The phosphines react with tricarbonyl(η^6-mesitylene)molybdenum(0) to give high yields of the potential cyclotrimerization precursor complexes *fac*-[Mo(CO)$_3$(**1**)$_3$] and *fac*-[Mo(CO)$_3$(**2**)$_3$]. 1-Phenylphosphirane also reacts with the iron complex [(η^5-C_5H_5)Fe(η^6-$C_6H_5CH_3$)]PF_6 in acetonitrile to give the cationic cyclotrimerization precursor complex [(η^5-C_5H_5)Fe(**2**)$_3$]-PF_6. The phenyl groups of the three- and four- membered phosphorus heterocycles are arranged in groups of three syn or anti to the auxiliary ligands in the three

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(16) Bennett, D. W.; Grubisha, D. S.; Cremer, S. E.; Peterson, A. C. *J. Crystallogr. Spectrosc. Res.* **1992**, *22*, 83.

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complexes, which could be an important factor in determining the outcome of cyclotrimerization reactions.

Experimental Section

All reactions were performed in an atmosphere of dry argon using the Schlenk technique. Solvents were purified by conventional literature methods; petroleum ether had a boiling point of 40−60 °C. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 25 °C on a Varian XL 200E or VXR 300 S spectrometer operating at 200.04 or 299.95 MHz and at 80.98 or 121.42 MHz, respectively. ^{13}C{^{1}H} NMR spectra were recorded at 25 °C on Varian XL 200E, VXR 300S, or VXR 500S spectrometer operating at 50.31, 75.43, or 125.70 MHz. The chemical shifts were referenced to Me_4Si (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P) with downfield chemical shifts being positive. IR spectra were recorded on a Model 683 Perkin-Elmer infrared spectrophotometer. Mass spectra were recorded on a VG Micromass 7070F double-focusing mass spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical ZAB-2SEQ mass spectrometer (ionization: 30 keV Cs^+ ions) in a matrix of 3-nitrobenzyl alcohol and methanol as solvent. Elemental analyses were performed by staff within the Research School of Chemistry.

1-Phenylphosphetane (1). Dilithium phenylphosphide was prepared from phenylphosphine (10.65 g, 96.74 mmol) and 2.2 equiv of *n*-butyllithium in THF. The pyrophoric yellow powder was suspended in THF (1 L), and 1,3-dichloropropane (10.00 g, 88.5 mmol) was added with stirring at −78 °C. After 30 min, the mixture was allowed to warm to room temperature and stirring was continued for 18 h. The solvent was removed from the reaction mixture in vacuo, and the residue was extracted with petroleum ether (150 mL). Filtration of the mixture, followed by removal of the solvent under reduced pressure and distillation of the residue, gave 1-phenylphosphetane as a clear mobile oil: bp 63 °C (0.05 mmHg); yield 1.71 g (13%, purity 80%). ^{1}H NMR (C_6D_6, 200.04 MHz): δ 1.55−2.60 (m, 6 H, CH_2), 6.90−7.45 (m, 5 H, aromatics). ^{13}C{^{1}H} NMR (C_6D_6, 50.30 MHz): δ 22.19 (d, ^{1}J(CP) = 6.0 Hz, $\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2}$), 24.63 (d, ^{2}J(CP) = 2.4 Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 127.77 (s, 4-Ar*C*), 128.57 (d, ^{3}J(CP) = 4.9 Hz, 3-Ar*C*), 130.58 (d, ^{2}J(CP) = 16.5 Hz, 2-Ar*C*), 143.54 (d, ^{1}J(CP) = 31.4 Hz, 1-Ar*C*). ^{31}P{^{1}H} NMR (C_6D_6, 80.98 MHz): δ 13.90 (s, 80%, monomer), −27.17 (s, 20%, polymer). MS: *m/e* 150.0 amu ([M]$^{\bullet+}$).

Selective Precipitation of Polymer from 1. A solution of *trans*-[$PdCl_2(SEt_2)_2$] in benzene (4 mL, 1.12% w/v) was added to a solution of distilled **1** (380 mg, 2.02 mmol, 80% purity) in benzene (50 mL). A voluminous yellow precipitate formed. Filtration of the reaction mixture afforded a clear colorless solution of pure **1**, as indicated by ^{31}P{^{1}H} NMR spectroscopy.

