

{(E)- and (Z)-2-[α,β -bis(methoxycarbonyl)vinyl]cyclopentadien-1-ylidene}triphenylphosphorane

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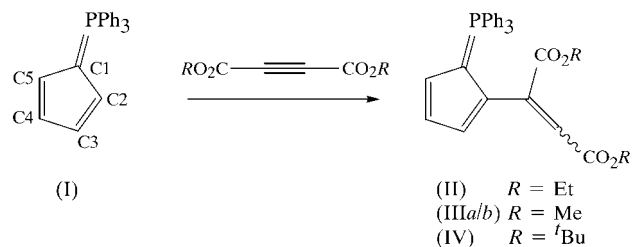
The Ramirez ylide undergoes electrophilic substitution with dialkyl acetylenedicarboxylates, yielding a mixture of the *Z* and *E* adducts. The crystal structure analyses of the two adducts formed using dimethylacetylene, *viz.* dimethyl (*E*)- and (*Z*)-1-[2-(triphenylphosphoranylidene)cyclopentadien-1-yl]ethylenedicarboxylate, both $C_{29}H_{25}O_4P$, explain an unusual chemical shift observed for the vinyl H atom of the *Z* adduct, which had previously precluded a definitive assignment of the isomers. In addition, the structures explain why only one of the isomers reacts further with acetylene esters to produce azulenes with a rare substitution pattern.

Comment

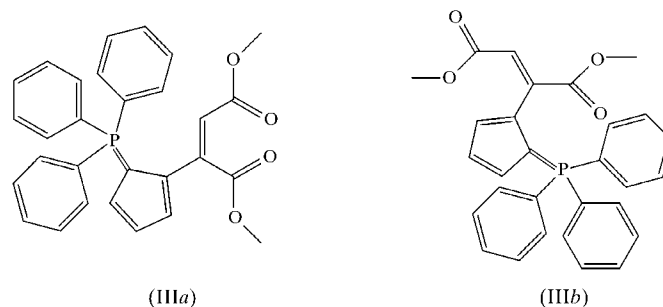
The ylide (cyclopentadien-1-ylidene)triphenylphosphorane (often referred to as the Ramirez ylide), (I), is known to be unreactive in the Wittig reaction because of the aromaticity present in the five-membered ring (Ramirez & Levy, 1957*a,b*). Instead, as shown by Yoshida *et al.* (1971*a,b*, 1973), (I) reacts with electrophiles, undergoing substitution at the 2-position. In one case, an activated acetylene (diethyl acetylenedicarboxylate) was used, which gave a putative vinyl adduct, (II), but the stereochemistry of the double bond was not established. We had cause to reinvestigate this reaction and we extended the study to other dialkyl acetylene esters [$R = Me$, Et and tBu , *i.e.* (IV)]. The reactions typically gave two isomeric adducts, one of which exhibits an unusual chemical shift (4.7 p.p.m.) in the 1H NMR spectrum. This behaviour precluded a definitive *E/Z* assignment of the isomers.

In addition, we have found that one isomer in each case reacts with further acetylene ester to give azulenes with a rare substitution pattern (Higham *et al.*, 2004). It was clear that an X-ray crystallographic study would identify the isomer stereochemistry, shed light on the unusual chemical shift and provide valuable information as to why only one isomer should react to form azulenes. To this end, we reacted (I) with dimethyl acetylenedicarboxylate and isolated the major

isomer by recrystallization. An X-ray crystallographic study proved this to be, somewhat surprisingly, the *Z* adduct, (III*a*) (Fig. 1).



The approximate planarity of the five-membered ring and the alkene function, together with the short distance between atoms C2 and C6 [1.438 (2) Å], suggests conjugation of the new alkene with the cyclopentadienyl ring. It is also clear that the vinyl H atom is in an unusual location, placing it within the bonding domain of the ylide bond (an ylide pocket), that provides some explanation, together with the extensive conjugation present, as to the unusual chemical shift of 4.71 p.p.m. We calculate the shortened contact distance between atom P1 and the vinyl H atom attached to atom C9 to be 2.81 (2) Å. This unusual H-atom position might be thought of as a factor in the elongation of the C1–C2 bond [1.4496 (19) Å] relative to the C1–C5 bond length [1.411 (2) Å]. On the other hand, there is also substantial elongation of the C1–C2 bond in the other adduct (see below) and in the Ramirez ylide itself. The internuclear P...H distance is 2.71 Å, calculated on the basis of an internuclear C–H distance of 1.08 Å.



