PERKIN 2

The solid state conformation of oxo stabilised ylides: X-ray structures of four new polyoxo phosphorus ylides

R. Alan Aitken, Nazira Karodia † and Philip Lightfoot

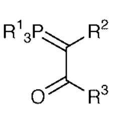
*School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife,
UK KY16 9ST. E-mail: raa@st-and.ac.uk and pl@st-and.ac.uk*

Received (in Cambridge, UK) 15th July 1999, Accepted 22nd November 1999

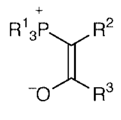
The first X-ray structure determinations of a trioxo ylide **7**, a tetraoxo ylide **8**, a tetraoxo bis(ylide) **10** and a hexaoxo bis(ylide) **9** show these compounds to exhibit unexpected effects as regards the relative alignment of the 4–8 contiguous C=X units present. Crystal-packing forces are sufficient to over-ride the normal preference for the P=C–C=O unit in such stabilised ylides to have the *syn* configuration. A survey of all previous X-ray structures of acyclic oxo-stabilised phosphorus and arsenic ylides is also presented.

Introduction

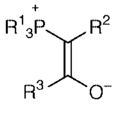
It is well established that phosphorus ylides **1** containing an adjacent carbonyl group are significantly stabilised and this may be attributed to a significant contribution from the phosphonium enolate structures **2** and **3**.[1,2] The fact that such delocalisation leads to the possibility of distinct geometrical isomers was demonstrated at an early stage by the observation of separate ^{1}H NMR signals for the isomers of **4**.[3] It is clear that, for effective delocalisation, the P=C–C=O system should be planar but whether the P=C and C=O functions are more likely to be *syn* as in **2** or *anti* as in **3** will depend on the nature of R^1, R^2 and R^3, although the favourable electrostatic interaction between P$^+$ and O$^-$ in **2** might reasonably be supposed to favour this form. Although the structure of such ylides has been investigated by a variety of techniques and the structures of **5** and **6** have been predicted using theoretical methods,[4] there has been no systematic survey of the pattern of *syn vs. anti* alignment of the P and O atoms as revealed by the many X-ray structures of this type which have been reported. From our studies of the synthetic application of pyrolytic extrusion of Ph$_3$PO from such compounds, we had available a range of stabilised ylides containing linear arrays of 4, 5, 6 and 8 contiguous P=C and C=O functions in which the relative alignment of the adjacent groups is much more difficult to predict. We present here the X-ray structures of **7**,[5] **8** and **9**,[6] and **10**,[7] but in order to understand the significance of the results, we first survey the values of the P=C–C=O torsion angle and the deviations of the bond lengths from normally expected values,[8] for compounds of this type in the Cambridge Structural Database (CSD). It should be noted that a previous comprehensive survey of average bond lengths determined by X-ray methods[8] did not include any ylides.



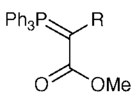
1



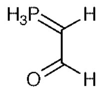
2



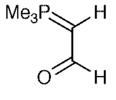
3



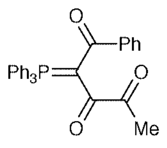
4



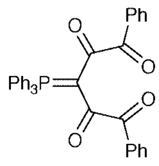
5



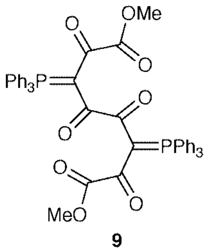
6



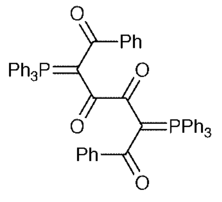
7



8



9



10

Previous structures of carbonyl stabilised phosphorus ylides

The structures of phosphorus ylides **11**–**27** are stabilised by an adjacent aldehyde or ketone carbonyl group and compound **28** is stabilised by an imine; relevant structural parameters together with the CCDC reference codes are presented in Table 1. In a few cases the figures may differ slightly from those reported by the original authors since they have been determined directly from the CSD which is believed to be more accurate. It should be noted that **15**/**16** exists as a 1 : 1 mixture of the two conformations shown and also that **19** is unsymmetrical in the crystal leading to two separate sets of values for the two ends. It is immediately obvious that all the structures of this type have the *syn* alignment of the P and O atoms corresponding to structure **2**. The bond lengths also show considerable delocalisation with all the P=C lengths considerably greater than the value of 1.66–1.67 Å determined for Ph$_3$P=CH$_2$.[25,26] Likewise the values for C–C and C=O may be compared with averages of 1.465 and 1.222 Å for the corresponding bonds in the fragment =C–C=O.[8]

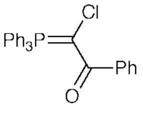
When we come to the ester-stabilised ylides **29**–**40** a quite different pattern is apparent. As shown in Table 2, the 12 examples are equally divided between the *syn* and *anti* forms corresponding to **2** and **3**. It appears that in the absence of

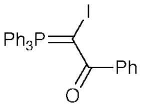
---

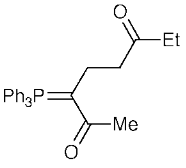
† *Present address*: Department of Chemistry, University of Bradford, Bradford, West Yorkshire, UK BD7 1DP.

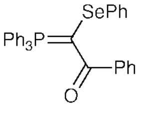
Table 1 Structural parameters for aldehyde, ketone and imine stabilised phosphorus ylides

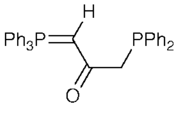
Compound	CCDC Reference Code	Bond lengths/Å			Torsion angle/°	Ref.
		P=C	C–C	C=O/N	P=C–C=O/N	
11	BOPOMC	1.736	1.361	1.301	10.2	9
12	BOPOMI	1.713	1.346	1.277	2.9	9
13	YUFKIT	1.736	1.396	1.271	7.1	10
14	DEPFAF	1.746	1.407	1.251	1.7	11
15	NAVDAP	1.708	1.391	1.241	4.1	12
16	NAVDAP	1.724	1.398	1.233	5.4	12
17	ZEBZEL	1.744	1.406	1.230	11.0	13
18	PRACFE	1.718	1.390	1.235	5.3	14
19	YECKOG	1.748	1.423	1.235	10.1	15
		1.755	1.435	1.226	4.5	
20	KETBAM	1.773	1.333	1.333	5.9	16
21	COPRAA	1.709	1.457	1.229	6.2	17
22	JEFVOF	1.710	1.384	1.249	0.5	18
23	PYLASN	1.750	1.363	1.269	2.1	19
24	BOTMAY	1.711	1.390	1.255	2.2	20
25	PUJJOT	1.755	1.370	1.290	0.2	21
26	YIKBOJ	1.770	1.426	1.234	1.9	22
27	DEVHIV	1.717	1.399	1.257	10.5	23
28	KOPMOR	1.734	1.359	1.333	0.6	24