***cis*-Tetracarbonylbis(1-phenylphosphetane)molybdenum(0) (4).** A solution of pure **1** in benzene (ca. 60 mL) was treated at room temperature with a solution of tetracarbonyl(η^4-norbornadiene)molybdenum(0) in benzene (0.053 M). The progress of the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. After the addition of 9.0 mL of the solution of the molybdenum complex (0.48 mmol) to the phosphine, the singlet for the free ligand at δ_P 13.9 ppm had disappeared and was replaced by the signal at δ_P 60.49 ppm for the product. The solvent was removed from the reaction mixture under reduced pressure, and the residue was chromatographed on a short column of silica gel with benzene as eluant. The solvent was removed from the eluate in vacuo, the residue was dissolved in diethyl ether (1.5 mL), and *n*-hexane (8 mL) was added. The solution was concentrated to ca. 8 mL in vacuo, and then it was cooled to −28 °C. The colorless, crystalline product was filtered off, washed twice with *n*-hexane at −78 °C, and dried in vacuo. Yield: 140 mg (58%); mp 91 °C. Anal. Calcd for $C_{22}H_{22}MoO_4P_2$: C, 52.0; H, 4.4; P, 12.2. Found: C, 51.9; H, 4.4; P, 12.3. ^{1}H NMR (CD_2Cl_2, 200.05 MHz): δ 2.10−2.75 (m, 12 H, CH_2), 7.30−7.60 (m, 10 H, aromatics). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.43 MHz): δ 23.65−24.50 (m, $\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 27.90−28.90 (m, $\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2}$), 128.74−128.95 (m, 3-Ar*C*), 128.99 (s, 4-Ar*C*), 129.24−129.54 (m, 2-Ar*C*), 141.38−141.73 (m, 1-Ar*C*), 209.62 (t, ^{2}J(CP) = 9.8 Hz, CO_{cis}), 216.02 (dd, $^{2}J(CP_{cis}) = {}^{2}J(CP_{trans})$ = 7.9 Hz, CO_{trans}). ^{31}P{^{1}H} NMR (CD_2Cl_2, 80.98 MHz): δ 60.49 (s). IR (*n*-hexane): 1912, 1933, 2022 cm^{-1} (ν_{CO}). MS: *m/e* 508 amu ([M]$^{\bullet+}$).

1-Phenylphosphirane (2). Dilithium phenylphosphide (from phenylphosphine (9.54 g, 86.66 mmol) and 2.2 equiv of *n*-butyllithium in THF) was suspended in THF (1 L), and 1,2-dichloroethane (7.65 g, 77.3 mmol) was added with stirring at −78 °C. After 30 min, the mixture was allowed to warm to room temperature and stirring was continued for 18 h. The solvent was removed from the reaction mixture in vacuo, and the residue was extracted with petroleum ether (150 mL). Filtration of the mixture, followed by removal of the solvent under reduced pressure and distillation of the residue, gave 1-phenylphosphirane as a clear mobile oil: bp 48 °C (1 mmHg) [lit.[2] bp 44−48 °C (1.5 mmHg); yield 2.21 g (21%). ^{1}H NMR (C_6D_6, 200.04 MHz): δ 0.78−1.09 (m, 4 H, CH_2), 6.90−7.27 (m, 5 H, aromatics). ^{13}C{^{1}H} NMR (C_6D_6, 50.30 MHz): δ 10.09 (d, ^{1}J(CP) = 40.3 Hz, CH_2), 128.37 (s, 4-Ar*C*), 128.50 (s, 3-Ar*C*), 131.88 (d, ^{2}J(CP) = 19.6 Hz, 2-Ar*C*), 139.81 (d, ^{1}J(CP) = 39.6 Hz, 1-Ar*C*), 216.75−217.03 (m, CO). ^{31}P{^{1}H} NMR (CD_2Cl_2, 80.98 MHz): δ −236.60 (s).

