Phosphorus Derivatives of Anthracene and Their Dimers[1]

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The syntheses of the (9-anthracenyl)phosphanes **2** to **7** and of the metal carbonyl complexes **8** and **9** are described. Both **1** and **4** undergo [4 + 4] cycloaddition when irradiated, forming the dimers **10** and **11**. Only one of the six possible rotamers for **10** is formed. For **11** one additional rotational isomer is observed. The relationship between the [4 + 4] dimerization and steric effects of the PR_2 group is discussed. The compounds **6**, **8** and **11** were characterized by X-ray diffraction. The structure of **6** was rendered imprecise by the presence of disordered toluene, but the influence of the bulky anthracenyl groups was clear, with wide C–P–C angles of 110.4°. The molecule displays imposed threefold symmetry. The two independent molecules of complex **8**, which crystallizes as a dichloromethane hemisolvate, are closely similar to each other; the W–P bond lengths are 254.3 and 253.4 pm. The W–C bonds *trans* to phosphorus are 4 pm shorter than those *cis*. The phosphane dimer **11** crystallizes with imposed centrosymmetry. The H atom positions, which could be tentatively identified from difference syntheses, indicate a different rotamer than was formed for the analogous fluorophosphane dimer **10**.

Since Fritzsche initiated studies of the photochemistry of anthracene[2] and the anthracene dimer was correctly determined to be the irradiation product[3], a large number of anthracene derivatives have been prepared and the effects of different substituents investigated[4]. Halogen, alkyl, aryl cyano, carbonyl, oxy, and silyl groups have been the commonly studied substituents. Substituents in the 9-position (see Figure 1) have the largest influence, be it steric or electronic[5].

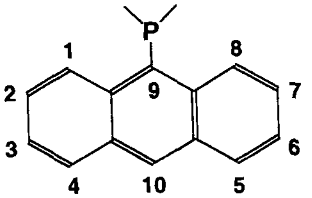

Figure 1. The numbered positions of 9-phosphorus-substituted anthracenes

Recently, the synthesis of (9-anthracenyl)difluorophosphane **1** (to the best of our knowledge the first anthracene derivative with phosphorus as a substituent in the 9-position), of its dimer, **10**, and of a Pt complex were reported[6]. We now report the synthesis of additional (9-anthracenyl)phosphanes, dimers, and complexes (compounds **2**–**9** and **11**–**13**). Like (9-anthracenyl)difluorophosphane, these compounds are relatively stable solids. (9-Anthracenyl)dichlorophosphane (**2**) and (9-anthracenyl)phosphane (**4**) in which the chlorine or hydrogen atoms can be easily replaced, are well-suited for further reactions. (9-Anthracenyl)phosphanes can be used as ligands in metal complexes. Surprisingly, despite the bulk of the anthracene ring, we were able to prepare and determine the crystal structure of tris(9-anthracenyl)phosphane (**6**) (Figure 2).

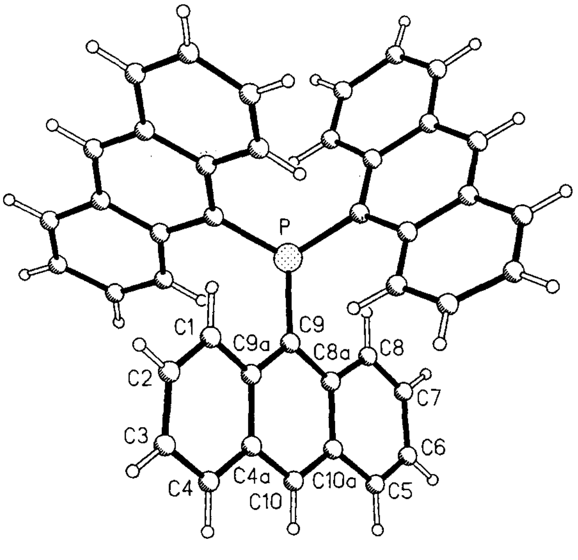

Figure 2. X-ray crystal structure of compound **6**, showing the numbering scheme of the asymmetric unit

Anthracene undergoes [2 + 4][7] and [4 + 4] cycloadditions[6]. After irradiating (9-anthracenyl)difluorophosphane (**1**) and (9-anthracenyl)phosphane (**4**), we observed [4 + 4]

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addition, as indicated in the ^{1}H-NMR spectra by the upfield shift of the proton in the 10-position[8]. When substituents are present, the anthracene rings can dimerize either head-to-head or head-to-tail[5]. Formation of the head-to-tail isomers of (9-anthracenyl)phosphanes was observed.

The rotamers of the dimers of (9-anthracenyl)phosphanes were also investigated. The PR_2 group, with its free electron pair, has the three possible rotamers shown in Figure 3, in relation to the 1- and 8-protons of one anthracene ring and the 10-proton of the other. Of these **B** and **C** are equivalent. The rotamers found in the anthracene dimers indicate which rotamers of the monomer are favoured. For the (9-anthracenyl)difluorophosphane dimer **10**, only isomer **A** is present, indicating that for the monomer both fluorine atoms are also located on one side of the anthracene ring. This corresponds to Parr's calculations as to the most stable rotamer of difluorophenylphosphane[9].

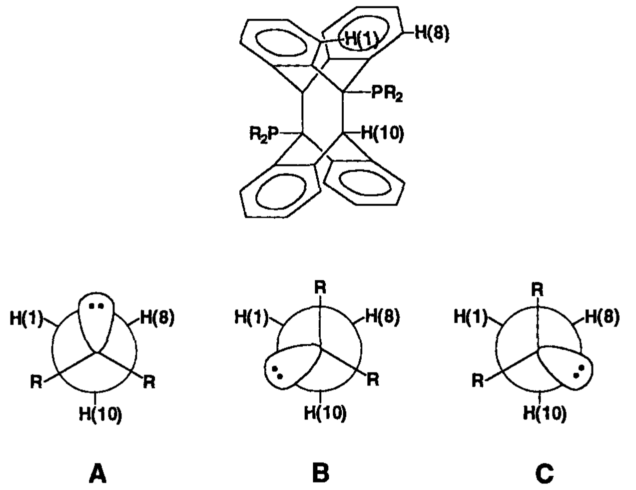


Figure 3. The rotamers of 9-phosphorus-substituted anthracenes are shown using Newman projections along the P—C(9) bond

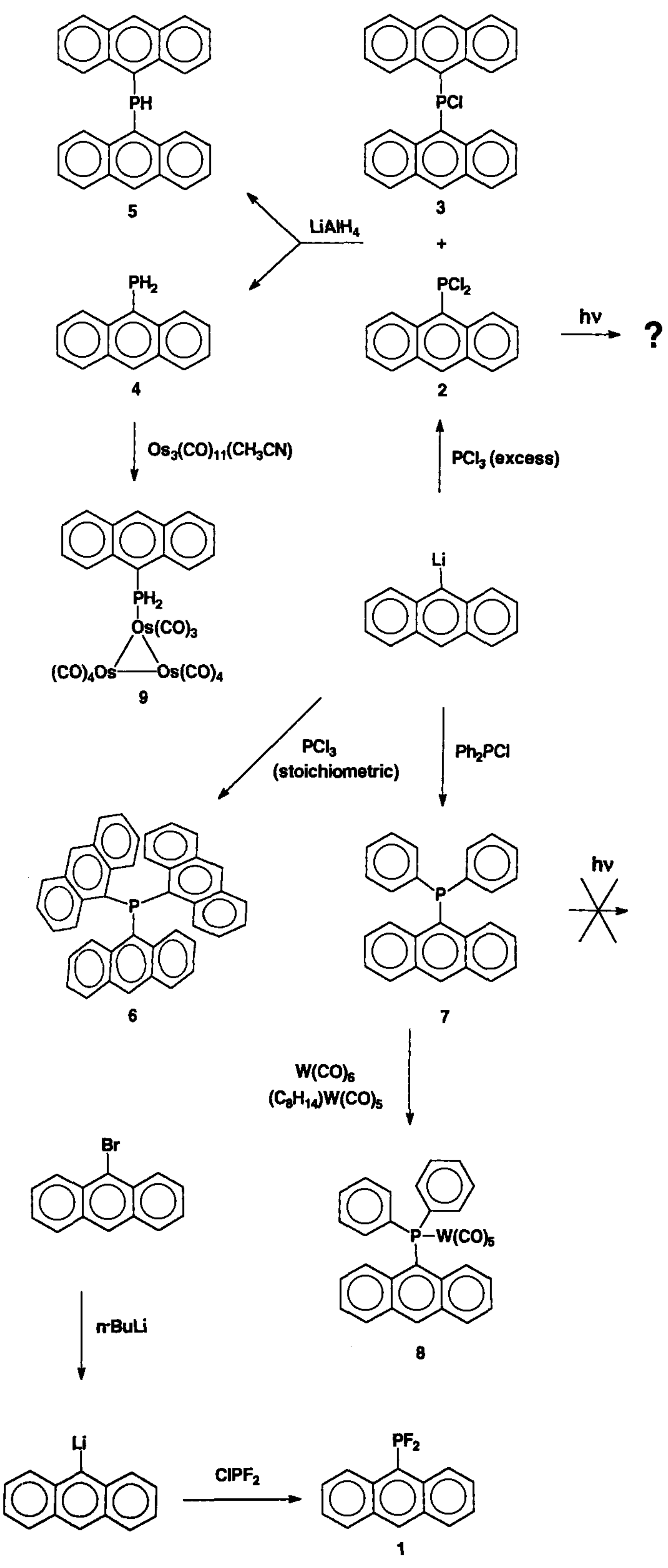
It was of interest to evaluate the ligand properties of (9-anthracenyl)-substituted phosphorus(III) compounds, and the reactions of **4** and **7** with $Os_3(CO)_{11}(CH_3CN)$ and $W(CO)_6$ were chosen as examples.