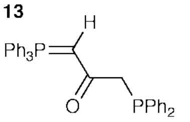

11

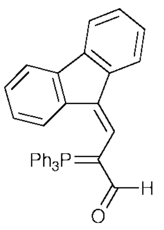

12

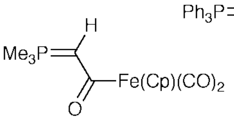

13

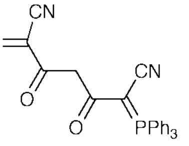

14

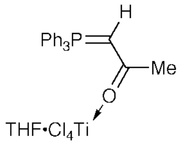

15

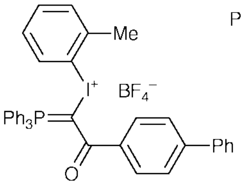

16

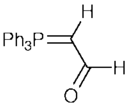

17

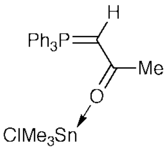

18

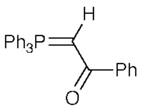

19

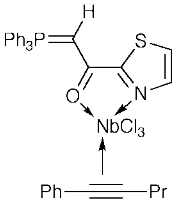

20

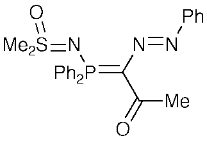

21

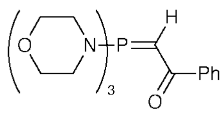

22

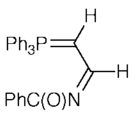

23

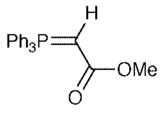

24

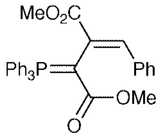

25

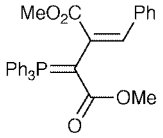

26

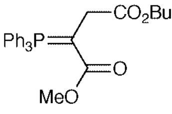

27

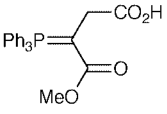

28

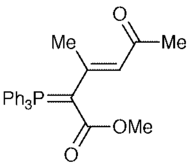

29

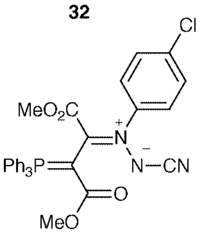

30

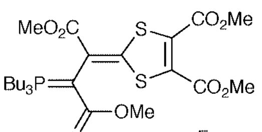

31

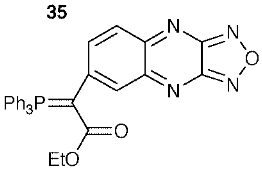

32

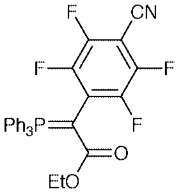

33

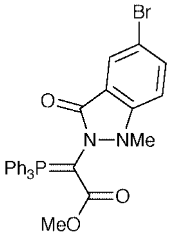

34

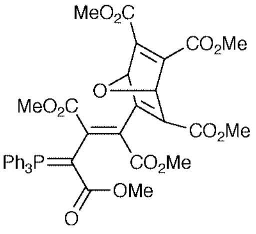

35


36


37


38


39


40

special features the *anti* arrangement is preferred and the *syn* arrangement only occurs for the simple P=CH case **29** and in examples where the ylide function is conjugated with a C=C bond on the other side to the ester function. The C–C and C=O bond lengths in these cases should be compared with average values of 1.488 and 1.199 Å for the fragment =C–C(=O)–OR.[8] There is no correlation between the extent of delocalisation as indicated by the bond lengths and whether a compound is *syn* or *anti* and delocalisation appears to be equally effective in both situations.

Table 2 Structural parameters for ester stabilised phosphorus ylides

		Bond lengths/Å				
Compound	CCDC Reference Code	P=C	C–C	C=O	Torsion angle/° P=C–C=O	Ref.
29	TPCMOM01	1.704	1.394	1.227	2.3	27
30	TMXPTP	1.752	1.424	1.351	7.9	28
31	CMXPTP	1.727	1.416	1.225	10.2	28
32	TBCMTP	1.715	1.415	1.221	177.5	29
33	CMXPPN	1.733	1.393	1.244	166.0	29
34	YUFKEP	1.747	1.424	1.224	0.7	30
35	TPEAZM10	1.752	1.442	1.216	166.0	31
36	SOCMOM	1.727	1.401	1.235	0.1	32
37	VEGRII	1.749	1.438	1.209	176.8	33
38	SUFMEL	1.722	1.441	1.222	177.6	34
39	BOWMAB	1.712	1.373	1.270	174.9	35
40	YIZSUV	1.748	1.445	1.216	2.3	36

Table 3 Structural parameters for phosphorus ylides stabilised by two carbonyl or carbonyl and imine groups

		Ester (imine for **53**, COPh for **54**)				Ketone (imine for **43**, **44**, COC_2F_5 for **54**)			
		Bond lengths/Å				Bond lengths/Å			
Compound	CCDC Reference Code	P=C	C–C	C=O/N	Torsion angle/° P=C–C=O/N	C–C	C=O/N	Torsion angle/° P=C–C=O/N	Ref.
41	BUTJEF	1.758	1.439	1.212	144	1.448	1.217	2	37
42	POSACE	1.698	1.473	1.201	177.7	1.484	1.318	15.5	38
43	LETGUM	1.760	1.453	1.210	163.3	1.426	1.237	6.05	39
	LETHAT	1.763	1.451	1.198	177.5	1.416	1.233	8.7	39
44	NAMREY	1.770	1.454	1.227	169.8	1.435	1.303	174.4	40
45	GOKBOX	1.751	1.451	1.205	173.6	1.425	1.257	2.9	41
46	JIKDEM	1.772	1.460	1.206	170.3	1.420	1.254	3.9	42
	JIKDEM01	1.749	1.449	1.212	154.9	1.412	1.254	3.0	42
47	JISTUA	1.766	1.472	1.203	150.0	1.404	1.279	0.9	43
		1.773	1.440	1.215	168.9	1.410	1.282	3.0	
48	JISVAI	1.763	1.439	1.216	168.2	1.423	1.259	7.4	43
49	KENSAX	1.759	1.449	1.224	32.0	1.431	1.247	0.1	44
50	KENROK	1.769	1.473	1.208	161.8	1.409	1.270	10.9	44
51	ZUBDAB	1.745	1.455	1.176	154.0	1.403	1.253	8.4	45
		1.749	1.449	1.188	153.7	1.407	1.255	8.6	
52	VAVWEU	1.754	1.441	1.199	170.5	1.421	1.246	1.2	46
	VAVWIY	1.759	1.452	1.212	152.7	1.416	1.268	8.3	46
53	NAMRAU	1.768	1.443	1.294	39.0	1.433	1.240	2.2	40
54	DENSIY	1.748	1.505	1.211	65.2	1.387	1.241	5.3	47

A considerable number of structures **41**–**54** have been determined with an ylide function stabilised by two flanking carbonyl groups or one carbonyl and an imine. For **43**, **46**, **47**, **51** and **52** the compounds exist in the crystal as two separate forms leading to two sets of structural parameters. Most of the examples contain one ester and one ketone or imine carbonyl group and from the data in Table 3, it is clear that in almost all cases the ester oxygen is *anti* to P while the ketone or imine oxygen is *syn* to P. The bond lengths also confirm that delocalisation occurs to a much more significant extent towards the ketone or imine function and hardly at all towards the ester. The only exceptions to this pattern are **44**, where steric problems are likely to prevent the imine function from being *syn* to P, and **49**, for which there is no obvious explanation. For **53** and **54** it can be seen that delocalisation is primarily towards the *syn* acetyl and perfluoropropionyl groups respectively and the imine and benzoyl groups are aligned at an intermediate angle with no significant delocalisation in the latter case.

