277. Transition Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. VI[1]). The Preparation of Some Diaryl- and Dialkyl Derivatives of 2,11-Bis(phosphinomethyl)benzo[*c*]phenanthrene

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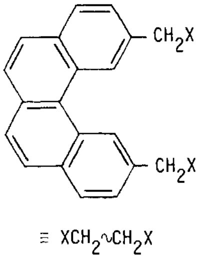
Summary

The preparation of the ditertiary phosphines 2,11-bis(di-*m*-tolylphosphinomethyl)benzo[*c*]phenanthrene (**1b**), 2,11-bis(di-*p*-anisylphosphinomethyl)benzo[*c*]phenanthrene (**1c**), 2,11-bis(di-*m*-trifluoromethylphenylphosphinomethyl)benzo[*c*]phenanthrene (**1d**), 2,11-bis(dicyclohexylphosphinomethyl)benzo[*c*]phenanthrene (**1e**) and 2,11-bis[di-(*t*-butyl)phosphinomethyl]benzo[*c*]phenanthrene (**1f**), by a combination of synthetic routes is described.

Introduction. - In earlier publications [1] the preparation of the ditertiary phosphine 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1a**) and some of its coordination chemistry were described. The development of this study required the preparation of complexes of analogous phosphines having different electronic and steric properties and/or different solubility characteristics. This paper describes the preparation of ligands **1b** to **1f**.



1a X = Ph_2P-
1b X = $(m\text{-}CH_3 \cdot C_6H_4)_2P$-
1c X = $(p\text{-}CH_3O \cdot C_6H_4)_2P$-
1d X = $(m\text{-}CF_3 \cdot C_6H_4)_2P$-
1e X = $(C_6H_{11})_2P$-
1f X = $t\text{-}Bu_2P$-
1g X = Br

Results and discussion. - The new ligands were prepared using a combination of the reactions shown in the *Scheme*. Relevant comments to these reactions are:

Reaction 1. The cleavage of a P–C bond in $(m\text{-}CH_3 \cdot C_6H_4)_3P$, using sodium in liquid ammonia [2], followed by hydrolysis, gave $(m\text{-}CH_3 \cdot C_6H_4)_2PH$ in good yield. The same reaction using $(m\text{-}CF_3 \cdot C_6H_4)_3P$, however, led only to the partial recovery of starting material.

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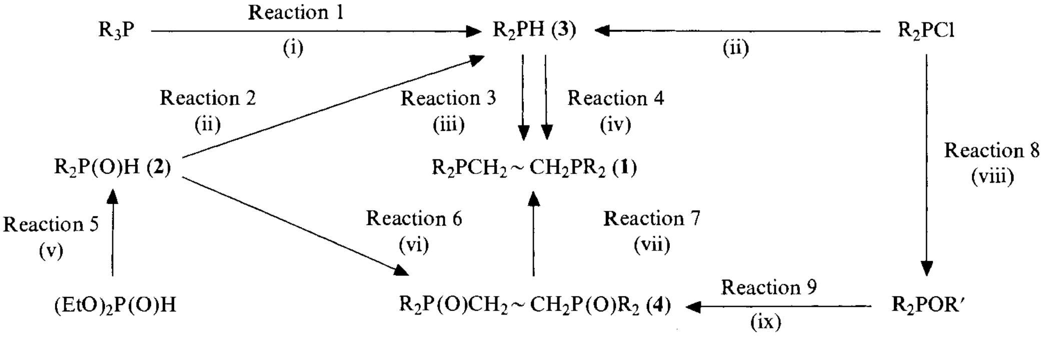
[1]) Part V: See [1].

Scheme



(i) Na in liq. NH_3 followed by hydrolysis. (ii) $LiAlH_4$ in Et_2O. (iii) *n*-BuLi in THF followed by **1g**. (iv) **1g** in *iso*-BuC(O)Me followed by NaOH. (v) RMgBr followed by HCl. (vi) *n*-BuLi in THF followed by **1g** in THF. (vii) $SiHCl_3$ and *n*-Bu_3N in MeCN. (viii) $R'O^-$ in R'OH. (ix) **1g**.