***fac*-Tricarbonyltris(1-phenylphosphetane)molybdenum(0) (7).** A solution of tricarbonyl(η^6-mesitylene)molybdenum(0) (230 mg, 0.76 mmol) in dichloromethane (20 mL) was slowly added to a solution of **1** (425 mg, 2.83 mmol, 80% purity) in benzene (25 mL). After being stirred at room temperature for 14 h, the reaction mixture was subjected to flash chromatography on silica with dichloromethane. Removal of the solvents from the eluate in vacuo afforded a colorless solid that was dissolved in THF (5 mL) and crystallized by the addition of petroleum ether (25 mL), giving the pure product as colorless prisms: mp 189 °C; yield 390 mg (81%). Anal. Calcd for $C_{30}H_{33}MoO_3P_3$: C, 57.2; H, 5.3; P, 14.9. Found: C, 57.0; H, 5.3; P, 14.7. ^{1}H NMR (CD_2Cl_2, 299.95 MHz): δ 1.89−2.50 (m, 18 H, CH_2), 7.23−7.42 (m, 15 H, aromatics). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.70 MHz): δ 24.46−24.52 (m, $\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 28.10−28.90 (m, $\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2}$), 128.56−128.64 (m, 4-Ar*C*), 128.74−128.87 (m, 3-Ar*C*), 129.88−130.04 (m, 2-Ar*C*), 143.20−143.37 (m, 1-Ar*C*), 219.86−220.06 (m, CO). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.42 MHz): δ 64.25 (s with satellites (sextet), $^{1}J(^{31}P^{95}Mo)$ = 126.7 Hz). IR (CH_2Cl_2): 1848, 1941 cm^{-1} (ν_{CO}). FAB-MS: *m/e* 630 amu ([M]$^{\bullet+}$).

***fac*-Tricarbonyltris(1-phenylphosphirane)molybdenum(0) (8).** A solution of tricarbonyl(η^6-mesitylene)molybdenum(0) (279 mg, 0.93 mmol) in dichloromethane (16 mL) was added to a solution of **2** (399 mg, 2.93 mmol) in benzene (40 mL). After being stirred at room temperature for 20 h, the mixture was heated under reflux for 150 min. Flash chromatography on silica with benzene, followed by removal of the solvents in vacuo and two recrystallizations of the residue from hot toluene, afforded the desired complex as almost colorless prisms: mp 141 °C; yield 380 mg (70%). Anal. Calcd for $C_{27}H_{27}MoO_3P_3$: C, 55.1; H, 4.6; P, 15.8. Found: C, 55.7; H, 4.7; P, 15.5. ^{1}H NMR (CD_2Cl_2, 200.04 MHz): δ 0.89−1.48 (m, 12 H, CH_2), 7.15−7.50 (m, 15 H, aromatics). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.70 MHz): δ 10.20−10.40 (m, CH_2), 128.73−128.85 (m, 3-Ar*C*), 129.54 (s, 4-Ar*C*), 132.30−132.42 (m, 2-Ar*C*), 138.14−138.35 (m, 1-Ar*C*), 216.75−217.03 (m, CO). ^{31}P{^{1}H} NMR (CD_2Cl_2, 80.98 MHz): δ −164.60 (s with satellites (sextet), $^{1}J(^{31}P^{95}Mo)$ = 143.5 Hz). IR (CH_2Cl_2): 1856, 1950 cm^{-1} (ν_{CO}). FAB-MS: *m/e* 588 amu ([M]$^{\bullet+}$).

(η^5-Cyclopentadienyl)tris(1-phenylphosphirane)iron(II) Hexafluorophosphate (9). The complex [(η^5-C_5H_5)Fe(η^6-$C_6H_5CH_3$)]PF_6 (0.93 g, 2.60 mmol) was dissolved in acetonitrile (10 mL), and the temperature of the solution was lowered to −40 °C in a refrigerated cold bath. The stirred solution was then irradiated with a 100 W mercury immersion lamp for ca. 15 h, whereupon the bright yellow solution became deep