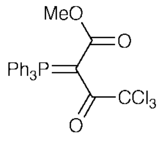
Previous structures of stabilised arsenic, nitrogen and sulfur ylides

For the arsenic ylides **55**–**66**, the data largely conform to the patterns already established for phosphorus ylides (Table 4). For **61** and **63** two separate forms occur in the crystal. It is clear that ester groups are generally *anti* to As while ketone groups are *syn*. It is interesting to note this is also the case for **58** which following the pattern of **30**, **31**, **34**, **36** and **40** might have been expected to be *syn*. The only exceptions are **59**, which like the keto analogue **60** exists in the *syn* configuration, and **65** for which a hydrogen bonding interaction with the NH favours the acetyl group adopting the *anti* configuration of the carbonyl with respect to P.

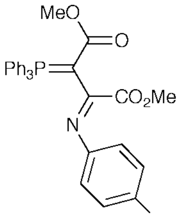
A few ylides of other elements **67**–**71** (Table 5) serve to illustrate the general principle that a single ketone carbonyl is always aligned *syn* to the heteroatom but once the heteroatom is satisfied by the resulting attractive interaction an additional carbonyl may be *anti*. It should be noted however that for **69**–**71** there is no significant difference in the extent of delocalisation into the *syn* and *anti* groups as indicated by the bond lengths. Again **68**–**70** each occur as two separate forms in the crystal.

Structures of polyketones

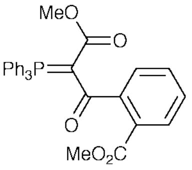
In considering the likely structure of the oxo ylides **7**–**10** it is not only the relative alignment of the P=C and C=O functions but also that of the adjacent carbonyls which is of interest. In contrast to the oxo ylide structure where there is a potential attractive interaction between P and O, the interaction between two adjacent carbonyl groups should be entirely repulsive. For this reason it might be expected that vicinal polycarbonyl compounds would have adjacent carbonyl groups aligned *anti* to one another. However, early UV and IR studies[61] showed that



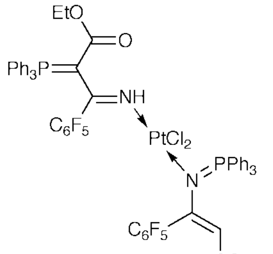
41



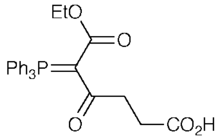
42



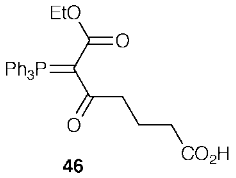
43



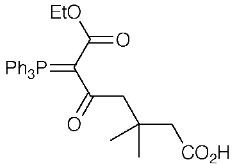
44



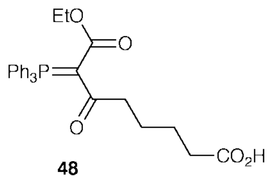
45



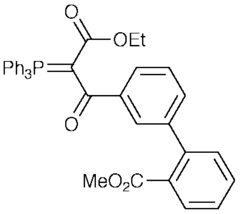
46



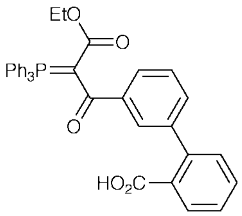
47



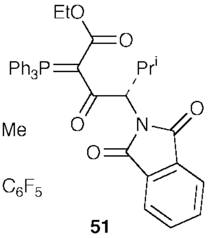
48



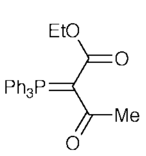
49



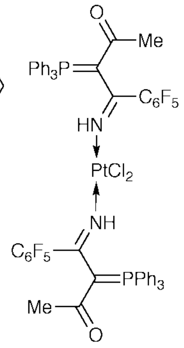
50



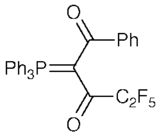
51



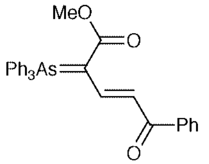
52



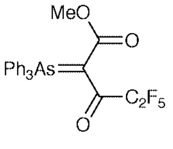
53



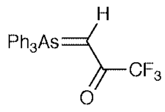
54



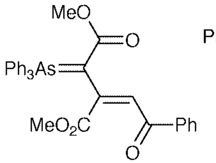
55



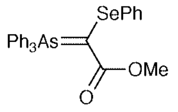
56



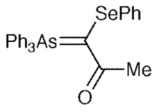
57



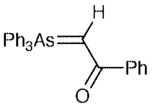
58



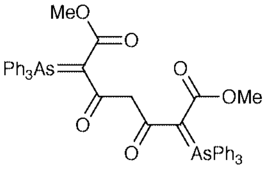
59



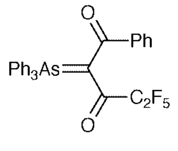
60



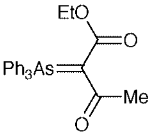
61



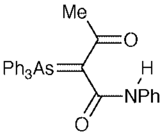
62



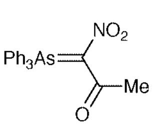
63



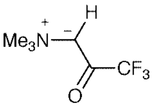
64



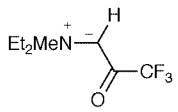
65



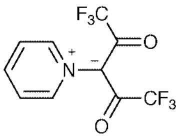
66



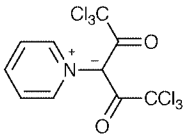
67



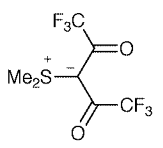
68



69



70



71

this is in fact unlikely and as shown in Chart 1, the data for the few compounds of this type which have been structurally characterised by X-ray methods confirm this. For benzil **72**,[62] and the vicinal triones **73**,[63] **74**,[64] and **75**,[65] the torsion angles are generally nearer to 90° than 180°. When we come to the tetraone **76**[63] the central two carbonyls are nearly *syn* to one another while the outer pairs are nearer *anti*, a pattern which is not repeated however with the dimesityl analogue **77**.[64] For the two known pentaones **78** and **79**,[66] the observed pattern of two small central angles and two large outer angles was supported by theoretical calculations based on dipole–dipole forces which gave idealised values of 25° and 180° respectively. The same method predicted two angles of 127° for triones and either 180°, 90° and 180° or 3 × 130° for tetraones.[66] Even in the cyclic tetraones **80**[67] and **81**[68] the adjacent carbonyl groups are at intermediate angles to one another.