Reaction 2. Compounds of the type $R_2P(O)X$ have been reduced to corresponding secondary phosphines using a variety of reducing agents, the most common being $LiAlH_4$ [3]. This reagent was successfully used for the reduction of $(m\text{-}CF_3 \cdot C_6H_4)_2P(O)H$ to **3d**. However, from the $LiAlH_4$ reduction of $(p\text{-}CH_3O \cdot C_6H_4)_2P(O)H$ no secondary phosphine was formed and only small amounts of $(p\text{-}CH_3O \cdot C_6H_4)_2PCH_3$ could be isolated. This type of reaction has been observed previously [3], *e.g.*, the reduction of $Ph(p\text{-}CH_3O \cdot C_6H_4)P(O)H$ gave a mixture of $Ph(p\text{-}CH_3O \cdot C_6H_4)PH$ and $Ph(p\text{-}CH_3O \cdot C_6H_4)PCH_3$. However, $(p\text{-}CH_3O \cdot C_6H_4)_2P(O)H$ was not reduced by $Li[AlH(O{-}t\,Bu)_3]$ in refluxing THF and its reaction with Si_2Cl_6 in benzene gave several products which were not investigated further.

Reaction 3. This is the standard method of preparation of ligand **1a** [4] and was successfully used for the preparation of ligands **1b** and **1d**. When R_2PH ($R = C_6H_{11}$ and *t*-Bu) were used in this reaction it was shown by ^{31}P-NMR. spectroscopy that mixtures of products were formed. The desired compounds **1e** and **1f** were present in significant amounts but could not be conveniently isolated.

Reaction 4. This reaction has been extensively used for the preparation of tertiary phosphines containing *t*-butyl groups [5]. Ligand **1f** was obtained by this method in *ca.* 30% yield. Preliminary results indicate that ligand **1e** can also be obtained by this reaction.

Reaction 5. This appears to be one of the most convenient methods for the selective introduction of two R-groups onto a phosphorus atom [6]. It was used to obtain intermediates **2c**, **2d** and **2e**.

Reaction 6. Hays [6] reports the successful preparation of tertiary phosphine oxides by the reaction of alkyl halides on $R_2P(O)MgX$ obtained *in situ* by reaction 5. Better results were obtained by starting from pure $R_2P(O)H$, adding *n*-BuLi followed by **1g**. While this reaction gave the desired product when R was $p\text{-}CH_3O \cdot C_6H_4$, when R was C_6H_{11} a complex mixture of products, containing some **4e**, was obtained.

Reaction 7. Although the reduction of tertiary phosphine oxides to the corresponding phosphines can be carried out using a variety of reagents [7], difficulties were encountered in reducing ditertiary bis-phosphine oxides. Thus, $Ph_2P(O)CH_2\sim CH_2P(O)Ph_2$ was not reduced by $SiHCl_3$, in benzene solution in the presence of p-$CH_3\cdot C_6H_4NEt_2$, while Si_2Cl_6 in $CHCl_3$ gave only incomplete reduction. The best reducing system for compounds of type **4** proved to be $SiHCl_3$ and n-Bu_3N in acetonitrile [8].

Reaction 8. Compounds of the type $R_2P(OR')$ are generally prepared by reaction of R_2PCl and R'OH in the presence of a nitrogen base and it is stated that the use of sodium alkoxides is less satisfactory [9]. We find that while $(C_6H_{11})_2P$(O-*iso*Pr) can be obtained from $(C_6H_{11})_2PCl$, *iso*-PrOH and Et_3N, the preparation of t-Bu_2P(O-*iso* Pr) requires the action of *iso*-PrONa on t-Bu_2PCl.

Reaction 9. This reaction [10] provides a very convenient method of preparation for compounds of type **4** from R_2P(O-*iso* Pr) and **1g** even when R = t-Bu.

The analytical and NMR. data for the new compounds characterized are given in *Tables 1* and *2* respectively.