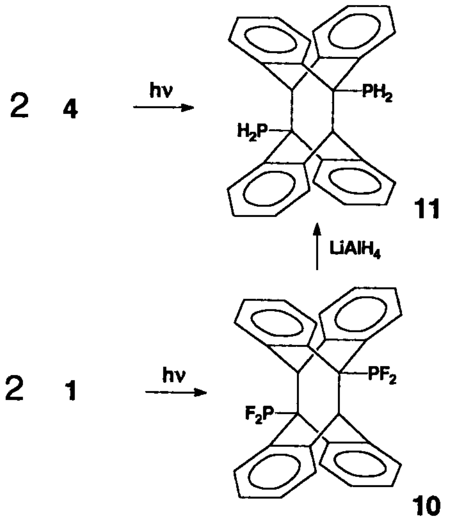
9-(Difluorophosphino)phenanthrene (**12**) was synthesized by a preparation similar to that for **1** from the appropriate 9-lithio precursor and PF_2Cl. Its use as a ligand in the platinum complex **13** is also reported.

Results and Discussion

The synthesis of **1** is a clean reaction with a yield of 96%[6]. **1** is indicated in the ^{31}P-NMR spectrum by a triplet at δ = 220.4 and in the ^{19}F-NMR spectrum by a doublet at δ = -94.7 with J_{PF} = 1157 Hz. The presence of ca. 1% of bis(9-anthracenyl)fluorophosphane is indicated by a doublet at δP = 175.6 and by a doublet at δF = -193.9 with J_{PF} = 881 Hz.

The preparation of **2**, similar to preparations of other dichlorophosphanes[10], by slow addition of 9-lithioanthracene to a large excess of PCl_3, results in a bright yellow solid with a ^{31}P-NMR resonance at δ = +159. This shift is very close to that for dichlorophenylphosphane (δP = 161). Purification of **2** is difficult, because of the impurities *n*-butylanthracene (from the side reaction of 9-lithioanthracene with *n*-butyl bromide) and anthracene. Bis(9-anthracenyl)chlorophosphane (**3**) is often a side product in this reaction,





as indicated in the ^{31}P-NMR spectrum by a signal at $\delta = +80$ (cf. δP = +80 for chlorodiphenylphosphane). Careful sublimation, with prior removal of anthracene, works best for the purification of **2**, although the process destroys **3**, making its full characterization impossible.

Chlorine–phosphorus bonds can readily be hydrogenated by $LiAlH_4$[11]. In this manner, (9-anthracenyl)phosphane (**4**) is prepared from **2** with a yield of 38%. Reaction of a mixture of **2** and **3** with $LiAlH_4$ gives both **4** and bis(9-anthracenyl)phosphane (**5**) as products. **4** can be purified by sublimation or by recrystallization from ethanol to give a yellow solid with $\delta P = -157$. Proton-coupled ^{31}P-NMR spectra show a triplet with $J_{PH} = 206$ Hz, as expected for PH_2 groups. A doublet at $\delta = 4.2$ with the same coupling constant was seen in the ^{1}H-NMR spectra. **5** remains in the sublimation residue and can be recrystallized from a mixture of CH_2Cl_2 and toluene. ^{31}P-NMR spectra of **5** show a doublet at $\delta = -100$ with $J_{PH} = 236$ Hz. The signal for PH with the corresponding coupling constant in the ^{1}H-NMR spectra was shifted downfield to $\delta = 6.7$.

(9-Anthracenyl)dichlorophosphane (**2**) decomposes with formation of anthracene when traces of water are present. This is evident in the mass spectrum for the product of the reaction of **2** and D_2O, which shows a peak at $m/z = 179$ ($C_{14}H_9D$). The ^{1}H-NMR spectrum is similar to that of anthracene, but with an integral ratio of 1:4:4 (9-deuterioanthracene) instead of the usual 2:4:4 ratio. When the experiment was repeated with liberal amounts of H_2O present, a yellow insoluble substance was obtained. Based on microanalyses, we believe that this substance is (9-anthracenyl)phosphonous acid.

Repeating the reaction of 9-lithioanthracene with PCl_3, using a 3:1 molar ratio, results in a deep red solution. The mass spectrum of the precipitated red solid, with a peak at $m/z = 562$, indicates the presence of tris(9-anthracenyl)phosphane (**6**). The ^{31}P-NMR spectrum, with a signal at $\delta = -44$, has a shift value reasonable for **6**. Because of the large size of the anthracene group, we had not expected to find three anthracene groups connected to phosphorus. However, the X-ray crystal structure investigation (see Figure 2) shows that the rings in **6** are not distorted.

Table 1. ^{1}H-NMR data of 9-anthracenylphosphanes (numbering see Figure 1)

Compound (Solvent)	1.8-H	10-H	4.5-H	2.7-H	3.6-H	R
$C_{14}H_9PF_2$[a] ($CDCl_3$) **1**	δ 8.97 dddd $J_{1,2} = 8.8$ $J = 4.4$ $J = 2.2$ $J_{1,3} = 1.1$	δ 8.56 s	δ 7.99 d(br) $J_{3,4} = 8.2$	δ 7.60 ddd $J_{1,2} = 8.8$ $J_{2,3} = 6.6$ $J = 1.6$	δ 7.50 ddd $J_{3,4} = 8.1$ $J_{2,3} = 6.6$ $J_{1,3} = 1.2$	
$C_{14}H_9PCl_2$[a] ($CDCl_3$) **2**	δ 9.04 ddd $J_{1,2} = 9.0$ $J = 1.8$ $J_{1,3} = 0.8$	δ 8.47 s	δ 7.89 dd $J_{3,4} = 8.3$ $J = 0.7$	δ 7.52 ddd $J_{1,2} = 9.0$ $J_{2,3} = 6.6$ $J = 1.5$	δ 7.37 ddd $J_{3,4} = 8.2$ $J_{2,3} = 6.7$ $J_{1,3} = 1.0$	
$C_{14}H_{11}P$[a] ($CDCl_3$) **4**	δ 8.4 d(m) $J_{1,2} = 8.5$	δ 8.33 s	δ 7.89 d(br) $J_{3,4} = 8.0$	δ 7.47 ddd $J_{1,2} = 8.6$ $J_{2,3} = 6.7$ $J = 1.7$	δ 7.3 ddd $J_{3,4} = 8.0$ $J_{2,3} = 6.6$ $J = 1.4$	δ 4.3 d $J_{PH} = 206.4$
$C_{28}H_{19}P$[b] ($CDCl_3$) **5**	δ 8.55 ddd $J_{1,2} = 8.8$ $J = 1.7$ $J_{1,3} = 0.9$	δ 8.32 s	δ 7.85 dd $J_{3,4} = 8.3$ $J = 0.5$	δ 7.21 ddd $J_{1,2} = 8.8$ $J_{2,3} = 6.6$ $J = 1.5$	δ 7.28 ddd $J_{3,4} = 8.3$ $J_{2,3} = 6.6$ $J_{1,3} = 1.0$	δ 6.73 d $J_{PH} = 235$
$C_{42}H_{27}P$[a] ($CDCl_3$) **6**	δ 8.5 ddd $J_{1,2} = 9.1$ $J = 3.3$ $J_{1,3} = 0.9$	δ 8.5 s	δ 7.95 dd $J_{3,4} = 8.4$ $J = 0.7$	δ 6.9 ddd $J_{1,2} = 9.1$ $J_{2,3} = 6.6$ $J = 1.4$	δ 7.25 ddd $J_{3,4} = 8.4$ $J_{2,3} = 6.5$ $J_{1,3} = 0.9$	
$C_{26}H_{19}P$[b] ($CDCl_3$) **7**	δ 8.66 ddd $J_{1,2} = 8.8$ $J = 4.9$ $J = 0.73$	δ 8.50 s	δ 7.91 dd $J_{3,4} = 8.4$ $J = 0.6$	δ 7.20 dd $J_{1,2} = 9.0$ $J = 1.4$	δ 7.32–7.26[c]	δ 7.15–7.08 m[d]
$C_{31}H_{19}O_5PW$ ($CDCl_3$)[a] **8**	δ 7.66 d $J_{1,2} = 9.06$	δ 8.50 s	δ 7.95 d(m) $J_{3,4} = 8.45$	δ 7.01 ddd $J_{1,2} = 9.1$ $J_{2,3} = 6.6$ $J = 1.4$	δ 7.28 ddd $J_{3,4} = 8.3$ $J_{2,3} = 6.6$ $J = 1$	
	δ 7.54 dd[d] $J = 11.45$ $J = 2.2$	δ 7.50dd[d] $J = 11.46$ $J = 0.9$	δ 7.18–7.11 m[d]			

[a] Recorded at 200.1 MHz. – [b] Recorded at 400.1 MHz. – [c] Multiplet due to both 3,6-H and phenyl protons according to H–H COSY. – [d] Signal for phenyl protons according to H–H COSY.

(9-Anthracenyl)diphenylphosphane (**7**) is prepared from 9-lithioanthracene and chlorodiphenylphosphane. This method is preferable to the reaction of phenyllithium with (9-anthracenyl)dichlorophosphane for stability reasons. **7** is a yellow solid. The amount of *n*-butylanthracene formed here is low, since the chlorodiphenylphosphane is added directly to the lithium reagent.