Results and discussion

The structure of the trioxo ylide **7** is shown in Fig. 1. It can be seen that the ylide function is approximately *syn* to the carbonyl group on both sides while the two adjacent carbonyls are at an intermediate angle to one another as in the polyketones **72**–**81**. Significant delocalisation into the two adjacent carbonyls is also apparent from the bond lengths given.

For the ylide **8** stabilised by two identical 1,2-diketone groups the structure is illustrated in Fig. 2. In this case it is rather surprising to see that one of the two carbonyl groups flanking

Table 4 Structural parameters for arsenic ylides

		Ester (COPh for **63**, COMe for **65**)				Ketone (COC_2F_5 for **63**, CONHPh for **65**)			
		Bond lengths/Å				Bond lengths/Å			
Compound	CCDC Reference Code	X=C	C–C	C=O	Torsion angle/° X=C–C=O	C–C	C=O	Torsion angle/° X=C–C=O	Ref.
55	SIRFUU	1.877	1.452	1.205	173.6	—	—	—	48
56	CUCYAA	1.899	1.454	1.164	172.0	1.391	1.237	7.7	49
57	FOFSOI	1.854	—	—	—	1.427	1.217	2.6	50
58	VANYAK	1.877	1.446	1.213	176.3	—	—	—	51
59	ZITZOR	1.824	1.437	1.227	2.6	—	—	—	52
60	RAXDUP	1.903	—	—	—	1.352	1.238	4.2	53
61	BOTLUR	1.871	—	—	—	1.382	1.251	1.3	20
		1.866	—	—	—	1.375	1.238	4.1	
62	ZOVDET	1.874	1.447	1.215	151.3	1.413	1.255	5.75	54
63	CARZEA	1.896	1.478	1.236	34.4	1.397	1.253	7.1	55
		1.896	1.469	1.219	37.7	1.395	1.255	7.8	
64	FOLNOJ	1.864	1.474	1.204	170.1	1.416	1.245	2.1	56
65	FOLNUP	1.864	1.436	1.240	176.8	1.467	1.241	0.5	56
66	FOLPAX	1.878	—	—	—	1.437	1.238	11.0	56

Table 5 Structural parameters for nitrogen and sulfur ylides

		anti-COR				*syn*-COR			
		Bond lengths/Å				Bond lengths/Å			
Compound	CCDC Reference Code	X=C	C–C	C=O	Torsion angle/° X=C–C=O	C–C	C=O	Torsion angle/° X=C–C=O	Ref.
67	CEDGOH	1.499	—	—	—	1.353	1.245	8.4	57
68	DANJUX	1.477	—	—	—	1.330	1.269	0.9	58
		1.477	—	—	—	1.329	1.264	2.2	
69	CEYWEI	1.460	1.405	1.226	175.0	1.418	1.222	3.0	59
		1.455	1.410	1.221	165.9	1.413	1.224	8.3	
70	CEYWIM	1.457	1.420	1.206	173.6	1.417	1.207	5.1	59
		1.455	1.409	1.195	171.9	1.420	1.218	3.1	
71	FECDUM	1.746	1.445	1.208	174.2	1.404	1.220	0.6	60

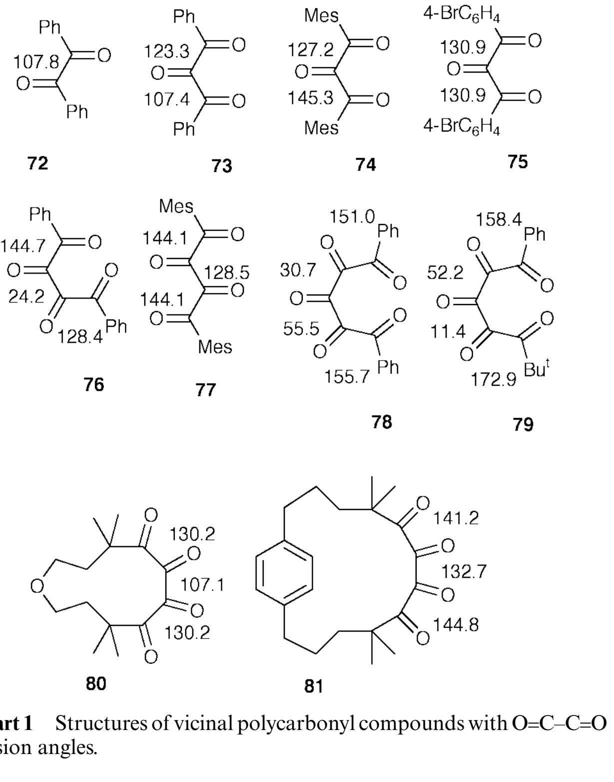


Chart 1 Structures of vicinal polycarbonyl compounds with O=C–C=O torsion angles.

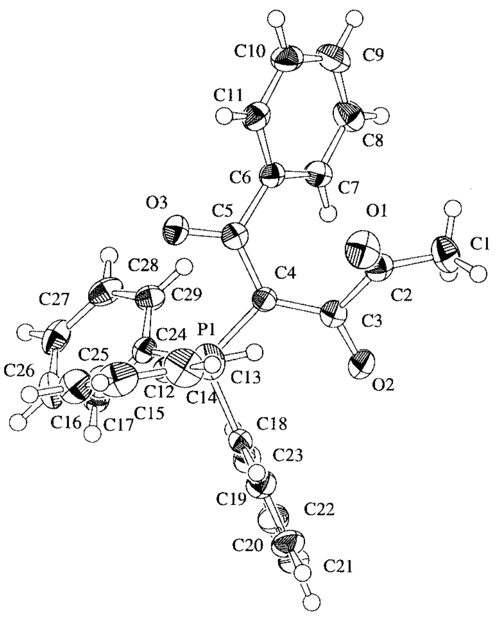


Fig. 1 X-Ray structure of the trioxo ylide **7**. Selected bond lengths and torsion angles; P(1)–C(4) 1.759(2), C(4)–C(5) 1.439(3), C(5)–O(3) 1.247(3), C(4)–C(3) 1.432(3), C(3)–O(2) 1.235(3), C(3)–C(2) 1.545(3), C(2)–O(1) 1.205(3) Å; P(1)–C(4)–C(5)–O(3) 11.1(3), P(1)–C(4)–C(23)–O(2) 25.9(3), O(2)–C(3)–C(2)–O(1) −126.1(2)°.

the ylide function is *syn* to it and the other *anti* while the adjacent carbonyls are almost at 90° to each other. As mentioned earlier for **69**–**71** the extent of delocalisation towards the two carbonyl functions as reflected in the bond lengths seems to be approximately equal whether the carbonyl is *syn* or *anti* to the ylide function.