Table 1. *Analytical Data for Ditertiary Phosphines and Their Precursors*

	Compound		C (%)	H (%)	P (%)	Mol. Wt.
1b	$(m\text{-}CH_3\cdot C_6H_4)_2PCH_2\sim CH_2P(m\text{-}CH_3\cdot C_6H_4)_2$	Found	84.78	6.15	8.94	668
		Calcd.	84.71	6.22	9.11	681
1c	$(p\text{-}CH_3O\cdot C_6H_4)_2PCH_2\sim CH_2P(p\text{-}CH_3O\cdot C_6H_4)_2$	Found	77.27	5.80	8.34	794
		Calcd.	77.40	5.68	8.32	745
1d	$(m\text{-}CF_3\cdot C_6H_4)_2PCH_2\sim CH_2P(m\text{-}CF_3\cdot C_6H_4)_2$	Found	64.40	3.34	7.22	877
		Calcd.	64.30	3.37	6.91	897
1e	$(C_6H_{11})_2PCH_2\sim CH_2P(C_6H_{11})_2$	Found	81.31	9.03	9.45	629
		Calcd.	81.44	9.00	9.56	649
1f	$(t\text{-}Bu)_2PCH_2\sim CH_2P(t\text{-}Bu)_2$	Found	79.36	9.29	11.28	537
		Calcd.	79.37	9.25	11.38	545
2c	$(p\text{-}CH_3O\cdot C_6H_4)_2P(O)H$	Found	64.01	5.78	11.73	
		Calcd.	64.14	5.73	11.83	
2d	$(m\text{-}CF_3\cdot C_6H_4)_2P(O)H$	Found	49.75	2.69	9.23	
		Calcd.	49.72	2.66	9.17	
2e	$(C_6H_{11})_2P(O)H$	Found	66.36	10.61		
		Calcd.	67.25	10.84		
3d	$(m\text{-}CF_3\cdot C_6H_4)_2PH$	Found	52.21	2.91	9.53	
		Calcd.	52.19	2.80	9.62	
4b	$(m\text{-}CH_3\cdot C_6H_4)_2P(O)CH_2$	Found	77.86	5.41		
	$\sim CH_2P(O)(m\text{-}CH_3\cdot C_6H_4)_2\cdot 0.25\,CHCl_3$	Calcd.	78.03	5.73		
4c	$(p\text{-}CH_3O\cdot C_6H_4)_2P(O)CH_2\sim CH_2P(O)(p\text{-}CH_3O\cdot C_6H_4)_2$	Found	74.26	5.46	8.12	
		Calcd.	72.21	5.44	7.98	
4d	$(m\text{-}CF_3\cdot C_6H_4)_2P(O)CH_2\sim CH_2P(O)(m\text{-}CF_3\cdot C_6H_4)_2$	Found	62.08	3.29	6.84	
		Calcd.	62.08	3.26	6.68	
4e	$(C_6H_{11})_2P(O)CH_2\sim CH_2P(O)(C_6H_{11})_2$	Found	77.05	8.55	8.97	
		Calcd.	77.61	8.59	9.10	
4f	$(t\text{-}Bu)_2P(O)CH_2\sim CH_2P(O)(t\text{-}Bu)_2$	Found	75.06	8.74	10.64	
		Calcd.	74.96	8.74	10.75	

Table 2. *NMR. Parameters for Ditertiary Phosphines and Their Precursors*

Compound	$^{\delta}1,12$[a] [ppm]	$^{\delta}CH_2$ [ppm]	$^{\delta}CH_3$ [ppm]	$^{\delta}{=}P{-}H$ [ppm]	$^1J(^{31}P,^1H)$[b] [Hz]	$^2J(^{31}P,^1H)$ [Hz]	$\delta^{31}P$[c] [ppm]
1b	8.92(*s*)	3.70(*s*)	2.19(*s*)				− 9.0
1c	8.94(*s*)	3.63(*s*)	3.74(*s*)				− 11.6
1d	9.15(*s*)	3.75(*s*)					− 8.6
1e	9.11(*s*)	3.16(*s*)					+ 3.8
1f	9.12(*s*)	3.20(*d*)	1.20(*d*)[d]			3.36	+ 35.6
2c			3.78(*s*)	8.03(*d*)	475.6		+ 20.5
2d				8.24(*d*)	492.7		+ 17.8
2e				6.22(*d*)	433.7		+ 49.5
3d				5.36(*d*)	219.7		− 40.9
4b	9.41(*s*)	4.12(*d*)	2.17(*s*)			13.80	+ 30.2
4c	9.34(*s*)	4.05(*d*)	3.74(*s*)			13.73	+ 30.3
4d	9.41(*s*)	4.30(*d*)				13.20	+ 28.8
4e	9.45(*s*)	3.52(*d*)				11.90	+ 49.2
4f	9.60(*s*)	3.68(*d*)	1.25(*d*)[e]			10.68	+ 48.4
5e			1.11(*d*)[f]				+ 138.5
5f			[g]				+ 150.7