The spectroscopic data for the minor product were consistent with a species formed quantitatively when dichloromethane solutions of (III*a*) were subjected to a source of UV light for 96 h (this process could not be duplicated by prolonged heating). Recrystallization from dichloromethane–ethanol yielded orange crystals, which, when analysed by X-ray diffraction, were found to be the *E* isomer, (III*b*) (Fig. 2). In contrast to (III*a*), there is a high steric hindrance inherent in (III*b*) which twists the alkene group and five-membered ring out of the same plane by 43.3 (2)°; the C2–C6 bond length increases to 1.464 (3) Å, concomitant with the associated loss of electron delocalization. The 1H NMR spectrum supports this result in giving a chemical shift closer to that expected for vinyl protons [6.29 p.p.m. compared with 4.71 p.p.m. in (III*a*)]. Pertinent bond lengths and angles for (I),

(IIIa) and (IIIb) are given in Table 1 [see Ammon *et al.* (1973) for comprehensive structural details of (I)].

It is striking that the bond lengths within the five-membered rings of (I), (IIIa) and (IIIb) are consistently unequal. Thus, the C1–C2 and C4–C5 bonds are both elongated, while the C3–C4 bond is truncated compared with the C1–C5 and C2–C3 bonds. It is not clear why the bond-length inequalities in the adducts (which might be expected) should also be reflected in the parent, and we assume that this behaviour is a coincidence. The P–C1 bond lengths should be more informative, being related to the nature of the ylide bond, and it is notable that, in the adducts, these bonds are elongated [1.7412 (14) Å in (IIIa), 1.7357 (18) Å in (IIIb) and 1.718 (2) Å in (I)]. Ordinarily, this elongation would mean (Gilheany, 1994) that the ylide carbanion in the adducts is

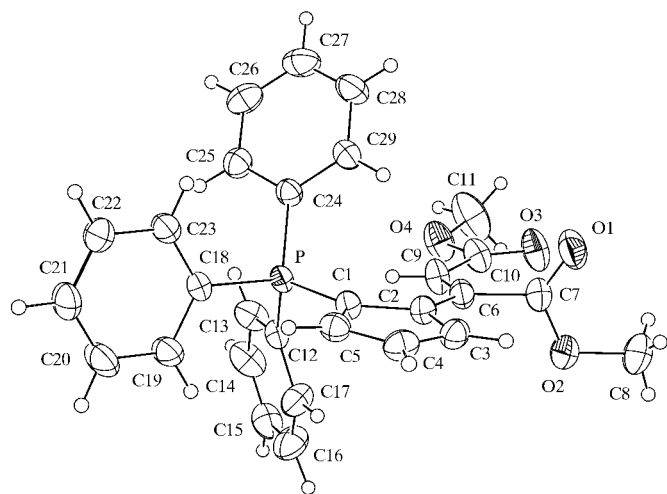


Figure 1
The molecule of (IIIa), with displacement ellipsoids drawn at the 40% probability level.

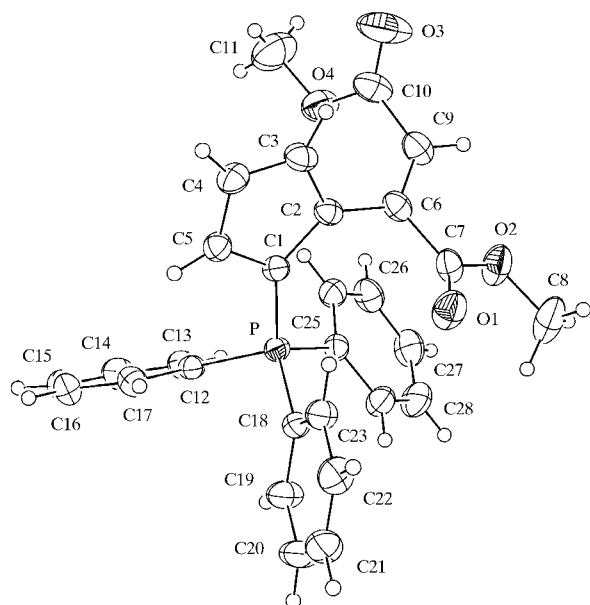


Figure 2
The molecule of (IIIb), with displacement ellipsoids drawn at the 40% probability level.

more delocalized than in the parent. However, this conclusion is not consistent with the lack of coplanarity between the five-membered ring and the vinyl substituent in (IIIb). It is also noteworthy that the external C2–C1–P angle is wider in the adducts [131.86 (11)° in (IIIa), 130.43 (14)° in (IIIb) and 125.3 (2)° in (I)].