The two ylide functions in the bis(ylides) **9** and **10** are effectively isolated from each other as far as delocalisation is concerned by the central oxalyl unit and these offer the opportunity

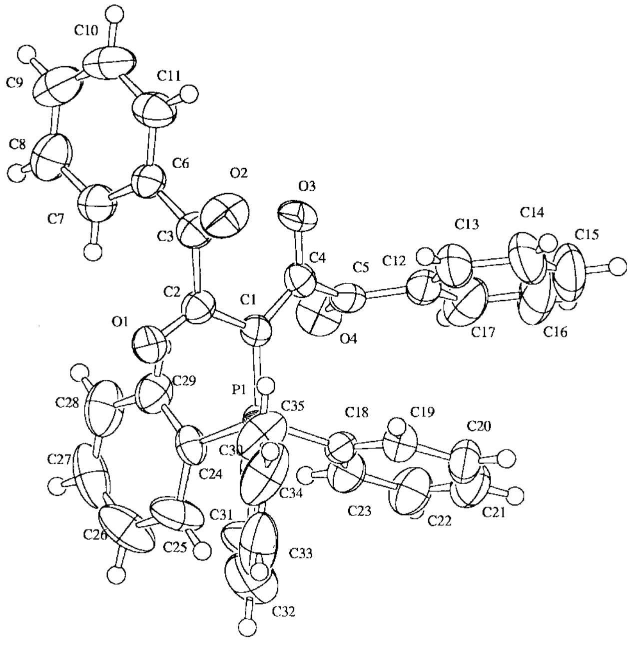


Fig. 2 X-Ray structure of the tetraoxo ylide **8**. Selected bond lengths and torsion angles; P(1)–C(1) 1.751(9), C(1)–C(2) 1.43(1), C(2)–O(1) 1.23(1), C(2)–C(3) 1.52(1), C(3)–O(2) 1.20(1), C(1)–C(4) 1.44(1), C(4)–O(3) 1.25(1), C(4)–C(5) 1.53(1), C(5)–O(4) 1.21(1) Å; P(1)–C(1)–C(2)–O(1) −6(1), O(1)–C(2)–C(3)–O(2) 91(1), P(1)–C(1)–C(4)–O(3) −178.6(8), O(3)–C(4)–C(5)–O(4) −105(1)°.

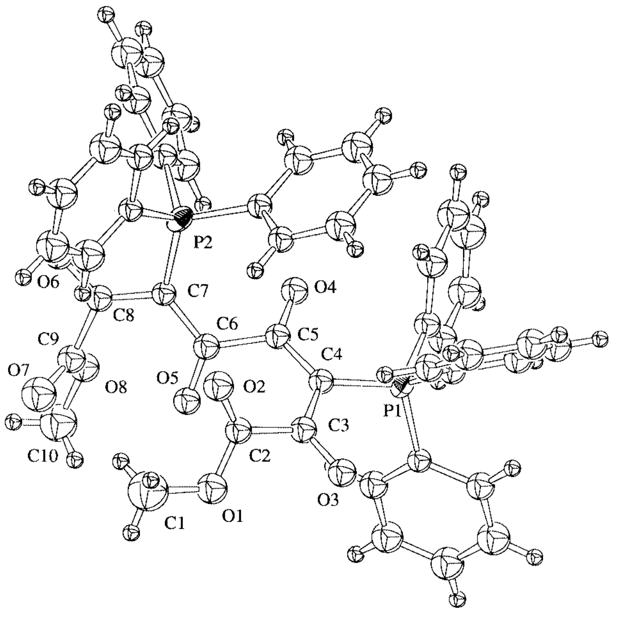


Fig. 3 X-Ray structure of the hexaoxo bis(ylide) **9**. Selected bond lengths and torsion angles; P(1)–C(4) 1.76(1), C(4)–C(3) 1.41(1), C(3)–O(3) 1.27(1), C(3)–C(2) 1.53(2), C(2)–O(2) 1.18(1), C(4)–C(5) 1.45(1), C(5)–O(4) 1.24(1), C(5)–C(6) 1.52(2), C(6)–O(5) 1.24(1), C(6)–C(7) 1.43(1), C(7)–P(2) 1.76(1), C(7)–C(8) 1.40(2), C(8)–O(6) 1.25(1), C(8)–C(9) 1.51(2), C(9)–O(7) 1.20(1) Å; P(1)–C(4)–C(3)–O(3) −3(1), O(3)–C(3)–C(2)–O(2) 122(1), P(1)–C(4)–C(5)–O(4) −11(2), O(4)–C(5)–C(6)–O(5) 129(1), O(5)–C(6)–C(7)–P(2) 163(1), P(2)–C(7)–C(8)–O(6) 3(2), O(6)–C(8)–C(9)–O(7) −77(2)°.

to examine the configuration of two separate ylide functions each stabilised by two adjacent carbonyls within the same molecule. In addition since these contain linear arrays of no fewer than 8 and 6 contiguous C=X units respectively they represent the longest such systems to be examined to date.

Suitable crystals of **9** were obtained by slow evaporation of an NMR solution and were found to contain two molecules of CDCl$_3$ per ylide. The structure is shown in Fig. 3. In this case one of the ylide functions has both flanking carbonyls *syn* while the other has one *syn* and one *anti*. All three 1,2-dicarbonyl functions are aligned at intermediate angles and as expected the bond lengths indicate pure single bond character for CO–CO. Again the extent of delocalisation as indicated by the bond lengths is approximately equal from the ylide functions towards all four flanking carbonyls whether they are *syn* or *anti*.