[a] Shift of protons at positions 1 and 12 of the benzo[*c*]phenanthrene ring.

[b] For H directly bonded to P.

[c] Relative to an external H_3PO_4 standard; shifts to higher fields are denoted as negative and those to lower fields as positive.

[d] $^3J(^{31}P,^1H) = 12.29$ Hz.

[e] $^3J(^{31}P,^1H) = 13.12$ Hz.

[f] $\delta_{CH} = 3.68$ ppm (doublet of septets); $^3J(^1H,^1H) = 6.10$ Hz; $^3J(^{31}P,^1H) = 9.33$ Hz.

[g] $\delta_{CH_3(t\text{-Bu})} = 1.09$(*d*) ppm; $^3J(^{31}P,^1H_{(t\text{-Bu})}) = 12.29$ Hz; $\delta_{CH_2(i\text{-Pr})} = 1.22$(*d*) ppm; $^3J(^1H_{CH},{}^1H_{CH_3(i\text{-Pr})}) = 6.10$ Hz; $\delta_{CH} = 3.83$ ppm (doublet of septets); $^3J(^{31}P,^1H) = 1.22$ Hz.

Experimental Part

Melting points were determined using a *Büchi* melting point apparatus and are uncorrected. ^1H- and ^{31}P-NMR. spectra were recorded on a *Bruker* HX 90 FT spectrometer at frequencies of 90.00 and 36.43 MHz respectively, the ^2H-resonance of the deuterated solvent being used as internal lock. ^1H-chemical shifts are in ppm with respect to an internal TMS standard whilst the ^{31}P-chemical shifts are in ppm relative to an external H_3PO_4-standard. Shifts to higher fields are denoted as negative and those to lower fields as positive. ^{31}P-NMR. spectra were obtained under conditions of broad-band ^1H-noise decoupling. Elemental analyses and molecular weight determinations were performed by the *Microanalytical Laboratory* of the ETH Zürich. All preparations were carried out under a nitrogen atmosphere in dried and de-oxygenated solvents.

1b. - $(m\text{-}CH_3 \cdot C_6H_4)_2PLi$ was prepared by the addition of 9.0 ml of a 1.67M solution (15.03 mmol) of *n*-BuLi in hexane to a stirred solution of 3.1 g (14.47 mmol) of $(m\text{-}CH_3 \cdot C_6H_4)_2PH$ [2] in 15 ml THF which had been cooled to 0°. The resulting orange-brown solution was stirred for 1 h at RT., cooled to 0° and treated with a solution of 3.0 g (7.24 mmol) **1g** in 10 ml THF. The resulting light yellow solution was stirred for 2 h at RT. and the solvent evaporated under reduced pressure. The residue was dissolved in 30 ml $CHCl_3$ and the solution washed with 3 × 20 ml water. The organic layer was dried over $MgSO_4$ and the solution was evaporated under reduced pressure. The resulting oil was washed first with methanol and then with light petroleum (40-60°) leaving a spongy solid which, after drying i.V., gave the product (3.3 g, 67%) as pale yellow powder. This became oily at 140° and melted to a clear liquid from 195 to 200°.