We were also interested in the details of the conformation of the ylide portion of the molecules. It is frequently observed in X-ray studies that the carbanion substituents tend to take up an orientation perpendicular to the plane of one of the P-substituent bonds, referred to as the unique substituent. This behaviour is illustrated in Fig. 3, the conformation being called perpendicular. In addition, it is common that a deviation from carbanion planarity occurs, of up to 20° from the plane perpendicular to the plane containing the P=C bond and the unique substituent. Where there is a deviation, it is usually towards the unique substituent, the P–C bond length of which is, in turn, lengthened. These observations are linked to the electronic structure of a typical phosphonium ylide (Gilheany, 1994), where there is overlap of the occupied *p* orbital on the carbanion into an antibonding orbital of the phosphorus substituent (called negative hyperconjugation). Therefore, it is notable that in both adducts there is no such deviation from planarity and no evidence that one of the P–C(Ph) bonds is unique.

The bond lengths, X-ray photoelectron spectra and ¹H NMR coupling constants previously obtained for the Ramirez ylide have been used to describe the amount of ylide–ylene character present (86% ylide), but this two-component bonding description has since fallen out of favour (Gilheany, 1994). It is sufficient to note for (IIIa) and (IIIb) that the increased P–C1 bond length and C2–C1–P bond angle suggest less ylene character than may be present in the parent compound. The bond lengths and angles within the PPh₃ group for the three compounds are as expected and unremarkable.

In conclusion, X-ray crystallographic studies of (IIIa) and (IIIb) have allowed the stereochemical assignment of the vinyl adducts. When diethyl and di-*tert*-butyl acetylenedicarboxylate were reacted with (I), a mixture of the *Z* and *E* isomers were again obtained in each case. A ¹H NMR resonance at 4.7 p.p.m. was observed in both reactions and assigned to the *Z* adduct. Therefore, the adduct initially reported by Yoshida *et al.* (1971a,b, 1973) can now confidently be said to have *Z* stereochemistry. Our mechanistic studies of the formation of azulenes (Higham *et al.*, 2004) reveal a step that is dependent on a Wittig reaction, and this is only feasible for the *E* isomer, (IIIb). For the *Z* isomer, (IIIa), this study illustrates why no

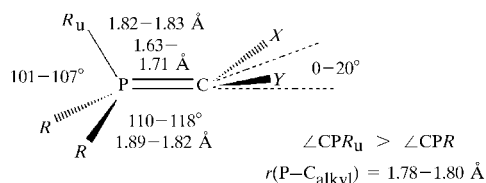


Figure 3
The ylide bonding model, in which R_u represents the unique substituent.

reaction takes place, namely because no rotation of the vinyl bond can bring the phosphorus and the requisite β -carbonyl group into close enough proximity.

Experimental

For the preparation of (IIIa), dimethyl acetylenedicarboxylate (0.43 g, 3.0 mmol) was added to a foil-enclosed solution of (I) (1.0 g, 3.0 mmol) in benzene (30 ml) and the mixture was stirred overnight under nitrogen. The resulting yellow precipitate was filtered off and stored. The filtrate was evaporated, yielding a solid that, when triturated with hot methanol, gave a fine yellow powder. ^1H NMR analysis showed that the two solids were identical and they were therefore combined. Recrystallization from carbon tetrachloride-ethanol yielded crystals suitable for X-ray analysis (yield 0.86 g, 60%; m.p. 517–518 K). For the preparation of (IIIb), phosphorane (IIIa) (1.0 g, 2.14 mmol) was dissolved in dichloromethane (40 ml) in a 50 ml Pyrex round-bottomed flask under nitrogen. The flask was placed 15 cm from the UV source (300 W lamp) and irradiated for 96 h. The wine-coloured solution was evaporated and the resulting brown-orange solid was recrystallized from dichloromethane-ethanol in a darkened flask, giving orange crystals (yield 0.9 g, 90%; m.p. 507–508 K).

Compound (IIIa)

Crystal data

$\text{C}_{29}\text{H}_{25}\text{O}_4\text{P}$ $D_x = 1.259 \text{ Mg m}^{-3}$
 $M_r = 468.46$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/n$ Cell parameters from 5590 reflections
 $a = 13.7622 (15) \text{ \AA}$ $\theta = 2.3\text{--}26.3^\circ$
 $b = 11.8849 (13) \text{ \AA}$ $\mu = 0.14 \text{ mm}^{-1}$
 $c = 15.8788 (17) \text{ \AA}$ $T = 293 (2) \text{ K}$
 $\beta = 107.914 (2)^\circ$ Prism, brown
 $V = 2471.3 (5) \text{ \AA}^3$ $0.50 \times 0.40 \times 0.36 \text{ mm}$
 $Z = 4$

Data collection

Bruker SMART CCD area-detector 6129 independent reflections
 diffractometer 5100 reflections with $I > 2\sigma(I)$
 φ and ω scans $R_{\text{int}} = 0.027$
 Absorption correction: multi-scan $\theta_{\text{max}} = 28.3^\circ$
 (SADABS; Sheldrick, 2002) $h = -18 \rightarrow 18$
 $T_{\text{min}} = 0.877$, $T_{\text{max}} = 0.950$ $k = -15 \rightarrow 15$
 43 496 measured reflections $l = -21 \rightarrow 21$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.5453P]$
 $R[F^2 > 2\sigma(F^2)] = 0.048$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.127$ $(\Delta/\sigma)_{\text{max}} = 0.005$
 $S = 1.05$ $\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
 6129 reflections $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
 407 parameters
 All H-atom parameters refined

