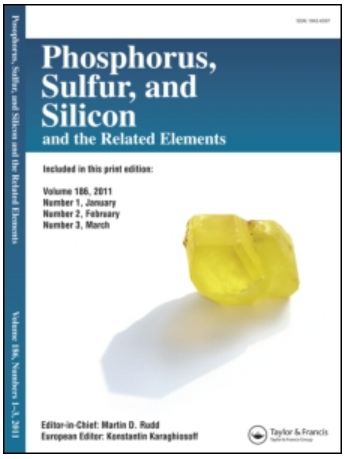

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An Efficient Synthesis of Stable Sulfur-Containing Phosphoranes Derived from 1-Methylimidazole-2-thiol

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AN EFFICIENT SYNTHESIS OF STABLE SULFUR-CONTAINING PHOSPHORANES DERIVED FROM 1-METHYLIMIDAZOLE-2-THIOL

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(Received March 22, 2002)

*Stable crystalline phosphorus ylides are obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 1-methylimidazole-2-thiol. These sulfur-containing phosphoranes exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. Using dibenzoylacetylene as Michael acceptor, yields 2-[1-methyl-1*H*-imidazole-2-yl)sulfanyl]-1,4-diphenyl-butane-1,4-dione.*

Keywords: Acetylenic esters; dibenzoylacetylene; NH-acid; 1-methylimidazole-2-thiol; triphenylphosphine

INTRODUCTION

The development of synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic synthesis.[1] Organophosphorus compounds, that is, those bearing a carbon atom bound directly to a phosphorus atom, are synthetic targets of interest, not least because of their value for a variety of industrial, biological, and chemical synthetic users.[2–8] Accordingly, many strategies have appeared describing novel synthesis of organophosphorus compounds. We report here an efficient synthetic route to sterically congested sulfur-containing phosphorus ylide **3** using triphenylphosphine, dialkyl acetylenedicarboxylates **1** and a SH-acid, such as 1-methylimidazole-2-thiol in good yields (see Scheme 1).

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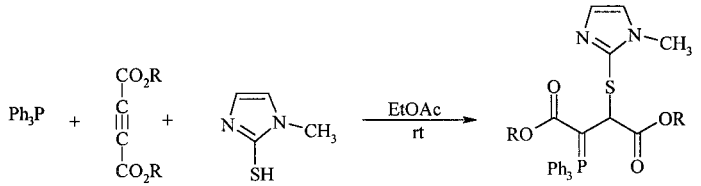


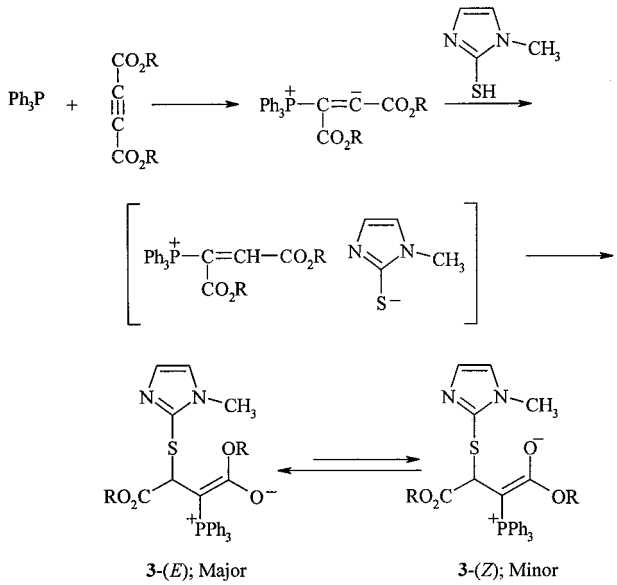
1 2 3

1, 3	R	%Yield of 3
a	Me	98
b	Et	96
c	^{i}Pr	98
d	^{t}Bu	97

SCHEME 1

RESULTS AND DISCUSSION

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[2–8] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the SH-acid **2**. Then the positively charged ion is attacked by the sulfur atom of the conjugate base of the SH-acid to from phosphoranes **3** (see Scheme 2).



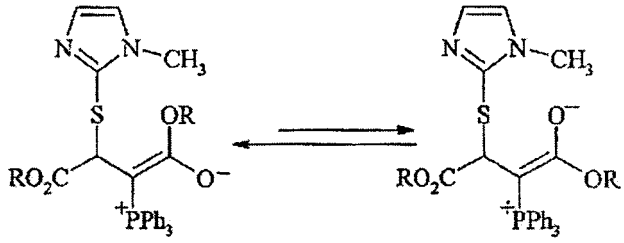
SCHEME 2

The structures of compounds **3a–3d** were deduced from their elemental analyses and their high-field ^{1}H-, ^{13}C-, and ^{31}P NMR and IR spectral data. The nature of the compounds as 1:1:1 adducts was apparent from their mass spectra which displayed molecular ion peaks at $m/z = 518$, 546, 574, and 602 respectively. Initial fragmentations involve loss from or complete loss of the side chains and scission of the heterocyclic ring system.