1c. - 6.8 g (5.0 ml, 50.1 mmol) $SiHCl_3$ and 9.1 g (7 ml, 49.0 mmol) *n*-Bu_3N were added to a suspension of 2.0 g (2.57 mmol) **4c** in 100 ml CH_3CN. The mixture was refluxed for 4 h and then left overnight at RT. The solvent was evaporated under reduced pressure and the waxy residue dissolved in 100 ml $CHCl_3$. The solution was washed successively with 80 ml 30% NaOH-solution and 2× 100 ml water and dried over $MgSO_4$. The yellow oil obtained after evaporation of the solvent was washed with light petroleum (30-60°) and the residual yellow solid was recrystallized from benzene/light petroleum. The product (1.1 g, 57%) melted over the range 145-148°.

1d. - It was prepared and purified as described for compound **1b**. 4.0 g (12.4 mmol) **3d**, 6.1 ml of a 2.04M solution of *n*-BuLi (12.4 mmol) and 2.57 g (6.2 mmol) **1g** gave, after drying i.V., a red-brown spongy solid which was recrystallised from MeOH giving 1.7 g (30%) of the white crystalline product with m.p. 109-110°.

1e. - It was prepared and purified as described for **1c**. 3.0 g **4e** gave a brown solid which was purified by washing with acetone and recrystallization from benzene/ethanol. The white crystalline product (1.7 g, 60%) had a m.p. 196-199°.

1f. - 1.4 g (9.6 mmol) t-Bu_2PH [11] was added to a hot solution of 2.0 g (4.83 mmol) **1g** in 40 ml isobutyl methyl ketone. The mixture was refluxed for 6 h and then left overnight. The liquid was decanted, the residue dissolved in 20 ml ethanol and treated with 20 ml 5% NaOH solution. The solvent was decanted from the oily precipitate which was dissolved in 40 ml $CHCl_3$. This solution was washed 3 times with 30 ml water, the organic layer dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The residual spongy solid was recrystallized from ethanol/benzene giving 0.9 g (30%) of the white crystalline product with m.p. 208-210°.

2c. - 19.6 g (76.03 mmol) $(EtO)_2P(O)H$ was added slowly to the *Grignard* reagent prepared from 10.5 g (431.89 m-atoms) Mg and 80.0 g (467.72 mmol) p-$CH_3 \cdot C_6H_4 \cdot Br$ in 250 ml ether which had been cooled to 0°. The very viscous solution was refluxed for 2 h and a waxy solid collected at the bottom of the flask. This mixture was hydrolysed with 200 ml 10% HCl-solution followed by 100 ml of water. The ether layer was separated and the residue was extracted with 6 50-ml portions of C_6H_6. The solid residue was then dissolved in ethanol and this solution extracted with a mixture of C_6H_6 and H_2O. The combined ether and benzene extracts were dried over $MgSO_4$, and the solvent evaporated i.V. The pale yellow crude product was purified by recrystallization from acetone/ether and gave 26.6 g (70%) of product with m.p. 115-116° and $\tilde{\nu}_{P-H} = 2340\ cm^{-1}$.

2d. - It was prepared as described for **2c** from 10.0 g (72.4 mmol) $(EtO)_2P(O)H$, 49.0 g (192.1 mmol) m-$CF_3 \cdot C_6H_4 \cdot Br$ and 5.4 g (222.1 m-atoms) Mg and recrystallised from Et_2O by cooling the solution to −60°. The white crystalline product (22.0 g, 90%) had m.p. 62° and $\tilde{\nu}_{P-H} = 2380\ cm^{-1}$.

2e. - It was prepared as described for **2c** from 20.0 g (144.82 mmol) $(EtO)_2P(O)H$, 85.2 g (522.50 mmol) $C_6H_{11}Br$ and 12.6 g (518.26 m-atoms) Mg and recrystallized from hexane. The white solid (18.2 g, 59%) had m.p. 71-72° (Lit. [12]: 73-75°).

3d. - 20.0 g (59.1 mmol) **2d** and 4 g (105.2 mmol) $LiAlH_4$ in 200 ml Et_2O were refluxed for 15 h. The red-brown solution was cooled to 0° and hydrolysed by the successive addition of 4 ml water, 4 ml 15% NaOH-solution and 12 ml water. The organic layer was separated, dried over Na_2SO_4 and fractionally distilled, the product being collected at 90-92°/0.4 Torr. Yield 10.5 g (54%). $\tilde{\nu}_{P-H} = 2290\ cm^{-1}$.