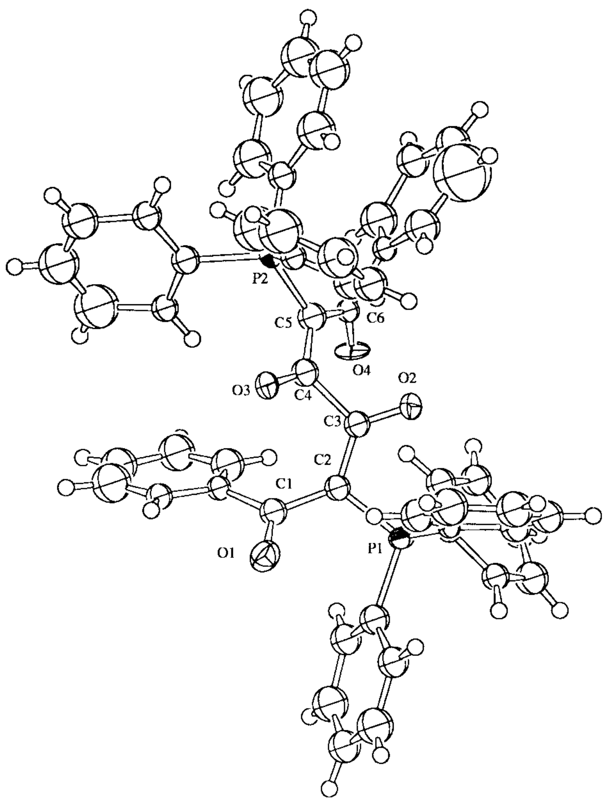


Fig. 4 X-Ray structure of the tetraoxo bis(ylide) **10** (Molecule A). Selected bond lengths and torsion angles; P(1)–C(2) 1.73(3), C(2)–C(1) 1.49(4), C(1)–O(1) 1.24(3), C(2)–C(3) 1.43(4), C(3)–O(2) 1.21(3), C(3)–C(4) 1.60(4), C(4)–O(3) 1.20(3), C(4)–C(5) 1.39(4), C(5)–P(2) 1.80(3), C(5)–C(6) 1.50(4), C(6)–O(4) 1.16(3) Å; P(1)–C(2)–C(1)–O(1) 29(3), P(1)–C(2)–C(3)–O(2) 7(3), O(2)–C(3)–C(4)–O(3) −128(2), O(3)–C(4)–C(5)–P(2) 16(4), P(2)–C(5)–C(6)–O(4) −146(2)°.

The structure solution of **10** was complicated by the fact that the structure was found to consist of a 1 : 1 ratio of two different molecules **10A** (Fig. 4) and **10B** (Fig. 5) which differ only in the alignment of one of the outer carbonyl groups. Thus, **10A** has one ylide function with two *syn* carbonyls and the other with one *syn* and one approximately *anti* while **10B** has both ylide functions with two approximately *syn* carbonyls. Because of the rather high *R* factor for this structure the bond lengths are subject to some error but it appears that the extent of delocalisation toward the lone *anti* carbonyl C(6)–O(4) in form **10A** is markedly reduced compared to normal.

Conclusion

The torsion angles between the adjacent C=P and C=O functions determined for **7**–**10** are summarised in Chart 2. While the observed pattern is in reasonable agreement with the patterns established for previously reported oxo ylide and polyketone structures described earlier, it is clear that the normal preference for *syn* alignment of the ylide and ketone carbonyl functions is reduced for a second carbonyl group to such an extent that one carbonyl group may be *anti* as seen for **8**–**10**. With the possible exception of **10A**, the extent of delocalisation does not appear to be affected by a stabilising carbonyl group being *anti* to the ylide and other factors such as crystal packing forces probably predominate in deciding how the adjacent C=X functions are aligned in the crystalline state.

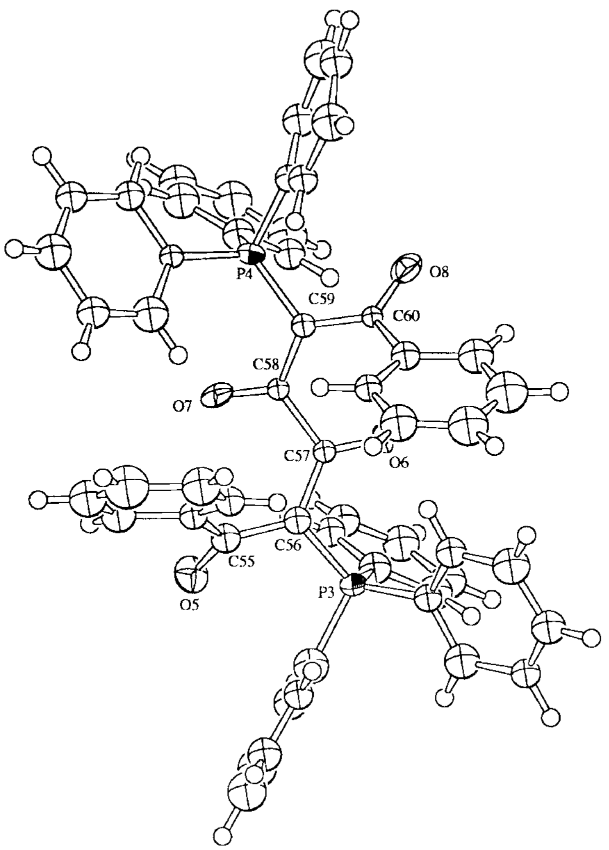


Fig. 5 X-Ray structure of the tetraoxo bis(ylide) **10** (Molecule B). Selected bond lengths and torsion angles; P(3)–C(56) 1.74(3), C(56)–C(55) 1.46(4), C(55)–O(5) 1.22(3), C(56)–C(57) 1.44(3), C(57)–O(6) 1.21(3), C(57)–C(58) 1.49(3), C(58)–O(7) 1.26(3), C(58)–C(59) 1.44(3), C(59)–P(4) 1.75(3), C(59)–C(60) 1.37(3), C(60)–O(8) 1.25(3) Å; P(3)–C(56)–C(55)–O(5) −42(3), P(3)–C(56)–C(57)–O(6) −4(3), O(6)–C(57)–C(58)–O(7) 139(2), O(7)–C(58)–C(59)–P(4) −11(3), P(4)–C(59)–C(60)–O(8) −35(3)°.

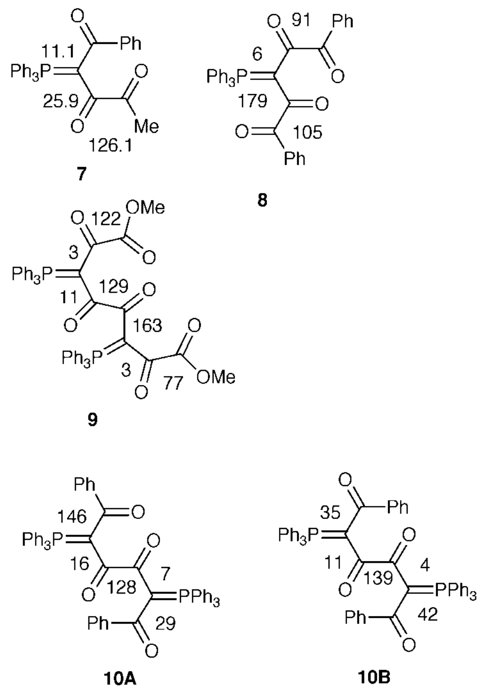


Chart 2 Structures of carbonyl stabilised phosphorus ylides **7**–**10** with P=C–C=O and O=C–C=O torsion angles.

Experimental

The ylides **7**,[5] **8** and **9**,[6] and **10**[7] were prepared as already described.

X-Ray structure determinations

Data were recorded on a Rigaku AFC7S diffractometer using Mo-Kα radiation and the structures were solved by direct methods and refined using full-matrix least squares analysis.