The ^{1}H-, ^{13}C-, and ^{31}P NMR spectra of ylides **3a–3c** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in **3**-(*E*) and **3**-(*Z*) geometrical isomers is slow on the NMR timescale at ambient temperature. Selected ^{1}H-, ^{13}C-, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **3a–3d** are shown in Table I.

Although, phosphoranes **3a–3d** are stable in common organic solvents, refluxing ylide **3a** in 80% aqueous ethanol resulted in dimethyl

TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, OR, CO_2R, C-2 and C-3 in the Major (M) and Minor (m) Diastereoisomers of Compounds **3a–c**



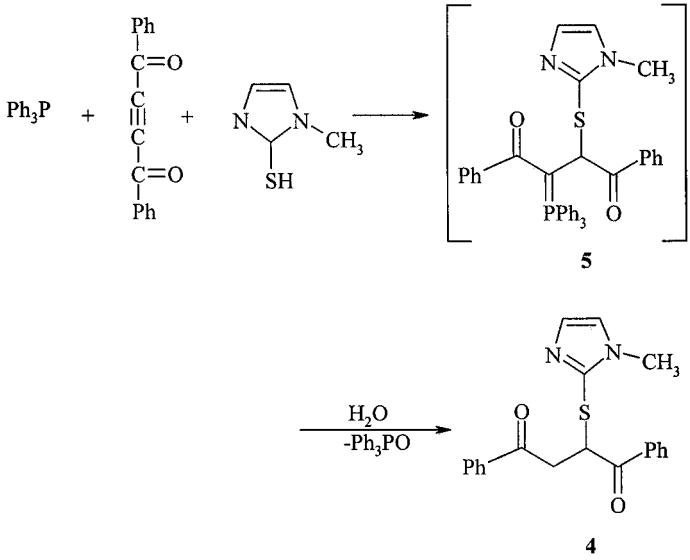
3-(*E*); Major **3**-(*Z*); Minor

Compound	Isomer (%)	^{1}H NMR data H-2 ($^{3}J_{PH}$)	OR	CO_2R	^{13}C NMR C-3 ($^{1}J_{PC}$)	C-2 ($^{2}J_{PC}$)	^{31}P NMR
3a	M (66)	5.48 (17.23)	3.06	3.67	43.26 (127.5)	60.4 (19)	24.06
	m (34)	5.42 (18.8)	3.31	3.72	43.0 (127.5)	60.2 (19)	24.20
3b	M (66)	5.49 (17.5)	3.67[a]	4.13[a]	42.97 (127.2)	60.4 (14.9)	23.99
	m (34)	5.44 (19.2)	4.02[a]	4.2[a]	43.15 (127.5)	60.0 (17.9)	24.89
3c	M (77)	5.46 (17.6)	4.7[b]	5.04[b]	42.75 (127.9)	60.5 (18.6)	23.77
	m (23)	5.4 (19.3)	4.89[b]	4.97[b]	43.25 (125.7)	60.0 (18.6)	25.00
3d	M (97)	5.32 (19.8)	0.92	1.49	42.36 (128.1)	61.0 (18.1)	23.56

[a]The methylene group of the OR moiety.
[b]The methine group of the OR moiety.

fumarate, dimethyl maleate, triphenylphosphine and the starting thiol **2**.

When dibenzoylacetylene was employed as Michael acceptor, in addition to triphenylphosphine oxide, 2-[1-methyl-1*H*-imidazol-2-yl)sulfanyl]-1,4-diphenlbutane-1,4-dione (**4**) was obtained in 98% yield. Addition of triphenylphosphine to dibenzoylacetylene in the presence the SH-acid **2** produces reactive ylied **5**, which is hydrolyzed to **4** under the reaction conditions employed (see Scheme 3).



SCHEME 3

Functionalized heterocyclic phosphorous ylides **3a–d** are considered as potentially useful synthetic intermediates. The procedure described here may be an acceptable method for the preparation of phosphoranes with variable functionalities. The one-pot nature of the present procedure makes it an interesting alternative to multistep approaches.[2–5]

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heracus CHN-O-Rapid analyzer. IR spectra were recorded as KBr discs on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a BRUKER DRX 500-AVANCE FT-NMR instrument

with $CDCl_3$ as solvent at 500.1, 125.7, and 202.5 MHz respectively. The reagents and solvents used in this work were obtained from Fluka (Buchs, Switzerland) and used without further purification.