4b. - 10 ml of 30% H_2O_2 was gradually added to 1 g of crude **1b** in 30 ml acetone²) at 0°. The reaction mixture was stirred overnight and the solid which had separated was filtered off, dissolved in 20 ml $CHCl_3$ and chromatographed over alumina using hexane/$CHCl_3$ 1:1 as eluant. Evaporation of the eluate left a yellow oil which was dissolved in a minimum of ethanol and cooled to −5°. 0.3 g of white crystalline product of m.p. 232-234° were thus obtained.

4c. - 2.0 g *n*-BuLi (31.2 mmol, 20 ml of a 1.56M solution in hexane) was gradually added to a tepid solution of 8.0 g (30.5 mmol) **2c** in 120 ml THF. The dark yellow solution was left at RT. for 2 h and treated with 6.4 g **1g** in 40 ml THF. The solution was refluxed for 2 h, left overnight and the solvent evaporated under reduced pressure. A residue-solution in $CHCl_3$ was washed with water, dried over $MgSO_4$ and the solvent evaporated again. The crude product was recrystallized from $CHCl_3$/hexane. The crystalline product (8.0 g, 67%) had m.p. 315-322°.

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2) The use of H_2O_2 in acetone solution mentioned in this preparation *should be avoided. Such a mixture is potentially explosive* and becomes particularly dangerous after evaporation of the solvent. During the course of subsequent work on a related compound a violent explosion of the oily residue occurred after the acetone had been evaporated. It was later discovered that the explosive nature of H_2O_2/acetone mixtures had been observed elsewhere, *e.g.*, see *A.D. Brewer*, Chem. in Britain, *1975*, 355.

4d. - It was prepared as described for **4b**. The solvent was evaporated under reduced pressure (*see Footnote to preparation of* **4b**) and the oily residue purified by chromatography over alumina using hexane/chloroform mixtures. The waxy solid thus obtained was recrystallized from ethanol by cooling the solution to −5°. 1 g crude **1b** gave 0.7 g of product with m.p. 204-205°.

4e. - 2.0 g (4.83 mmol) **1g** and 2.5 g (9.76 mmol) $(C_6H_{11})_2P$(O-*iso*Pr) were heated together at 140-160° for 2 h, the *iso*-PrBr formed being allowed to distil off. The reaction mixture was then heated to 160-170° for 1 h, cooled and washed with 100 ml Et_2O. The white residual solid was recrystallized from $CHCl_3$/hexane giving 2.7 g (83%) of product melting from 318 to 322°.

4f. - It was prepared and purified as **4e**. 3.6 g (17.56 mmol) *t*-Bu_2P(O-*iso*Pr) and 2.5 g (6 mmol) **1g** gave 2.4 g (68.6%) of product melting over the range 270-273°.

$(C_6H_{11})_2P$(O-isoPr) (**5e**). - 18.0 g (77.4 mmol) $(C_6H_{11})_2PCl$, 4.7 g (77.4 mmol) *iso*-PrOH and 7.8 g (77.1 mmol) Et_3N in 50 ml benzene were refluxed for 4 h. After cooling, the solid formed was filtered off and the solution fractionally distilled. The product (15.4 g, 78%) was collected at 110-115°/1.0 Torr and was characterized through its ^{1}H-NMR. spectrum.

t-Bu_2P(O-isoPr) (**5f**). - A solution of *iso*-PrONa, prepared by adding 1.2 g (52.1 m-atoms) Na to 20 ml *iso*-PrOH, was gradually added to 8.9 g (49.3 mmol) *t*-Bu_2PCl in 20 ml benzene. The mixture was refluxed for 14 h, cooled down and the solid filtered off. The solution was fractionally distilled and the product (4.5 g, 43%) was collected at 50°/1.5 Torr. It was characterized through its ^{1}H-NMR. spectrum.

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