Compound (IIIb)

Crystal data

$\text{C}_{29}\text{H}_{25}\text{O}_4\text{P}$ Mo $K\alpha$ radiation
 $M_r = 468.46$ Cell parameters from 8862 reflections
 Orthorhombic, $Pbca$ $\theta = 2.8\text{--}22.3^\circ$
 $a = 14.8041 (9) \text{ \AA}$ $\mu = 0.15 \text{ mm}^{-1}$
 $b = 18.0337 (12) \text{ \AA}$ $T = 293 (2) \text{ K}$
 $c = 18.1151 (12) \text{ \AA}$ Plate, orange
 $V = 4836.2 (5) \text{ \AA}^3$ $0.30 \times 0.25 \times 0.10 \text{ mm}$
 $Z = 8$
 $D_x = 1.287 \text{ Mg m}^{-3}$

Data collection

Bruker SMART CCD area-detector 4261 independent reflections
 diffractometer 3428 reflections with $I > 2\sigma(I)$
 φ and ω scans $R_{\text{int}} = 0.054$
 Absorption correction: multi-scan $\theta_{\text{max}} = 25.0^\circ$
 (SADABS; Sheldrick, 2002) $h = -17 \rightarrow 17$
 $T_{\text{min}} = 0.856$, $T_{\text{max}} = 0.985$ $k = -21 \rightarrow 21$
 65 646 measured reflections $l = -21 \rightarrow 21$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 1.0912P]$
 $R[F^2 > 2\sigma(F^2)] = 0.043$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.106$ $(\Delta/\sigma)_{\text{max}} = 0.005$
 $S = 1.06$ $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
 4261 reflections $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
 407 parameters
 All H-atom parameters refined

Table 1

Comparative geometric data for (IIIa), (IIIb) and (I).

| Bond lengths (Å) | (IIIa) | (IIIb) | (I) |
|------------------|-------------|-------------|-----------|
| P–C1 | 1.7412 (14) | 1.7357 (18) | 1.718 (2) |
| C1–C2 | 1.4496 (19) | 1.436 (2) | 1.430 (3) |
| C1–C5 | 1.411 (2) | 1.393 (3) | 1.392 (4) |
| C2–C3 | 1.409 (2) | 1.388 (3) | 1.401 (4) |
| C3–C4 | 1.389 (2) | 1.376 (3) | 1.376 (4) |
| C4–C5 | 1.411 (2) | 1.416 (3) | 1.419(3) |
| P1–C12 | 1.8173 (15) | 1.8213 (18) | – |
| P1–C18 | 1.8045 (14) | 1.8074 (17) | – |
| P1–C24 | 1.8044 (15) | 1.7995 (18) | – |
| C2–C6 | 1.438 (2) | 1.464 (3) | – |
| C6–C7 | 1.513 (2) | 1.498 (3) | – |
| C6–C9 | 1.344 (2) | 1.335 (3) | – |
| C9–C10 | 1.456 (2) | 1.476 (3) | – |

| Bond angles (°) | (IIIa) | (IIIb) | (I) |
|-----------------|-------------|-------------|-----------|
| C2–C1–P | 131.86 (11) | 130.43 (14) | 125.3 (2) |
| C5–C1–P | 120.84 (11) | 122.47 (14) | 125.3 (2) |
| C5–C1–C2 | 107.29 (12) | 107.08 (16) | 107.4 (2) |
| C1–C2–C3 | 105.89(13) | 106.18(16) | 106.8 (2) |
| C2–C3–C4 | 109.65 (14) | 109.89 (18) | 108.9(2) |
| C2–C6–C7 | 114.76 (13) | 118.15 (16) | – |
| C6–C9–C10 | 124.08 (15) | 124.9 (2) | – |

Crystals of (IIIa) are monoclinic and space group $P2_1/n$ was chosen from the systematic absences. Crystals of (IIIb) are orthorhombic and space group $Pbca$ was chosen from the systematic absences. All H atoms were located in a difference Fourier map and their positional and isotropic displacement parameters were allowed to refine independently. Refined C–H distances in (IIIa) are in the range 0.89 (2)–1.01 (2) Å and refined C–H distances in (IIIb) are in the range 0.89 (4)–1.05 (4) Å, with individual standard uncertainties of between 0.02 and 0.04 Å.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002) and *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1050). Services for accessing these data are described at the back of the journal.

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