7, like triphenylphosphane, acts as a ligand in metal complexes. [(9-Anthracenyl)diphenylphosphane]pentacarbonyltungsten (**8**) was formed by irradiating **7** in the presence of

Table 2. ^{13}C-NMR data of 9-anthracenylphosphanes

Compound (Solvent)	C-1,8	C-4a,10a*	C-8a,9a*	C-2,7	C-3,6	C-4,5	C-10	C-9
$C_{14}H_9PF_2$[a] ($CDCl_3$) **1** [c]	δ 124.3 dt $^3J_{CP}$ = 28.6	δ 130.7 d $^3J_{CP}$ = 3.6 $^4J_{CF}$ = 4.4	δ 134.6 dt $^2J_{CP}$ = 18.2	δ 127.6 dt J = 3 $^3J_{CF}$ = 4.8	δ 125.3 d J = 1.5	δ 129.3	δ 134.4 d J = 1.5	δ 129.8 dt $^1J_{CP}$ = 52.9 $^2J_{CF}$ = 8.8
$C_{14}H_9PCl_2$[b] ($CDCl_3$) **2** [c,d]	δ 126.1 d J = 12	δ 131.1 d J = 3.8	δ 134.0 J = 21.4	δ 127.5 d J = 3.7	δ 125.4	δ 129.8	δ 135.1	δ 128.2[e] J = 74
$C_{14}H_{11}P$[a] ($CDCl_3$) **4** [c,d]	δ 127.2 d $^3J_{CP}$ = 14.6	δ 131.2 d $^3J_{CP}$ = 2.8	δ 134.9 d $^2J_{CP}$ = 8.9	δ 126.1 d J= 1.4	124.9	δ 129.3	δ 129.0	not located
$C_{28}H_{19}P$[a] ($CDCl_3$) **5**	δ 126.7 d J = 15.1	δ 131.4 d J = 2.6	δ 134.7 d J = 10.0	δ 126.3 d J = 1.6	δ 124.9	δ 129.5	δ 129.7	δ 130.2 d J = 24.1
$C_{42}H_{27}P$[a] ($CDCl_3$) **6** [d]	δ 127.0 d J = 20.4	δ 131.6 d J = 3.8	δ 134.8 d J ≈ 16.1	δ 126.1 d J = 1.7	δ 124.9	δ 129.4	δ 130.6	δ 131.4[e]
$C_{26}H_{19}P$[b] ($CDCl_3$) **7** [c,d]	δ 128.4 d J = 24.5	δ 136.78 d J ≈ 13.4	δ 136.72 d J ≈ 14.0	δ 125.97 d	δ 125.1 d J = 1.1	δ 129.28	δ 131.9 d	δ 126.0[e]
$C_{31}H_{19}O_5PW$ ($CDCl_3$)[a] **8** [c]	δ 127.7 d J = 9.5	δ 132.0 d J = 6.4	δ 131.6 d J = 7.0	δ 124.9	δ 125.0	δ 129.6	δ 132.0 d	δ 127.0 d[e] J = 36

[a] Recorded at 100.6 MHz. — [b] Recorded at 50.3 MHz. — [c] Determined by using H—C COSY. — [d] Determined by using $^{13}C\{^{31}P\}$. — [e] Tentatively assigned to C-9. — * Tentative assignments; may have to be interchanged with other values marked similarly. The resonance of the ^{13}C-atoms of the phenyl rings in **7** and **8** are assigned as follows (δ values): **7**: Phenyl-1 (131.8, d, J = 4.7); 128.4, d*, J = 5.5; 127.5*, 131.5, d*, J = 18.4. — **8**: Phenyl-1 (138.7, d, J = 41); 132.4, d*, J = 13.1; 129.7, d*, J = 2.2; 128.8, d*, J = 10.6.

$W(CO)_6$. To avoid difficulties in separating **7** and **8**, pentacarbonyl (η^2-1-cyclooctene)tungsten was added to react with remaining **7**. The excess tungsten carbonyls were easily removed with the solvent under vacuum. The ^{31}P-NMR spectrum of **8** shows a singlet at $\delta = +16.0$ with ^1J(PW) = 242. This is comparable to a resonance of $\delta = 20.9$ and a coupling constant of ^1J(PW) = 243 for triphenylphosphanepentacarbonyltungsten[12,13]. ^{13}C-NMR and IR data are compared in Table 3.

Compound **4** also acts as a ligand, replacing acetonitrile in $Os_3(CO)_{11}(CH_3CN)$ to form the triosmiumdodecacarbonyl cluster **9**. A comparison of its IR data with those of related clusters is given in Table 4.

(9-Anthracenyl)phosphanes, when irradiated, enter an excited state and, when there is no steric hindrance between the R groups and the 1- and 8-protons of the first anthracene ring and the 10-proton of the second, may dimerize. Our investigations involved four different PR_2 anthracene derivatives, with R = F, H, Cl, Ph where H and F are known to have similar van der Waals radii.

Compound **10**, the dimer of **1**, is prepared by irradiation. The ^{1}H-NMR signal at $\delta = 4.9$ indicates that [4 + 4] addi-

Table 3. ^{13}C and IR data for the 9-anthracenyldiphenyl- and the triphenylphosphane-$W(CO)_5$ complexes

	$C_{26}H_{19}P$[a]	$C_{18}H_{15}P$[a]
δ(<u>C</u>O)trans	198.77 ppm	199.27 ppm
δ(<u>C</u>O)cis	197.04 ppm	197.28 ppm
$^1J_{WC}$cis	–	143.8 Hz
$^1J_{WC}$trans	–	126.2 Hz
$^2J_{PC}$trans	22.2 Hz	22.0 Hz
$^2J_{PC}$cis	6.7 Hz	7.2 Hz
ν (CO)	2078 cm^{-1}	2070 cm^{-1}
ν (CO)	1935 cm^{-1}	1935 cm^{-1}

[a] NMR data are from a $CDCl_3$ solution and IR data from a CH_2Cl_2 solution (data for $C_{18}H_{15}P$ are found in ref.[13]).

Table 4. IR data for osmium carbonyl clusters with phosphane ligands

$Os_3(CO)_{11}PH_3$[a]	2112 w	2058 ms	2038 ms	2022 vs		1989 m	
$Os_3(CO)_{11}PH_2Ph$[b]	2110 m	2055 s	2036 s	2021 s	2003 m	1991 s	1976 m
$Os_3(CO)_{11}PH_2(Ant)$[c] Ant = $C_{14}H_9$	2109 m	2054 s	2038 s	2019 vs		1990 m	1980 ms

[a] In CH_2Cl_2, ref.[27]. — [b] In cyclohexane, ref.[28]. — [c] In CH_2Cl_2.

tion occurs, and the one signal in the ^{31}P-NMR spectrum indicates that only one isomer is present. As seen in the X-ray structure of **10** (ref.[16]), this is the head-to-tail isomer and the rotamer **A**, where both fluorines on each PF_2 group are located between the rings and the lone pairs of electrons above and below. Even at temperatures up to 105°C no other signals appear in the ^{31}P-NMR spectrum. The rotation barrier of the PF_2 group in **10** seems to be high enough to make other rotamers impossible.

Compound **11**, the dimer of (9-anthracenyl)phosphane, is prepared by irradiation of the monomer in a saturated toluene solution. The dimer, being less soluble in toluene, precipitates. After 22.5 h of irradiation, a large amount of the monomer still remains. The ^{31}P-NMR spectrum shows three signals, one for the monomer, and two at $\delta = -105$ and -107 in a ratio of ca. 1:2, indicating that two isomers of the dimer are present. The ^1H-NMR spectrum shows a doublet for the PH_2 group, shifted from that of the monomer, as well as additional peaks attributed to a second isomer.

Compound **11** can also be prepared by hydrogenating **10**. This method of preparation gave two ^{31}P-NMR signals at $\delta = -105$ and -107, also in a ratio ca. 1:2, corresponding to the signals seen above. The (9-anthracenyl)difluorophosphane dimer, **11**, being head-to-tail, would only give head-to-tail hydrogenated products. Thus, the signals must be due to different rotamers. The possible rotamers of the PR_2 are shown in Figure 3. Since two rotamers are present, the PH_2 group must have a relatively low rotational energy barrier. If one rotamer is not favoured over the other, the ratio of **A** to **B** and **C** (which are equivalent) is 1:2. The **B**/**C** isomers seem to be the more stable of the two rotamers, as seen in the X-ray structure (see below and Figures 5 and 6). With respect to the whole molecule possible combinations are **A**/**A**, **A**/**B**, **A**/**C**, **B**/**A**, **B**/**B**, **B**/**C**, **C**/**A**, **C**/**B**, and **C**/**C**. Of these, **A**/**B**, **B**/**A**; **A**/**C**, **C**/**A**; and **B**/**C**, **C**/**B** are identical. **A**/**A** (*2/m*) and **B**/**C** (= **C**/**B**) (*i*) are achiral. **A**/**B** (= **B**/**A**) (*1*) and **A**/**C** (= **C**/**A**) (*1*) as well as **C**/**C** (*2*) are enantiomeric (axial chirality).

The irradiation of (9-anthracenyl)dichlorophosphane in benzene is not as simple as in the case of (9-anthracenyl)difluorophosphane. After 35 h of irradiation, the ^{31}P-NMR resonance for the monomer **1** barely exists, and a number of other signals appear, among them the signal for PCl_3 at $\delta = +220$, suggesting that a radical reaction takes place.