Preparation of Dimethyl 2-[(1-Methyl-1*H*-imidazole-2-yl)sulfanyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)-succinate (3a): General Procedure

To a magnetically stirred solution of 0.52 g triphenylphosphine (2 mmol) and 0.23 g 1-methylimidazole-2-thiol (2 mmol) in 10 mL of ethyl acetate was added dropwise a mixture of 0.28 g dimethyl acetylenedicarboxylate (2 mmol) in 3 mL of ethyl acetate at room temperature over 10 min. After 5 h stirring, the product was filtered off, washed with ethyl acetate, and dried in vacuum. White powder, m.p. 205–207°C, yield 1.01 g, 98%. IR (KBr) (ν_{max}, cm^{-1}): 1739 (CO_2Me), 1616 (C=C), 1425 (P–Ph), 1293 (C–O), 1101 (P–Ph), 994 (P–Ph). Analysis: calcd for $C_{28}H_{27}N_2O_4PS$ (518.6): C, 64.85; H, 5.25; N, 5.40%. Found: C, 64.7; H, 5.3; N, 5.4%. MS (*m/z*, %): 518 (M^+, 1), 405 (M^+-$C_4H_5N_2S$, 100), 262 (Ph_3P, 51), 197 ($C_8H_9N_2O_2S$, 9), 183 ($C_{12}H_8P$, 43), 152 ($C_7H_8N_2S$, 5), 114 ($C_4H_6N_2S$, 11), 108 (C_6H_5P, 41), 74 (C_6H_2, 15).

Major isomer (*E*)-**3a** (66%), ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 3.06 (3H, s, OCH_3), 3.41 (3H, s, NCH_3), 3.67 (3H, s, OCH_3), 5.48 (1H, d, $^3J_{HP}$ 17.2 Hz, CH), 6.50 (1H, s, CH of imidazole), 7.53 (1H, s, CH of imidazole), 7.42–7.62 (15H, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 34.54 (N–CH_3), 43.26 (d, $^1J_{CP}$ 127.5 Hz, C–P), 49.16 (OCH_3), 52.54 (OCH_3), 60.35 (d, $^2J_{CP}$ 19.0 Hz, CH), 116.77 (CH of imidazole), 117.27 (CH of imidazole), 126.27 (d, $^1J_{CP}$ 92.3 Hz, C_{ipso} of 3 C_6H_5), 128.95 (d, $^3J_{CP}$ 12.0 Hz, C_{meta} of 3 C_6H_5), 132.20 (d, $^4J_{CP}$ 1.8 Hz, C_{para} of 3 C_6H_5), 133.54 (d, $^2J_{CP}$ 10.0 Hz, C_{ortho} of 3 C_6H_5), 161.97 (C_2 of imidazole), 170.28 (d, $^2J_{CP}$ 12.7 Hz, CO_2CH_3), 171.48 (d, $^3J_{CP}$ 11.7 Hz, CO_2CH_3). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 24.06 (Ph_3P^+-C).

Minor isomer (*Z*)-**3a** (34%). ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 3.31 (3H, s, OCH_3), 3.42 (3H, s, NCH_3), 3.72 (3H, s, OCH_3), 5.42 (1H, d, $^3J_{HP}$ 18.8 Hz, CH), 6.61 (CH of imidazole), 7.21 (CH of imidazole), 7.42–7.62 (15H, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 34.50 (N–CH_3), 43.00 (d, $^1J_{CP}$ 127.5 Hz, C–P), 50.15 (OCH_3), 52.26 (OCH_3), 60.22 (d, $^2J_{CP}$ 19.0 Hz, CH), 116.02 (CH of imidazole), 116.80 (CH of imidazole), 125.54 (d, $^1J_{CP}$ 90.9 Hz, C_{ipso} of 3 C_6H_5), 128.46 (d, $^3J_{CP}$ 12.2 Hz, C_{meta} of 3 C_6H_5), 131.91 (d, $^4J_{CP}$ 2.7 Hz, C_{para} of 3 C_6H_5), 132.00 (d, $^2J_{CP}$ 10.0 Hz, C_{ortho} of 3 C_6H_5), 162.37 (C_2 of imidazole), 170.34 (d, $^2J_{CP}$ 12.7 Hz, CO_2CH_3), 171.23 (d, $^3J_{CP}$ 11.7 Hz, CO_2CH_3). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 24.20 (Ph_3P^+-C).