1-Phenyl-2-triphenylphosphoranylidenepentane-1,3,4-trione 7

A colourless block suitable for X-ray diffraction was obtained by recrystallisation from ethyl acetate–toluene. The following crystal data were obtained: $C_{29}H_{23}O_3P$, $M = 450.47$, monoclinic space group $P2_1/n$ (#14); $a = 12.915(3)$, $b = 10.298(3)$, $c = 17.648(3)$ Å, $\beta = 101.08(2)°$, $V = 2303.5(9)$ Å^3, $Z = 4$, $D_c = 1.299$ g cm^{-3}, $R = 0.040$, $R_w = 0.040$ for 3267 data with $I > 3\sigma(I)$ and 299 parameters. Data were recorded at 200 K.

1,5-Diphenyl-3-triphenylphosphoranylidenepentane-1,2,4,5-tetraone 8

A colourless block suitable for X-ray diffraction was obtained by recrystallisation from ethyl acetate–CH_2Cl_2. The following crystal data were obtained: $C_{35}H_{25}O_4P{\cdot}0.5CH_2Cl_2$, $M = 583.02$, triclinic space group $P\bar{1}$ (#2); $a = 11.681(2)$, $b = 14.540(2)$, $c = 10.415(2)$ Å, $\alpha = 101.15(1)$, $\beta = 115.38(1)$, $\gamma = 91.95(1)°$, $V = 1554.5(6)$ Å^3, $Z = 2$, $D_c = 1.25$ g cm^{-3}, $R = 0.116$, $R_w = 0.156$ for 3569 data with $I > 3\sigma(I)$ and 383 parameters. Data were recorded at 293 K.

The quality of the refinement suffers from the presence of a disordered solvent molecule. An NMR spectrum of the crystal used suggests this to be CH_2Cl_2 (δ_H 5.30). Several models of disorder were tested, but this moiety was finally refined as a 50% occupied CH_2Cl_2 with C isotropic and Cl anisotropic, which satisfactorily accounts for most of the scattering density. The nature of the solvent models tested makes no significant difference to the refined parameters of the ylide molecule.

Dimethyl 3,6-bis(triphenylphosphoranylidene)-2,4,5,7-tetraoxo-octanedioate 9

A colourless plate suitable for X-ray diffraction was obtained by slow evaporation of a solution in $CDCl_3$. The structure showed that two molecules of $CDCl_3$ of crystallisation were present. The following crystal data were obtained: $C_{46}H_{36}O_8P_2{\cdot}2CDCl_3$, $M = 1017.5$, triclinic space group $P\bar{1}$ (#2); $a = 10.08(1)$, $b = 14.23(2)$, $c = 17.18(1)$ Å, $\alpha = 85.5(1)$, $\beta = 81.4(1)$, $\gamma = 76.20(7)°$, $V = 2364(4)$ Å^3, $Z = 2$, $D_c = 1.429$ g cm^{-3}, $R = 0.062$, $R_w = 0.064$ for 1999 data with $I > 3\sigma(I)$ and 298 parameters. Data were recorded at 293 K.

Due to the complexity of this structure, and its poor scattering, all C and O atoms were refined isotropically, with Cl and P only being refined anisotropically.

2,5-Bis(triphenylphosphoranylidene)-1,6-diphenylhexane-1,3,4,6-tetraone 10

A yellow crystal suitable for X-ray diffraction was obtained by recrystallisation from ethyl acetate–toluene. The structure showed a partly occupied toluene solvent molecule to be present. The following crystal data were obtained: $C_{54}H_{40}O_4P_2{\cdot}0.25\ C_7H_8$, $M = 839.9$, monoclinic space group Cc (#9); $a = 32.65(1)$, $b = 15.601(5)$, $c = 19.141(8)$ Å, $\beta = 102.95(3)°$, $V = 9500(6)$ Å^3, $Z = 8$, $D_c = 1.17$ g cm^{-3}, $R = 0.107$, $R_w = 0.142$ for 3178 data with $I > 3\sigma(I)$ and 568 parameters. Data were recorded at 220 K.

This material crystallises in the non-centrosymmetric space group Cc, with two independent molecules in the asymmetric unit. Attempts to solve the structure in centrosymmetric $C2/c$ with one independent molecule were unsuccessful. The lowering of symmetry is genuine, and is clearly related to the differences in conformation caused by crystal packing effects. Consequently a low data/parameter ratio was again obtained, and all C atoms were refined isotropically.

CCDC reference number 188/205. See http://www.rsc.org/suppdata/p2/a9/a905747a for crystallographic files in .cif format.