The phenyl groups of (9-anthracenyl)diphenylphosphane appear too bulky for the monomer to dimerize. After 48 h of irradiation, no changes in the ^1H- or ^{31}P-NMR spectra are seen.

Our investigations indicate that only **1** and **4** dimerize, presumably due to their limited steric hindrance. In both dimers, **10** and **11**, the PR_2 groups do not rotate at high temperatures, as seen in the high-temperature ^{31}P- and ^1H-NMR spectra. This, as well as the close contact between F and H in **10** and H and H in **11**, as seen in the X-ray structures of the dimers, suggest that PF_2 and PH_2 are the largest groups allowing the derivatives to dimerize. Since the initial isomer ratio for **11** prepared by dimerization is the same as for **11** prepared by hydrogenation, and this is the expected statistical 1:2 ratio, we believe that there is only a small difference in the energies of the rotamers.

X-ray Crystal Structures of Compounds 6, 8 and 11

Tris(9-anthracenyl)phosphane (**6**): In the crystal the phosphane molecule (Figure 2, Table 5) displays exact C_3-symmetry. The observed arrangement of the three bulky ligands leads to a "dense" packing of the anthracenyl substituents around the phosphorus atom. Thus, the carbon atom C(9) directly bound to phosphorus has a distance of only 230 pm from the hydrogen at C(1) of the neighbouring substituent (compare the sum of the van der Waals radii 290 pm[14]). The least squares planes of the two outer rings of the anthracenyl group display a dihedral angle of 7.6°. This slight deviation from planarity might also be caused by non-bond-

Table 5. Selected bond lengths [pm] and angles [°] for compound **6**. Symmetry operator (i): $-y, x - y, z$

P-C(9)	183.9 (4)	C(1)-C(2)	135.6 (10)
C(1)-C(9A)	142.4 (9)	C(2)-C(3)	138.4 (8)
C(3)-C(4)	136.8 (12)	C(4)-C(4A)	142.9 (10)
C(4A)-C(9A)	142.2 (7)	C(4A)-C(10)	136.8 (10)
C(5)-C(6)	132.7 (11)	C(5)-C(10A)	143.8 (11)
C(6)-C(7)	141.5 (8)	C(7)-C(8)	134.1 (10)
C(8)-C(8A)	142.9 (8)	C(8A)-C(9)	143.3 (8)
C(8A)-C(10A)	141.9 (7)	C(9)-C(9A)	143.3 (8)
C(10)-C(10A)	140.6 (10)		
C(9)-P-C(9i)	110.4(2)	P-C(9)-C(8A)	113.8(4)
P-C(9)-C(9A)	127.1(5)		

ing interactions. C–C bonding distances in the rings lie between 134 pm [C(5)–C(6)] and 144 pm [C(5)–C(10a)].

The high steric demand of the three ligands also has a significant influence on the bonding geometry at the central phosphorus atom. Although the P–C distance of 183.9 pm lies in the normal range (cf. 183 pm in Ph_3P[15]), the bond angles at phosphorus (110.4°) are clearly increased with respect to normal values; they are ca. 7° larger than in Ph_3P. The only comparable values for triorganophosphanes are found in trimesitylphosphane[16].

The angles at C(9) are also affected; P–C(9)–C(8a) narrows to 113.8°, whereas P–C(9)–C(9a) widens to 127.1°.

[(9-Anthracenyl)diphenylphosphane]pentacarbonyltungsten (**8**): Compound **8** crystallizes with two independent molecules (and one dichloromethane) in the asymmetric unit (see Figure 4, Table 6). This is the first X-ray crystal structure determination of a metal-anthracenylphosphane complex. The two molecules show no major differences; the orientations of the rings differ by up to 8°, with the anthracene moiety approximately perpendicular to the $W(CO)_3P$ plane (dihedral angles 96 and 85°).

Table 6. Selected bond lengths [pm] and angles [°] for the two molecules of compound **8**

W(1)-P(1)	254.3 (1)	253.4 (2)	W(1)-C(31)	200.2 (6)	200.0 (7)
W(1)-C(32)	203.8 (6)	203.8 (6)	W(1)-C(33)	204.6 (6)	203.7 (5)
W(1)-C(34)	204.9 (6)	204.2 (7)	W(1)-C(35)	203.7 (6)	204.4 (6)
C(1)-C(2)	136.5 (6)	137.1 (8)	C(1)-C(9A)	143.0 (8)	142.7 (7)
C(2)-C(3)	141.7 (8)	141.3 (9)	C(3)-C(4)	134.3 (9)	133.9 (8)
C(4)-C(4A)	142.6 (6)	143.0 (8)	C(4A)-C(9A)	144.3 (7)	143.6 (8)
C(4A)-C(10)	138.6 (8)	140.2 (7)	C(5)-C(5A)	143.7 (8)	143.5 (7)
C(5)-C(6)	135.1 (6)	134.5 (8)	C(5A)-C(8A)	144.1 (7)	143.9 (9)
C(5A)-C(10)	139.4 (6)	138.3 (8)	C(6)-C(7)	140.5 (8)	142.1 (9)
C(7)-C(8)	136.1 (9)	136.9 (7)	C(8)-C(8A)	143.0 (5)	143.5 (7)
C(8A)-C(9)	142.5 (8)	141.6 (6)	C(9)-C(9A)	143.6 (5)	141.7 (7)
P(1)-W(1)-C(31)	177.7(2)	177.9(1)	P(1)-W(1)-C(32)	91.5(2)	90.5(2)
C(31)-W(1)-C(32)	90.7(2)	88.7(3)	P(1)-W(1)-C(33)	91.4(2)	92.1(2)
C(31)-W(1)-C(33)	88.6(2)	89.8(2)	C(32)-W(1)-C(33)	89.1(2)	90.7(2)
P(1)-W(1)-C(34)	88.2(2)	90.3(2)	C(31)-W(1)-C(34)	89.5(2)	90.6(3)
C(32)-W(1)-C(34)	179.3(2)	177.3(2)	C(33)-W(1)-C(34)	90.3(2)	86.6(2)
P(1)-W(1)-C(35)	91.9(2)	90.4(2)	C(31)-W(1)-C(35)	88.1(2)	87.8(2)
C(32)-W(1)-C(35)	91.7(2)	91.6(2)	C(33)-W(1)-C(35)	176.6(3)	176.6(2)
C(34)-W(1)-C(35)	89.0(2)	91.0(2)	W(1)-P(1)-C(9)	110.6(2)	111.9(2)
W(1)-P(1)-C(11)	117.0(2)	118.0(2)	C(9)-P(1)-C(11)	106.0(2)	103.7(2)
W(1)-P(1)-C(21)	119.1(1)	117.5(2)	C(9)-P(1)-C(21)	104.5(2)	105.9(3)
C(11)-P(1)-C(21)	98.0(2)	97.9(2)			

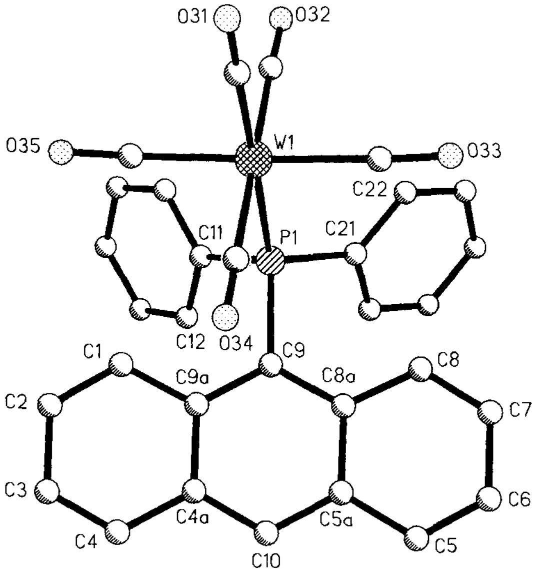


Figure 4. X-ray crystal structure of compound **8**, showing the atom numbering scheme. Only one of the two independent molecules is shown

The W–P bond lengths [254.3, 253.4(1) pm] in **8** are similar to those of 251.6(2) pm observed in $(Me_3P)W(CO)_5$[17] and 253.5(2) pm in $(iPr_3P)W(CO)_5$[18]. However, we have observed a shorter $(CO)_5W$–P bond [248.5(3) pm] in a diphosphorus derivative[19]. The additional precision associated with low temperature measurements shows clearly that the W–C bonds (esd ca. 0.6 pm) *trans* to phosphorus (av. 200.1 pm) are shorter than those *cis* (av. 204.1 pm); in the other $W(CO)_5$ derivatives the differences were less significant.

The anthracene ring systems are folded slightly about the central axis C9···C10 (dihedral angles between outer ring planes 9° and 8°). The folding is more pronounced at C9, with ring torsion angles C1–C9a–C9–C8a being 168, 170° and C9a–C9–C8a–C8 being −168, −168°. Additionally, the pattern of C–C bond lengths (all esd's <1 pm) is typical of anthracene systems[20], involving short bonds C1–C2, C3–C4, C5–C6 and C7–C8 (av. of eight 136 pm), long bonds C1–C9a, C2–C3, C4–C4a, C4a–C9a, C9–C9a, C8a–C9, C6–C7 and C5–C5a (av. of sixteen 143 pm) and "normal" aromatic bond lengths C4a–C10 and C5a–C10 (av. of four 139 pm, cf. av. 139 pm for the phenyl rings; in the standard anthracene system the bond at C9 should also be ca. 139 pm, but in **8** these bonds may be lengthened by interaction with the formally positive phosphorus atom). Similar features can be discerned in the structure of tris(anthracenyl)phosphane **6** (see above), but are less clear-cut in the statistical scatter.