Diethyl 2-[(1-Methyl-1*H*-imidazole-2-yl)sulfanyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (3b)

White powder, m.p. 130–134°C, yield 1.05 g, 96%. IR (KBr) (ν_{max}, cm^{-1}): 1738 (CO_2Me), 1617 (C=C), 1429 (P–Ph), 1287 (C–O), 1098 (P–Ph), 989 (P–Ph). Analysis: calcd for $C_{20}H_{31}N_2O_4PS$ (546.6): C, 65.92; H, 5.72; N, 5.12%. Found: C, 65.9; H, 5.7; N, 5.1%. MS (*m/z*, %): 546 (M^+, 2), 433 (M^+-$C_4H_5N_2S$, 100), 381 ($C_{22}H_{26}N_2PS$, 8), 333 ($C_{21}H_{18}O_2P$, 10), 284 (M^+-Ph_3P, 20), 262 (Ph_3P, 79), 211 ($C_9H_{11}N_2O_2$, 14), 183 ($C_{12}H_8P$, 70), 139 ($C_6H_7N_2S$, 6), 114 ($C_4H_6N_2S$, 12), 108 (C_6H_5P, 42), 76 (C_6H_4, 2), 49 (C_4H, 4).

Major isomer (*E*)-**3b** (66%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.42 (3H, t, $^3J_{HH}$ 7.0 Hz, CH_3), 1.24 (3H, t, $^3J_{HH}$ 7.0 Hz, CH_3), 3.44 (3H, s, N–CH_3), 3.67 (2H, ABX_3 system, OCH_2CH_3), 4.13 (2H, ABX_3 system, OCH_2CH_3), 5.49 (1H, d, $^3J_{HP}$ 17.5 Hz, CH), 6.57 (1H, s, CH of imidazole), 7.57 (1H, s, CH of imidazole), 7.40–7.64 (15H, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 13.89 (CH_2CH_3), 14.07 (CH_2CH_3), 34.57 (N–CH_3), 42.97 (d, $^1J_{CP}$ 127.2, C–P), 57.85 (OCH_2CH_3), 60.35 (d, $^2J_{CP}$ 14.9 Hz, CH), 61.26 (OCH_2CH_3), 116.90 (CH of imidazole), 117.53 (CH of imidazole), 126.57 (d, $^1J_{CP}$ 92.4 Hz, C_{ipso} of 3 C_6H_5), 128.85 (d, $^3J_{CP}$ 12.0 Hz, C_{meto} of 3 C_6H_5), 132.12 (d, $^4J_{CP}$ 2.5 Hz, C_{para} of 3 C_6H_5), 133.64 (d, $^2J_{CP}$ 9.4 Hz, C_{ortho} of 3 C_6H_5), 161.99 (C_2 of imidazole), 169.82 (d, $^2J_{CP}$ 12.7 Hz, CO_2CH_3), 170.71 (d, $^3J_{CP}$ 11.2 Hz, CO_2CH_3). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 23.99 (Ph_3P^+-C).

Minor isomer (*Z*)-**3b** (34%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.13 (3H, t, $^3J_{HH}$ 6.5 Hz, CH_3), 1.27 (3H, t, $^3J_{HH}$ 7.0 Hz, CH_3), 3.40 (3H, s, N–CH_3), 4.02 (2H, ABX_3 system, OCH_2CH_3), 4.20 (2H, ABX_3 system, OCH_2CH_3), 5.44 (1H, d, $^3J_{CP}$ 19.2 Hz, CH), 6.62 (1H, s, CH of imidazole), 7.30 (1H, s, CH of imidazole), 7.40–7.62 (15H, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 14.07 (CH_3), 14.87 (CH_3), 34.57 (N–CH_3), 43.15 (d, $^1J_{CP}$ 127.5, C–P), 58.44 (OCH_2CH_3), 60.03 (d, $^2J_{CP}$ 17.9 Hz, CH), 60.15 (OCH_2CH_3), 116.28 (CH of imidazole), 116.70 (CH of imidazole), 125.84 (d, $^1J_{CP}$ 91.8 Hz, C_{ipso} of 3 C_6H_5), 128.47 (d, $^3J_{CP}$ 12.0 Hz, C_{meta} of 3 C_6H_5), 131.94 (d, $^4J_{CP}$ 2.5 Hz, C_{para} of 3 C_6H_5), 132.05 (d, $^2J_{CP}$ 10.0 Hz, C_{ortho} of 3 C_6H_5), 162.39 (C–S), 170.00 (d, $^2J_{CP}$ 12.6 Hz, CO_2CH_3), 170.30 (d, $^3J_{CP}$ 9.4 Hz, CO_2CH_3), ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 24.89 (Ph_3P^+-C).