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purple, consistent with the formation of $[(\eta^5\text{-}C_5H_5)Fe(NCCH_3)_3]PF_6$.[17] A solution of **2** (1.18 g, 8.67 mmol) in toluene (5 mL) was added to the cold acetonitrile solution of the intermediate, and stirring was continued for 10 min at this temperature, followed by 8 h stirring at room temperature. The acetonitrile was removed under reduced pressure, and the orange oil was dissolved in dichloromethane (ca. 3 mL) and transferred to a 2 mm silica gel Chromatotron plate. The product was eluted as a deep orange band with use of an acetone−dichloromethane (10/90) mixture. Removal of solvents from the eluate afforded the crude product, which after recrystallization from dichloromethane−diethyl ether formed orange prisms: mp 182−185 °C; yield 0.36 g (21%). Anal. Calcd for $C_{29}H_{32}F_6FeP_4$: C, 51.7; H, 4.8; P, 18.4. Found: C, 51.8; H, 4.8; P, 18.2. ^{1}H NMR (CD_2Cl_2, 299.95 MHz): δ 0.93−1.66 (m, 12 H, CH_2), 4.49 (q, ^2J(HP) = 2.1 Hz, 5 H, C_5H_5), 7.36−7.47 (m, 15 H, aromatics). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.43 MHz): δ 9.95−10.03 (m, CH_2), 80.78 (s, C_5H_5), 129.38−129.51 (m, 3-Ar*C*), 131.00 (s, 4-Ar*C*), 131.87−132.02 (m, 2-Ar*C*), 135.86−136.33 (m, 1-Ar*C*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.42 MHz): δ −121.62 (s). FAB-MS: *m/e* 529 amu ($[M-PF_6]^{\bullet+}$).

Crystal Structure Analyses. Crystal data for **7**−**9** are given in Table 1. Data sets for **7** and **8** were collected using $\omega-2\theta$ scans of width $(1.0 + 0.3 \tan \theta)°$ with a scan speed in ω of 0.5° min^{-1} for **7** and 1° min^{-1} for **8**. Data for **9** were collected at −60 ± 1 °C using $\omega-2\theta$ scans of width $(0.90 + 0.30 \tan \theta)°$ with a scan speed of 8.0° min^{-1}. The intensities of three representative reflections were measured periodically. Whereas no significant decrease in intensities during data collection was observed for **8** or **9**, a decay correction of 4% was applied to **7**. Data were also corrected for absorption (transmission ranges: 0.886−0.887 for **7**, 0.890−0.895 for **8**, and 0.86−1.00 for **9**).[18] The structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques. The hydrogen atoms were included in calculated positions ($r_{C-H} = 0.95$ Å). For **7** and **9** these parameters were not refined; for **8**, however, they were allowed to refine in the crystallographic least-squares procedure but with one common isotropic displacement factor for the methylene and the phenyl hydrogen atoms. Individual anisotropic displacement factors were employed for all non-hydrogen atoms in compounds **7** and **8** and for all non-carbon and non-hydrogen atoms in **9**, including the major component of the PF_6^- ion. The PF_6^- ion in **9** was refined over two positions, with bond and angle restraints imposed on the ill-behaved minor component. The displacement factor on C(3) in **7** was observed to be elongated at right angles to the C(2), C(3), C(4) plane, suggesting that this atom was disordered over two or more sites. A model was tested with two isotropic sites, C(3A) and C(3B) of occupancy *p* and $1 - p$, respectively, one above and one below the plane. This model, however, was not significantly better than the ordered representation at the corresponding stage of refinement, suggesting that C(3) may be disordered over more than two sites. Accordingly, the atom was described by using the anisotropic displacement factors of the former (“ordered”) model. Interpolated form factors were introduced, and refinement was continued until all shift/error ratios were <0.02. Refinement for **8** was also continued until all shift/error ratios were <0.02. Least-squares refinement was performed for all three structures using full-matrix methods. Maximum and minimum heights in a final difference map were 0.31 and −0.25 e $Å^{-3}$ for **7**, 0.30 and −0.21 e $Å^{-3}$ for **8**, and 0.71 and −0.46 e $Å^{-3}$ for **9**. Data reduction and refinement computations for **7** and **8** were performed with XTAL3.2;[19] data reduction and refinement computations for **9** were performed with teXsan.[20] Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 21.

Supporting Information Available: For **7**−**9**, text describing X-ray procedures, tables of data collection parameters, bond distances and angles, thermal parameters for non-hydrogen atoms, calculated hydrogen atom parameters, least-squares planes, and selected torsion angles, and ORTEP diagrams (52 pages). Ordering information is given on any current masthead page.

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