References

1 A. W. Johnson, *Ylides and Imines of Phosphorus*, Wiley, Chichester, 1993.
2 S. M. Bachrach and C. I. Nitsche, in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, Chichester, 1994, vol. 3, p. 273.
3 H. I. Zeliger, J. P. Snyder and H. J. Bestmann, *Tetrahedron Lett.*, 1969, 2199.
4 S. M. Bachrach, *J. Org. Chem.*, 1992, **57**, 4367.
5 R. A. Aitken, H. Hérion, A. Janosi, N. Karodia, S. V. Raut, S. Seth, I. J. Shannon and F. C. Smith, *J. Chem. Soc.*, *Perkin Trans. 1*, 1994, 2467.
6 R. A. Aitken and N. Karodia, *Liebigs Ann./Recl.*, 1997, 779.
7 R. A. Aitken, H. Hérion, C. E. R. Horsburgh, N. Karodia and S. Seth, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 485.
8 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.
9 A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, 1965, **87**, 5603; F. S. Stephens, *J. Chem. Soc.*, 1965, 5640, 5658.
10 H. J. Bestmann, A. Gross and F. Hampel, *Z. Kristallogr.*, 1995, **210**, 239.
11 S. Husebye, E. A. Meyers, R. A. Zingaro, A. L. Braga, J. V. Comasseto and N. Petragnani, *Acta Crystallogr.*, *Sect. C*, 1986, **42**, 90.
12 D. Soulivong, C. Wieser, M. Marcellin, D. Matt, A. Harriman and L. Toupet, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2257.
13 M. F. Braña, M. Morán, M. J. Pérez de Vega, I. Pita-Romero and N. Walker, *Tetrahedron*, 1995, **51**, 9127.
14 H. Blau, W. Malisch, S. Voran, K. Blank and C. Krüger, *J. Organomet. Chem.*, 1980, **202**, C33.
15 L. Pandolfo, G. Facchin, R. Bertani, P. Ganis and G. Valle, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 576.
16 J. A. Albanese, D. L. Staley, A. L. Rheingold and J. L. Burmeister, *Inorg. Chem.*, 1990, **29**, 2209.
17 R. M. Moriarty, I. Prakash, O. Prakash and W. A. Freeman, *J. Am. Chem. Soc.*, 1984, **106**, 6082.
18 M. Geoffroy, G. Rao, Z. Tancic and G. Bernardinelli, *J. Am. Chem. Soc.*, 1990, **112**, 2826.
19 J. Buckle, P. G. Harrison, T. J. King and J. A. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 1552.
20 M. Shao, X. Jin, Y. Tang, Q. Huang and Y. Huang, *Tetrahedron Lett.*, 1982, **23**, 5343.
21 E. Diez-Barra, J. Fernández-Baeza, M. M. Kubicki, A. Lara-Sánchez, A. Otero, N. Poujaud and J. Tejeda, *J. Organomet. Chem.*, 1997, **542**, 291.
22 A. N. Chekhlov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1992, 2737.
23 G. O. Nevstad, K. Maartmann-Moe, C. Rømming and J. Songstad, *Acta Chem. Scand.*, *Ser. A*, 1985, **39**, 523.
24 S. A. Touré, A. Voglozin, E. Degny, R. Danion-Bougot, D. Danion, J. P. Pradère, L. Toupet and Y. T. N'Guessan, *Bull. Soc. Chim. Fr.*, 1991, **128**, 574.
25 J. C. J. Bart, *Angew. Chem.*, *Int. Ed. Engl.*, 1968, **7**, 730; *J. Chem. Soc.* (*B*), 1969, 350.
26 H. Schmidbaur, J. Jeong, A. Schier, W. Graf, D. L. Wilkinson and G. Muller, *New J. Chem.*, 1989, **13**, 341.
27 P. D. Boyle, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 2859.
28 U. Lingner and H. Burzlaff, *Acta Crystallogr.*, *Sect. B*, 1974, **30**, 1715.
29 A. F. Cameron, F. D. Duncanson, A. A. Freer, V. W. Armstrong and R. Ramage, *J. Chem. Soc.*, *Perkin Trans. 2*, 1975, 1030.
30 H. J. Bestmann, A. Gross and F. Hampel, *Z. Kristallogr.*, 1995, **210**, 237.
31 R. D. Gilardi and I. L. Karle, *Acta Crystallogr.*, *Sect. B*, 1972, **28**, 3420.
32 R. A. Aitken, G. Ferguson and S. V. Raut, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 812.
33 C. A. Kavounis, A. P. Bozopoulos and C. J. Cheer, *Z. Kristallogr.*, 1989, **188**, 299.
34 J. Vincente, M. T. Chicote, J. Fernández-Baeza, A. Fernández-Baeza and P. G. Jones, *J. Am. Chem. Soc.*, 1993, **115**, 794.
35 A. Alemagna, P. Del Buttero, E. Licandro, S. Maiorana and C. Guastini, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 337.
36 M. B. Hocking and F. W. van der Voort Maarschalk, *Can. J. Chem.*, 1994, **72**, 2428.
37 C. He, Q. Zheng, F. Shen, S. Dou and G. Lin, *Wuli Xuebao*, 1982, **31**, 825.
38 T. C. W. Mak and J. Trotter, *Acta. Crystallogr.*, 1965, **18**, 81.
39 F. D. Rochon, R. Melanson and M. M. Kayser, *Acta Crystallogr.*, *Sect. C*, 1994, **50**, 1165.
40 J. Vincente, M. T. Chicote, M. A. Beswick and M. C. R. de Arellano, *Inorg. Chem.*, 1996, **35**, 6592.
41 A. D. Abell, B. M. Clark and W. T. Robinson, *Aust. J. Chem.*, 1988, **41**, 1243.
42 A. D. Abell, J. O. Trent and W. T. Robinson, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 362.
43 A. D. Abell, J. O. Trent and K. B. Morris, *J. Chem. Soc. Perkin Trans. 2*, 1991, 1077.
44 A. D. Abell, K. B. Morris and V. McKee, *Aust. J. Chem.*, 1990, **43**, 765.
45 R. A. Aitken, H. R. Cooper and A. P. Mehrotra, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 475.
46 A. D. Abell, B. M. Clark and W. T. Robinson, *Aust. J. Chem.*, 1989, **42**, 2225.
47 Z.-X. Xia, Z.-M. Zhang and Y.-C. Shen, *Huaxue Xuebao*, 1984, **42**, 1223.
48 R. A. Aitken, A. J. Blake, I. Gosney, R. O. Gould, D. Lloyd and R. A. Ormiston, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 1801.
49 Z. Fan and Y. Shen, *Huaxue Xuebao*, 1984, **42**, 759.
50 Y. Shen, Z. Fan and W. Qiu, *J. Organomet. Chem.*, 1987, **320**, 21.
51 Q. Huang, Y. Huang, M. Shao and Y. Tang, *Youji Huaxue*, 1987, 181.
52 W.-M. Lu, Z.-Z. Huang and X. Huang, *Acta Crystallogr.*, *Sect. C*, 1996, **32**, 89.
53 W.-M. Lu, Z.-Z. Huang, X. Huang and J.-M. Gu, *Jiegou Huaxue*, 1997, **16**, 52.
54 L. Pandolfo, R. Bertani, G. Facchin, L. Zanotto, P. Ganis, G. Valle and R. Seraglia, *Inorg. Chim. Acta*, 1995, **237**, 27.
55 Z.-X. Xia and Z.-M. Zhang, *Huaxue Xuebao*, 1983, **41**, 577.
56 G. Ferguson, I. Gosney, D. Lloyd and B. L. Ruhl, *J. Chem. Res.* (*S*), 1987, 260; *J. Chem. Res.* (*M*), 1987, 2140.
57 E. Ziegler, H. Wittmann and K. Peters, *Monatsh. Chem.*, 1983, **114**, 783.
58 K. Peters, E. M. Peters, H. G. von Schnering, E. Ziegler and H. Wittmann, *Z. Kristallogr.*, 1984, **169**, 305.
59 H. Wittmann, E. Ziegler, K. Peters, E. M. Peters and H. G. von Schnering, *Monatsh. Chem.*, 1983, **114**, 1097.
60 H. Wittmann, E. Ziegler, H. Stork, K. Peters, E. M. Peters and H. G. von Schnering, *Monatsh. Chem.*, 1985, **116**, 1189.
61 L. Horner and F. Maurer, *Chem. Ber.*, 1968, **101**, 1783.
62 C. J. Brown and R. Sadanaga, *Acta Crystallogr.*, 1965, **18**, 158.
63 R. L. Beddoes, J. R. Cannon, M. Heller, O. S. Mills, V. A. Patrick, M. B. Rubin and A. H. White, *Aust. J. Chem.*, 1982, **35**, 543.
64 M. Khaftory and M. B. Rubin, *J. Chem. Soc.*, *Perkin Trans. 2*, 1983, 149.
65 J. R. Cannon, K. T. Potts, C. L. Raston, A. F. Sierakowski and A. H. White, *Aust. J. Chem.*, 1978, **31**, 297.
66 R. Gleiter, E. Litterst, T. Oeser and H. Irngartinger, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 1048.
67 R. Gleiter, U. Ackermann, T. Oeser and H. Irngartinger, *Chem. Eur. J.*, 1996, **2**, 271.
68 R. Gleiter, R. Krämer, H. Irngartinger and C. Bissinger, *J. Org. Chem.*, 1992, **57**, 252.

Paper a905747a