The bond angles at phosphorus follow a pattern to some extent dependent on electronic effects; the W–P–C angles

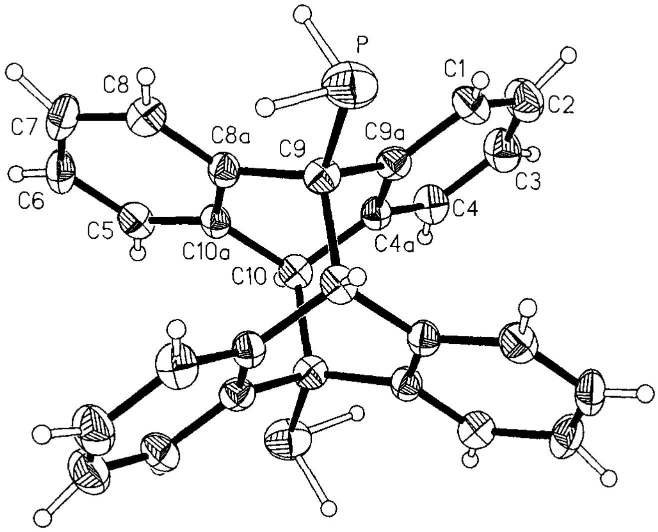


Figure 5. X-ray crystal structure of compound **11**, showing the numbering scheme of the asymmetric unit. Selected bond lengths [pm] and angles [°]: C(9)–C(10) 162.6(6) (symmetry operator 1 − *x*, 1 − *y*, 1 − *z*), P–C(9) 186.4(5), P–H(01) 132(5), P–H(02) 136(3), C(9)–P–H(01) 89(2), C(9)–P–H(02) 97(2), H(01)–P–H(02) 94(3)

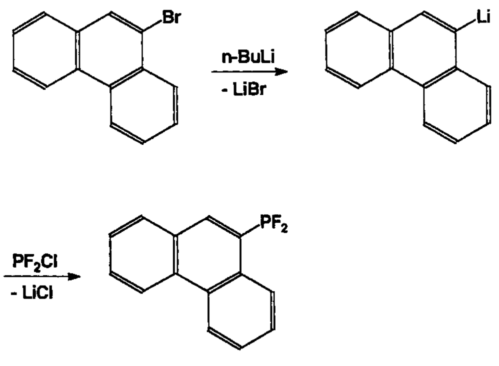
are larger than C—P—C, consistent with the electropositive nature of the metal atom. The extreme values are W1—P1—C21 119.1(1), C11′—P2—C21′ 97.9(1)°. Steric effects obviously play a role, but are less easy to rationalize; although the smallest phosphorus substituents (the phenyl groups) subtend the smallest angle, the W—P—phenyl angles are larger than W—P—anthracenyl.

(9-Anthracenyl)phosphane Dimer **11**: In the X-ray structure of **11** (Figure 5), only rotamer **B**/**C** (= **C**/**B**) was found. **11** crystallizes with imposed inversion symmetry in $P2_1/c$. The hydrogen atoms of the PH_2 group could be identified with reasonable certainty from difference syntheses. All angles at phosphorus are ca. 90°, although necessarily with high esd's. The single bonds C(9)—C(10i), formed on dimerization, are long [162.6(6) pm], presumably because of unfavourable steric interactions.

It is possible that this isomer crystallizes preferentially; alternatively, all isomers may crystallize in similar cells and this isomer may have been investigated by chance selection of crystals. However, **11** is not isostructural to **10** (see Experimental). The difference between **10** and **11** is demonstrated by the stereoview of both molecules, showing that **10** is an example of rotamer **A**/**A** and **11** an example of **B**/**C** (= **C**/**B**) (see Figure 6).

In a manner similar to **1**, the difluorophosphane **12** was synthesized by lithiation of 9-bromophenanthrene with *n*-BuLi, followed by reaction with PF_2Cl.

12 reacted, as other difluorophosphanes, with dichlorocyclooctadiene platinum(II), with formation of the complex **13**.



12

$$2\ \mathbf{12} + (COD)PtCl_2 \xrightarrow[-COD]{} (C_{14}H_9PF_2)_2PtCl_2$$

13

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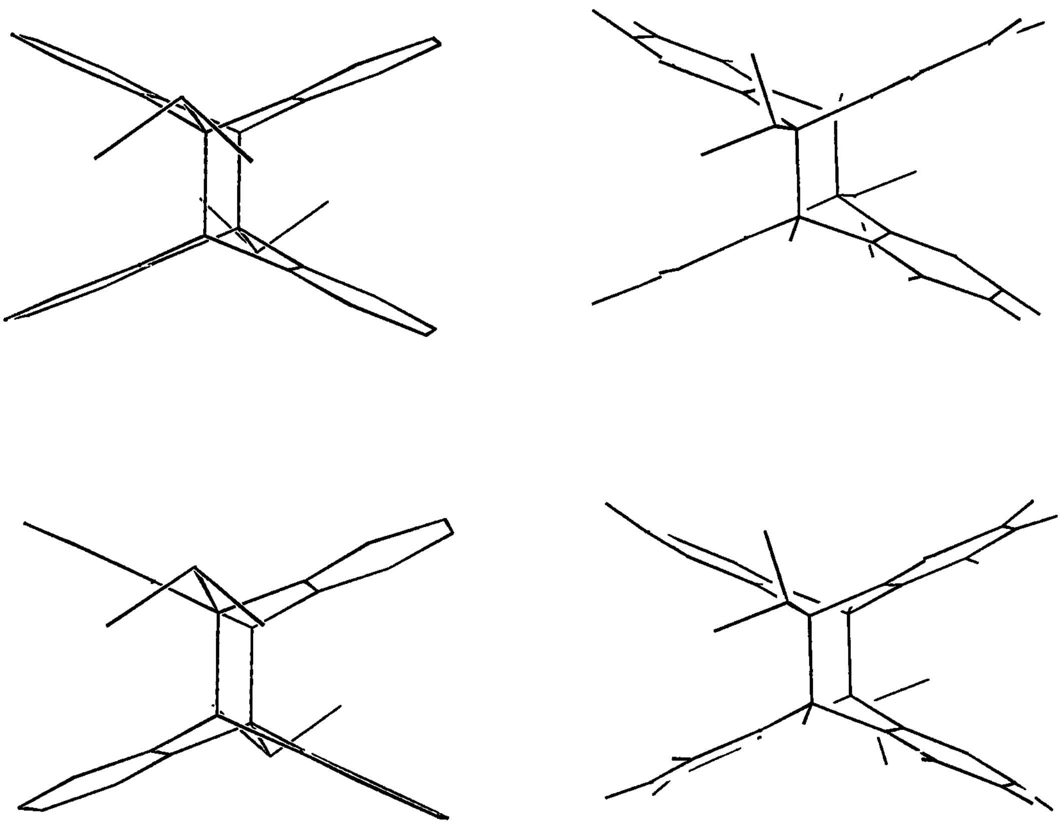

Figure 6. Stereoviews of **10** (above), rotamer **A**/**A**, and **11** (below), rotamer **B**/**C**

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Experimental

Inert atmosphere Schlenk line techniques were employed during the preparations with the exception of the air-stable osmium complexes. The nitrogen was dry and oxygen-free. Solvents were dried using standard procedures[21]. 9-Bromoanthracene (95%) was purchased from Aldrich Chemical Co. and was used without further purification. 15% *n*-butyllithium in hexane was from Chemetall GmbH. Substances were irradiated with a Hanau high-pressure mercury lamp. Melting points were determined on a Büchi 530 melting point apparatus using 0.1 mm capillary tubes, and are uncorrected. NMR spectra were recorded on the following instruments: Bruker AC 200 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz, ^{19}F: 188.3 MHz, ^{31}P: 81.0 MHz) and Bruker AM 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz), with $CDCl_3$, TMS, H_3PO_4, and $CFCl_3$ as references. IR spectra were recorded on a Beckman 4260-IR spectrometer. EI mass spectra were recorded on a FINNIGAN MAT 8430 mass spectrometer using EI-ionization. Atomic numbers were calculated based on the isotopes ^{12}C, ^{35}Cl, and ^{183}W. Microanalyses were performed in the Analytical Laboratory of the Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig.

Preparation of **2** *and* **3**. – *Isolation of (9-Anthracenyl)dichlorophosphane* (**2**): 9-Bromoanthracene (2.47 g, 9.6 mol; 2.60 g of the 95% pure substance) was added over a period of 30 min via a dropping funnel to *n*-BuLi (0.615 g, 10 mmol) as a 15% solution in hexane (4.10 g) at −30°C, preparing 9-lithioanthracene[6,22], which was added slowly over a period of 3.5 h to a vigorously stirred solution of PCl_3 (26.53 g, 193 mmol) in diethyl ether (60 ml) cooled in an ice bath. After refluxing for 1 h the mixture was cooled and pumped dry in vacuo (10^{-2} Torr). ^{31}P-NMR spectra showed a signal at $\delta = 159.6$ for **2** and often exhibited additional signals at $\delta = 80$ for **3** and at $\delta = 10$. **2** was sublimed (160°C/10^{-3} Torr) from the mixture yielding 1.27 g (47.6%), m.r. 117–125°C. – ^{31}P NMR (80.1 MHz, $CDCl_3$): $\delta = 159.61$.

$C_{14}H_9Cl_2P$ (279.1) Calcd. C 60.25 H 3.25 P 11.10
Found C 60.55 H 3.38 P 10.80

Decomposition of **2** *with Water:* Phosphane **2** (0.45 g, 1.61 mmol) was dissolved in ca. 10 ml of CH_2Cl_2. Addition of 2 ml of H_2O resulted in a yellow precipitate. After removing the solvent, the solid was washed twice with 2 ml of CH_2Cl_2 and dried in vacuo yielding 0.3 g (77%) of the corresponding phosphonous acid, m.p. 215°C.

$C_{14}H_{11}O_2P$ (242.2) Calcd. C 69.42 H 4.58
Found C 68.50 H 4.64

Synthesis of (9-Anthracenyl)phosphane (**4**): Phosphane **2** (0.95 g, 3.4 mmol) in 80 ml of diethyl ether was slowly added over a period of 30 min via a dropping funnel to a suspension of lithium aluminium hydride (0.70 g, 18.4 mmol) in diethyl ether (30 ml) cooled to −70°C. The mixture was allowed to warm to room temperature, refluxed for 2 h, and cooled in an ice bath. A solution of ammonium chloride (0.78 g, 20.5 mmol) in water (70 ml) was carefully added dropwise over 1 h, the rate being monitored by the evolution of gaseous HCl through an oil bubbler. The organic layer was removed and the aqueous layer was washed with diethyl ether. The organic layer and washes were dried with ca. 2 g of potassium carbonate and filtered. The solvent was removed in vacuo (10^{-2} Torr). The product **4** was recrystallized from ethanol with a yield of 0.27 g (38%), m.r. 68–73°C. – ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): $\delta = -157.8$ (t, $J_{PH} = 206.2$ Hz).

$C_{14}H_{11}P$ (210.2) Calcd. C 79.99 H 5.28
Found C 79.88 H 5.31

Formation of Bis(9-anthracenyl)phosphane (**5**): Phosphane **5** was prepared from a mixture of **2** and **3** treated with lithium aluminium hydride as described above. Phosphane **4** was removed by sublimation at 10^{-3} Torr at 110°C. The remaining orange solid was recrystallized from toluene and CH_2Cl_2 to give **5**; m.r. 155–156°C. – MS (70 eV): *m/z* (%) = 386 (23) $[M]^+$, 208 (base peak) $[M - C_{14}H_9]^+$, 176 (10) $[M - C_{14}H_9 - PH_2]^+$. – ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): $\delta = -100$ (d, $J_{PH} = 236$ Hz).

$C_{28}H_{19}P$ (386.4) Calcd. C 87.03 H 4.96
Found C 86.54 H 4.98

Synthesis of Tris(9-anthracenyl)phosphane (**6**): A solution of 9-bromoanthracene (5.91 g, 21.8 mmol) in 100 ml of diethyl ether was added over a period of 15 min to *n*-butyllithium (1.42 g, 22.1 mmol; 9.45 g of a 15% solution in hexane) in 40 ml of ether at −30°C. After stirring for 30 min, and warming to 0°C, the lithium reagent was added over a period of 1.5 h to PCl_3 (1.00 g, 7.2 mmol) in 30 ml of ether. The solution underwent colour changes from yellow to orange to orange-brown. It was refluxed for 1.5 h. The orange solution was filtered, and the remaining solid was washed with 20 ml of ether. The ether was removed in vacuo (10^{-2} Torr), and the remaining red-orange sludge was dissolved in 30 ml of hot toluene. Red crystals of **6** were obtained upon cooling; 0.37 g (7%); m.p. 218°C. – ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = -44$.

$C_{42}H_{27}P$ (652.7) Calcd. C 89.66 H 4.84
Found C 89.76 H 5.02

Synthesis of (9-Anthracenyl)diphenylphosphane (**7**): 9-Lithioanthracene was prepared from 9-bromoanthracene (11.00 g, 43 mmol; 11.58 g of the commercial product of 95% purity) as in the above preparations. Chlorodiphenylphosphane (9.49 g, 43 mmol) in diethyl ether (50 ml) was added via a dropping funnel and the resulting mixture was refluxed for 3.5 h. Removing the solvent in vacuo left an orange solid, which was dissolved in ca. 250 ml of dichloromethane and filtered over 5 g of degassed Al_2O_3 (Woelm, basic). Ca. 100 ml of ethanol was added to aid recrystallization. As the dichloromethane was removed with a rotation evaporator, **7** was obtained as a yellow precipitate with a yield of 11.02 g (71%); m.r. 195–198°C. – ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = -24.08$. – MS (70 eV): *m/z* = 362 $[M]^+$.

$C_{26}H_{19}P$ (362.4) Calcd. C 86.16 H 5.29 P 8.55
Found C 85.80 H 5.50 P 8.57

Reaction of **7** *with* $W(CO)_6$. – *Synthesis of [(9-Anthracenyl)-diphenylphosphane]pentacarbonyltungsten* (**8**): (9-Anthracenyl)diphenylphosphane (9.35 g, 25.8 mmol) was dissolved in ca. 500 ml of toluene. $W(CO)_6$ (9.90 g, 28 mmol) was added, and the mixture was irradiated for 34 h with a Hg lamp. Evolution of CO was observed. The $W(CO)_6$ did not dissolve completely and the ^{31}P-NMR spectrum indicated that the reaction had not gone to completion. (η^2-1-Cyclooctene)pentacarbonyltungsten (5.6 g, 13 mmol) was added and the mixture was stirred for 4 d. The solvent, excess $W(CO)_6$ and (η^2-1-cyclooctene)pentacarbonyltungsten were removed in vacuo (10^{-3} Torr) over a period of 4 h. The pale yellow solid was recrystallized from 70 ml of CH_2Cl_2 and 10 ml of toluene, with a yield of 3.23 g (18%), m.r. 195–197°C. – MS (70 eV): *m/z* (%) = 686 (17) $[M]^+$, 658 (10) $[M - CO]^+$, 630 (25) $[M - 2\,CO]^+$, 602 (47) $[M - 3\,CO]^+$, 574 (2) $[M - 4\,CO]^+$, 546 (base peak) $[M - 5\,CO]^+$, 466 (36) $[M - 5\,CO - Ph]^+$, 362 (63) [ligand]$^+$, 283 (15) [ligand − Ph]$^+$. − ^{31}P NMR (81 MHz, $CDCl_3$): δ = +16.0 ($^1J_{PW}$ = 120.7 Hz).

$C_{31}H_{19}O_5PW$ (686.3) Calcd. C 54.25 H 2.79 P 4.51
Found C 54.07 H 2.84 P 4.01

Reaction of **4** *with $Os_3(CO)_{11}(MeCN)$. − Synthesis of [(9-Anthracenyl)phosphane]undecacarbonyltriosmium* (**9**): A solution of phosphane **4** (40 mg, 0.19 mmol) and (acetonitrile)undecacarbonyltriosmium[23] (175 mg, 0.19 mmol) in 6 ml of CH_2Cl_2 was stirred at 25°C for 15 min. IR spectra showed complete transformation to **9**. The solvent was removed to give 207 mg (100%) of **9**, m.r. 138−140°C. − MS (70 eV): *m/z* (%) = 1088 (26) [M]$^+$, 1060 (14) [M − CO]$^+$, 1032 (42) [M − 2 CO]$^+$, 1004 (48) [M − 3 CO]$^+$, 976 (26) [M − 4 CO]$^+$, 948 (60) [M − 5 CO]$^+$, 920 (46) [M − 6 CO]$^+$, 892 (38) [M − 7 CO]$^+$, 864 (26) [M − 8 CO]$^+$, 836 (32) [M − 9 CO]$^+$, 808 (24) [M − 10 CO]$^+$, 780 (78) [M − 11 CO]$^+$, 389 (base peak). − ^{31}P NMR (81 MHz, CD_2Cl_2): δ = −141.

$C_{25}H_{11}O_{11}Os_3P$ (1088.9) Calcd. C 27.58 H 1.02
Found C 27.65 H 1.13

Dimerization of **4** *to* **11**: Phosphane **4** (2.02 g, 9.6 mmol) was dissolved in a Schlenk tube in ca. 25 ml of toluene. The solution was irradiated for 22.5 h with a Hg lamp, the precipitated solid being periodically scratched from the side of the reaction vessel. The solution was heated for 15 min to the boiling point of toluene, dissolving as much of the solid as possible, and filtered over silica gel. Removal of the solvent under vacuum gave 1.09 g (54%) of **11**. − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.54−7.42 (m), 6.87−6.72 (m, 12H), 4.45 (d, 2H, *J* = 2.56 Hz), 3.66 (d, 4H, PH_2, J_{PH} = 196.1). − ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = −105.5 (s), −106.8 (s). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 134.9 (d, C-8a, C-9a, $^2J_{CP}$ = 8.8 Hz), 131.27 (d, C-4a, C-10a, $^3J_{CP}$ = 2.7 Hz), 127.15 (d, C-1, C-8, $^3J_{CP}$ = 14.6 Hz), 129.3, 129.0, 126.15 (d, J_{CP} = 1.4 Hz), 125.0.

Hydrogenation of the (9-Anthracenyl)difluorophosphane Dimer **10** *to* **11**: A suspension of **10** (1.250 g, 2.6 mmol) and $LiAlH_4$ (1.00 g, 26.3 mmol) in 10 ml of diethyl ether was refluxed for 24 h. Half-concentrated hydrochloric acid was carefully added until the aluminium hydroxide was just dissolved (ca. 30 ml). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (8 times 30 ml). The combined organic layers were filtered through a 1-cm layer of Al_2O_3 (Woelm, basic). The Al_2O_3 was washed twice with ca. 15-ml portions of CH_2Cl_2. After evaporation of the solvent, the remaining yellow crystals were dissolved in hot toluene (ca. 150 ml) and slowly cooled to room temperature. Yield: 1.01 g (93%) of white crystals, m.p. 218°C. Recrystallization from toluene gave single crystals suitable for X-ray diffraction studies. − MS (70 eV): *m/z* (%) = 420 (<1) [M]$^+$, 419 (<1) [M − H]$^+$, 418 (<1) [M − 2 H]$^+$, 386 (<1) [M − PH_2 − H]$^+$, 354 (<1) [M − 2 PH_2]$^+$, 210 (39) [M/2]$^+$.

$C_{28}H_{22}P_2$ (420.4) Calcd. C 79.99 H 5.28
Found C 81.21 H 5.05

Note: The presence of anthracene made satisfactory microanalyses and mass spectra difficult to obtain.

Attempted Dimerization of (9-Anthracenyl)dichlorophosphane (**2**): Phosphane **2** (0.65 g, 2.25 mmol) was dissolved in 2.5 ml of C_6D_6 in a 10-mm NMR tube. The NMR tube was sealed and irradiated with a Hg lamp for 35 h. ^{31}P NMR (81 MHz, C_6D_6) showed signals at δ = 219.6, 205.6, 203.0, 176.5, 176.3, 175.8, 175.5, 175.2, 175.1, and 159.6. The signal for **2** (δP = 159.6) was of low intensity, indicating that **2** had reacted. Attempts to recrystallize the orange solid which had precipitated were unsuccessful.

Synthesis of (9-Difluorophosphano)phenanthrene (**12**): *n*-Butyllithium (2.5 g, 39 mmol) and 9-bromophenanthrene (10 g, 38.9 mmol) were allowed to react for 30 min in 120 ml of ether[24]. PF_2Cl (10.0 g, 95.8 mmol) was condensed onto the lithium reagent at −196°C at 10^{-2} Torr. After removing the solvent in vacuo, redissolving the residue in CH_2Cl_2, removing the LiCl by centrifugation, and removing the solvent again, a yellow oil remained. Upon cooling it became partially crystalline. The product was heated for 4 d to 120°C at 10^{-3} Torr. It condensed and crystallized in a sublimation column to give a white solid, yield 4.91 g (51%), m.p. 42°C. − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 8.75−8.62 (m, 2H), 7.97−7.92 (m, 2H), 7.79−7.64 (m, 5H). − ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 215.7 (t, J_{PF} = 1159 Hz). − ^{19}F NMR (188.3 MHz, $CDCl_3$): δ = −91.2 (d, J_{PF} = 1159 Hz). − ^{13}C-NMR spectra were recorded but could not be assigned with certainty.

$C_{14}H_9F_2P$ (246.2) Calcd. C 68.3 H 3.7
Found C 68.31 H 3.84

Synthesis of cis-Dichlorobis(9-difluorophosphanophenanthrene)-platinum(II) (**13**): A solution of (COD)$PtCl_2$ (1.0 g, 2.67 mmol) and **12** (1.6 g, 6.50 mmol) in 50 ml of CH_2Cl_2 was left standing for 20 h. Colourless crystals of **13** were precipitated; Yield 1.83 g (91%), m.r. 264−271°C. − ^{1}H NMR: δ = 9.1 (d, *J* = 25 Hz, 2H), 8.80−7.62 (m, 16H). − MS (70 eV): *m/z* (%) = 758 (2) [M]$^+$, 722 (2) [M − HCl]$^+$, 686 (8) [M − 2 HCl]$^+$, 246 (base peak) [$C_{14}H_9F_2P$]$^+$, 177 (48) [$C_{14}H_9$]$^+$.

$C_{28}H_{18}Cl_2F_4P_2Pt$ (758.4) Calcd. C 44.3 H 2.4
Found C 44.3 H 2.5

X-ray Analyses of Compounds 6, 8 and 11

X-ray Crystal Structure Determination of the Toluene Solvate of **6**: $C_{42}H_{27}P \times 1.5\ C_7H_8$, M_r = 700.9, rhombohedral, $R\bar{3}$, *a* = *b* = 1661.3(6), *c* = 2598.2(10) pm (hexagonal axes), *U* = 6.210 nm^3, *Z* = 6, D_x = 1.12 Mg m^{-3}, λ(Cu-K_α) = 154.18 pm, μ = 0.8 mm^{-1}, *T* = 20°C, *F*(000) = 2214. − A red prism 0.5 × 0.3 × 0.3 mm was mounted in a glass capillary. Data were collected on a Syntex $P2_1$ four-circle diffractometer to $2\Theta_{max}$ = 135° and corrected for absorption. Of 2126 independent measured reflections, 1526 with *F* > 4σ(*F*) were used for all calculations (program system Siemens SHELXTL PLUS). The orientation matrix was refined from 15

Table 7. Atomic coordinates (× 10^4) and equivalent isotropic temperature factors [pm^2 × 10^{-1}] for compound **6**. *U*(eq) is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor. Atoms X represent the disordered solvent (see text)

	x	y	z	U(eq)
P	0	0	971(1)	43(1)
C(1)	1515(4)	640(4)	1944(2)	62(3)
C(2)	2178(5)	855(5)	2307(3)	79(4)
C(3)	2951(5)	1733(5)	2352(3)	83(4)
C(4)	3022(5)	2438(5)	2047(3)	82(4)
C(4A)	2336(4)	2252(4)	1663(2)	62(3)
C(5)	1755(5)	3578(4)	713(3)	81(4)
C(6)	1138(5)	3439(5)	349(3)	76(4)
C(7)	431(5)	2523(5)	234(2)	68(3)
C(8)	359(4)	1793(4)	495(2)	54(3)
C(8A)	994(4)	1906(3)	897(2)	48(2)
C(9)	917(3)	1145(4)	1196(2)	47(2)
C(9A)	1585(3)	1331(4)	1593(2)	49(2)
C(10)	2390(5)	2970(4)	1377(3)	72(3)
C(10A)	1724(4)	2823(4)	1000(2)	62(3)
X(1)	595(24)	5418(22)	622(12)	171(11)
X(2)	-720(21)	4420(18)	218(11)	139(7)
X(3)	1329(27)	5696(28)	804(15)	248(17)
X(4)	-22(26)	4928(24)	401(12)	169(10)
X(5)	1239(21)	5901(20)	121(13)	181(11)

Table 8. Atomic coordinates (× 10^4) and equivalent isotropic temperature factors [pm^2] for compound **8**. *U*(eq) is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor

	x	y	z	U(eq)
W(1)	10696.2(2)	1041.8(1)	2447.1(1)	220(1)
P(1)	8822(1)	-70(1)	2570(1)	208(5)
C(1)	7246(5)	-1246(3)	522(3)	276(22)
C(2)	6644(5)	-1810(3)	-360(3)	318(24)
C(3)	5331(5)	-1946(3)	-849(3)	336(24)
C(4)	4681(5)	-1495(3)	-450(3)	306(22)
C(4A)	5268(4)	-889(3)	468(3)	236(20)
C(5)	4555(5)	799(3)	2127(3)	307(24)
C(5A)	5226(5)	255(3)	1753(3)	262(22)
C(6)	5162(5)	1464(3)	2965(3)	338(26)
C(7)	6467(5)	1630(3)	3478(3)	344(24)
C(8)	7127(5)	1117(3)	3158(3)	291(22)
C(8A)	6535(4)	386(3)	2286(3)	222(20)
C(9)	7168(4)	-180(3)	1915(3)	212(20)
C(9A)	6578(4)	-776(3)	986(3)	208(19)
C(10)	4622(5)	-392(3)	873(3)	273(22)
C(11)	8740(4)	-1236(3)	2221(3)	228(20)
C(12)	7548(5)	-1979(3)	1929(3)	288(22)
C(13)	7548(5)	-2834(3)	1694(3)	356(24)
C(14)	8711(5)	-2973(3)	1732(3)	394(26)
C(15)	9890(5)	-2248(3)	2021(3)	401(26)
C(16)	9917(5)	-1382(3)	2270(3)	303(22)
C(21)	8775(4)	154(3)	3663(3)	224(21)
C(22)	9856(5)	840(3)	4427(3)	258(21)
C(23)	9787(5)	1019(3)	5241(3)	305(23)
C(24)	8664(5)	521(3)	5311(3)	324(25)
C(25)	7600(5)	-181(3)	4559(3)	330(25)
C(26)	7653(5)	-353(3)	3742(3)	257(21)
C(31)	12117(5)	1921(3)	2315(3)	266(22)
C(32)	12123(5)	961(3)	3355(3)	279(23)
C(33)	10690(5)	2115(3)	3441(3)	354(26)
C(34)	9255(5)	1131(4)	1547(3)	352(26)
C(35)	10769(5)	26(3)	1440(3)	356(26)
O(31)	12939(4)	2425(2)	2245(2)	379(18)
O(32)	12928(4)	938(3)	3877(3)	449(20)
O(33)	10737(5)	2726(3)	4007(3)	607(24)
O(34)	8472(4)	1189(3)	1040(3)	569(24)
O(35)	10847(4)	-519(3)	867(3)	574(22)
W(2)	4891.6(2)	5456.1(1)	3535.5(1)	253(1)
P(2)	2875(1)	5661(1)	2741(1)	222(5)
C(1')	3522(4)	5451(3)	1045(3)	275(22)
C(2')	3711(5)	5259(3)	270(3)	309(23)
C(3')	3957(5)	5919(4)	-34(3)	349(25)
C(4')	4012(5)	6743(4)	438(3)	327(25)
C(4A')	3822(4)	6975(3)	1251(3)	253(21)
C(5')	3922(5)	8996(3)	3068(3)	294(23)
C(5A')	3805(4)	8096(3)	2560(3)	262(21)
C(6')	3896(5)	9256(3)	3878(3)	337(24)
C(7')	3832(5)	8660(3)	4267(3)	344(24)
C(8')	3709(5)	7794(3)	3800(3)	297(22)
C(8A')	3617(4)	7453(3)	2908(3)	243(21)
C(9')	3363(4)	6541(3)	2374(3)	224(20)
C(9A')	3549(4)	6312(3)	1568(3)	225(20)
C(10')	3896(4)	7843(3)	1745(3)	267(22)
C(11')	1552(5)	4673(3)	1737(3)	262(21)
C(12')	602(5)	4767(4)	1129(3)	346(25)
C(13')	-387(5)	4021(4)	391(3)	463(29)
C(14')	-473(6)	3162(4)	238(4)	490(28)
C(15')	441(6)	3049(4)	833(4)	458(27)
C(16')	1441(5)	3804(3)	1580(3)	346(24)
C(21')	1796(5)	5954(3)	3338(3)	282(22)
C(22')	1868(5)	5804(3)	4066(3)	382(26)
C(23')	1034(6)	6007(4)	4515(4)	520(33)
C(24')	181(6)	6378(4)	4254(4)	516(32)
C(25')	98(6)	6535(4)	3534(4)	485(31)
C(26')	891(5)	6317(3)	3076(3)	375(26)
C(31')	6459(6)	5250(4)	4127(3)	418(28)
C(32')	3672(5)	4466(3)	3703(3)	332(24)
C(33')	5149(6)	6412(4)	4722(3)	392(27)
C(34')	6142(6)	6488(4)	3430(3)	414(28)
C(35')	4754(5)	4531(4)	2365(3)	366(27)
O(31')	7333(4)	5089(3)	4443(3)	602(25)
O(32')	3005(4)	3921(3)	3812(3)	517(21)
O(33')	5305(5)	6948(3)	5388(3)	630(24)
O(34')	6849(4)	7073(3)	3390(3)	723(28)
O(35')	4691(5)	4018(3)	1717(3)	550(23)
Cl(1)	7804(3)	4153(2)	2027(2)	1792(23)
Cl(2)	8081(3)	3020(2)	2806(2)	1242(17)
C(100)	8834(11)	3831(7)	2511(7)	1145(33)

reflections in the 2Θ range 25–40°. – The structure was solved by direct methods. Early in the refinement it became clear that a large region of characterless electron density, associated with symmetry centres, could not be adequately refined. The five largest peaks were refined as half-occupied carbon sites, but several peaks of height ca. 0.5×10^{-6} e pm^{-3} remained. The program BYPASS[25], which is specially designed to refine solvent regions, indicated a solvent volume per symmetry centre corresponding to one toluene molecule (this composition was used to derive the crystal data given above). However, although the *R* value was reduced, the esd's of bond lengths and angles were scarcely affected; the arbitrary refinement of the five peaks (atoms X in the coordinate table) was therefore retained. In view of these problems, the structure determination is necessarily imprecise. Hydrogen atoms were included using a riding model. The final *R* value was 0.096, with $R_w = 0.099$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00175\,F^2$. 150 parameters, $S = 2.4$, max. $\Delta/\sigma = 0.08$. Final atomic coordinates are given in Table 7.

X-Ray Crystal Structure Determination of **8**: $C_{31}H_{19}O_5PW \times 0.5\ CH_2Cl_2$, $M_r = 728.7$, triclinic, space group $P\bar{1}$, $a = 1121.0(2)$, $b = 1723.0(4)$, $c = 1763.0(4)$ pm; $\alpha = 110.96(2)$, $\beta = 104.29(2)°$, $\gamma = 105.80(2)°$. $U = 2.8265\ nm^3$, $Z = 4$, $D_x = 1.71\ Mg\ m^{-3}$, $\lambda(Mo\text{-}K_\alpha) = 71.069$ pm, $\mu = 4.36\ mm^{-1}$, $T = -95\,°C$, $F(000) = 1420$. – A yellow prism 0.6 × 0.35 × 0.2 mm was mounted on a glass fibre and transferred to a Nicolet R3 diffractometer with LT-2 low-temperature attachment. The temperature was maintained at −95 °C.

Table 9. Atomic coordinates (× 10^4) and equivalent isotropic temperature factors [pm^2] for compound **11**. *U*(eq) is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor

	x	y	z	U(eq)
P	3398(2)	3025(1)	6114(2)	450(6)
H(01)	3944(49)	2341(30)	5423(60)	339(91)
H(02)	4519(46)	2932(33)	7765(50)	339(91)
C(1)	1967(5)	3789(3)	2363(7)	316(18)
C(2)	1180(6)	4014(4)	587(7)	397(19)
C(3)	1815(6)	4617(4)	-259(7)	387(19)
C(4)	3246(5)	4995(4)	671(6)	308(17)
C(4A)	4050(5)	4763(3)	2453(5)	230(15)
C(5)	8053(5)	4166(3)	4713(6)	294(17)
C(6)	8902(5)	3407(4)	5671(6)	323(17)
C(7)	8285(5)	2780(4)	6485(6)	350(18)
C(8)	6824(5)	2934(3)	6392(6)	294(17)
C(8A)	5965(5)	3697(3)	5444(5)	237(15)
C(9)	4364(5)	3936(3)	5275(6)	239(15)
C(9A)	3404(5)	4151(3)	3313(5)	244(15)
C(10)	5621(5)	5138(3)	3517(5)	229(15)
C(10A)	6591(5)	4322(3)	4577(5)	234(15)

10499 reflections ($2\Theta_{max} = 50°$) were measured, of which 9950 were independent ($R_{int} = 0.015$); 8082 were considered observed [$F > 4\sigma(F)$] and used for all calculations. The orientation matrix was refined from the setting angles of 50 reflections in the range $2\Theta = 20-23°$. – The structure was solved by the heavy atom method. After isotropic refinement, an absorption correction was applied using the program DIFABS[26] (transmissions 0.90–1.13). Non-H atoms were then refined anisotropically; H atoms were included using a riding model. The final R value was 0.027, with $w_R = 0.032$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002\ F^2$. 707 parameters, S 1.4, max. Δ/σ 0.001, max. $\Delta\varrho = 1.6 \times 10^{-6}$ e pm^{-3}. Final atomic coordinates are given in Table 8.

X-Ray Crystal Structure Determination of **11**: $C_{28}H_{22}P_2$, M_r = 420.44, monoclinic, space group $P2_1/c$, $a = 963.6(4)$, $b = 1393.6(5)$, $c = 823.4(3)$ pm, $\beta = 113.68(3)°$, $U = 1.013$ nm^3, $Z = 2$, D_x = 1.38 Mg m^{-3}, λ(Mo-K_α) = 71.069 pm, $\mu = 0.22$ mm^{-1}, T = –95°C, $F(000) = 440$. – Most crystals proved unusable because of wide and irregular reflection profiles, but eventually a suitable pale yellow prism 0.45 × 0.35 × 0.3 mm was mounted as for compound **6**. Because of the wide reflection profiles, ω-scans of 1.5° were used to register 2255 reflections ($2\Theta_{max} = 53°$), of which 2092 were independent ($R_{int} = 0.013$); 1515 were considered observed [$F > 4\sigma(F)$] and used for all calculations. The orientation matrix was refined from the setting angles of 33 reflections in the range $2\Theta = 20-23°$. – The structure was solved by routine direct methods. Non-H atoms were refined anisotropically, H attached to C isotropically using a riding model. At this stage, the H atoms bonded to phosphorus were the largest peaks in a difference synthesis; they were refined with equal temperature factors and subjected to the constraint of equal P–H bond lengths (with a weight corresponding to an e.s.d. of 2 pm). The final R value was 0.079, with R_w = 0.083. The poor residuals can be attributed to the poor crystal quality. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004\ F^2$. 171 parameters, $S = 3.1$, max. $\Delta/\sigma = 0.001$, max. $\Delta\varrho = 0.5 \times 10^{-6}$ e pm^{-3}. Final atomic coordinates are given in Table 9.

Further details of all structure determinations (complete bond lengths and angles, H atom coordinates, temperature factors, structure factors, torsion angles) have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2. Any request for this material should quote a full literature citation and the reference number CSD-56299.

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[1] Dedicated to Professor *F. H. Westheimer* on the occasion of his 80th birthday.

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1: 121314-15-6 / **2**: 141982-25-4 / **2** [$(OH)_2$ statt Cl_2]: 141982-33-4 / **3**: 141982-26-5 / **4**: 141982-27-6 / **5**: 141982-28-7 / **6**: 141982-29-8 / **6** · 1.5 C_7H_8: 141982-30-1 / **7**: 110954-35-3 / **8**: 141982-34-5 / **8** · 0.5 CH_2Cl_2: 141982-36-7 / **9**: 141982-35-6 / **10**: 121289-97-2 / **11**: 141982-31-2 / **12**: 141982-32-3 / **13**: 142003-20-1 / $C_8H_{14}W(CO)_5$: 93040-30-3 / $Os_3(CO)_{11}CH_3CN$: 65702-94-5 / (COD)$PtCl_2$: 12080-32-9 / PCl_3: 7719-12-2 / Ph_2PCl: 1079-66-9 / $W(CO)_6$: 14040-11-0 / 9-bromoanthracene: 1564-64-3 / 9-bromophenanthrene: 9014-10-1