Diisopropyl 2-[(1-Methyl-1*H*-imidazol-2-yl)sulfanyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (3c)

White powder, m.p. 175–178°C, yield 1.12 g, 98%. IR (KBr) (ν_{max}, cm^{-1}): 1729 (CO_2CH_3), 1613 (C=C), 1432 (P–Ph), 1280 (C–O), 1102 (P–Ph),

993 (P—Ph). Analysis: calcd for $C_{32}H_{35}N_2O_4PS$ (574.67): C, 66.88; H, 6.14; N, 4.87%. Found: C, 67.0; H, 6.1; N, 4.8%. MS (*m/z*, %): 574 (M^+, 1), 461 (M^+-$C_4H_5N_2S$, 55), 287 ($C_{20}H_{16}P$, 22), 262 (Ph_3P, 93), 225 ($C_{10}H_{13}N_2O_2S$, 4), 183 ($C_{12}H_8P$, 100), 139 ($C_6H_7N_2S$, 10), 114 ($C_4H_6N_2S$, 25), 108 (C_6H_5P, 64), 38 (C_3N, 7).

Major isomer (*E*)-**3c** (77%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.42 (3H, d, $^3J_{HH}$ 6.0 Hz, CH_3), 0.62 (3H, d, $^3J_{HH}$ 6.1 Hz, CH_3), 1.24 (3H, d, $^3J_{HH}$ 6.2 Hz, CH_3), 1.27 (3H, d, $^3J_{HH}$ 6.1 Hz, CH_3), 3.44 (3H, s, N—CH_3), 4.70 (1H, heptet, 6.0 Hz, CH of isopropyl), 5.04 (1H, heptet, 6.2 Hz, CH of isopropyl), 5.46 (1H, d, $^3J_{HP}$ 17.6 Hz, CH), 6.57 (1H, s, CH of imidazole), 7.58 (1H, s, CH of imidazole), 7.40–7.65 (15H, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 21.49 (CH_3), 21.67 (CH_3), 22.03 (CH_3), 22.11 (CH_3), 34.57 (N—CH_3), 42.75 (d, $^1J_{CP}$ 127.9 Hz, C—P), 60.47 (d, $^2J_{CP}$ 18.6 Hz, CH), 64.90 (O*C*H(CH_3)$_2$), 68.68 (O*C*H(CH_3)$_2$), 116.50 (CH of imidazole), 117.65 (CH of imidazole), 126.77 (d, $^1J_{CP}$ 92.0 Hz, C_{ipso} of 3 C_6H_5), 128.77 (d, $^3J_{CP}$ 12.3 Hz, C_{meta} of 3 C_6H_5), 132.04 (d, $^4J_{CP}$ 2.5 Hz, C_{para} of 3 C_6H_5), 133.73 (d, $^2J_{CP}$ 9.7 Hz, C_{ortho} of 3 C_6H_5), 161.97 (C_2 of imidazole), 169.13 (d, $^2J_{CP}$ 12.5 Hz, *C*O_2CH(CH_3)$_2$), 170.0 (d, $^3J_{CP}$ 10.8 Hz, *C*O_2CH(CH_3)$_2$). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 23.77 (Ph_3P^+-C).

Minor isomer (*Z*)-**3c** (23%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.09 (3H, d, $^3J_{HH}$ 5.0 Hz, CH_3), 1.10 (3H, d, $^3J_{HH}$ 5.0 Hz, CH_3), 1.21 (3H, d, $^3J_{HH}$ 5.2 Hz, CH_3), 1.30 (3H, d, $^3J_{HH}$ 5.2 Hz, CH_3), 3.46 (3H, s, N—CH_3), 4.89 (1H, heptet, $^3J_{HH}$ 5.4 Hz, CH of isopropyl), 4.97 (1H, heptet, $^3J_{HH}$ 5.8 Hz, CH of isopropyl), 5.4 (1H, d, $^3J_{HP}$ 19.3 Hz, CH), 6.60 (CH of imidazole), 7.35 (CH of imidazole), 7.43–7.65 (15H, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 21.50 (CH_3), 21.70 (CH_3), 22.26 (CH_3), 22.43 (CH_3), 34.57 (N—CH_3), 43.25 (d, $^1J_{CP}$ 125.7 Hz, C—P), 60.00 (d, $^2J_{CP}$ 18.6 Hz, CH), 65.55 [O*C*H(CH_3)$_2$], 68.85 [O*C*H(CH_3)$_2$], 126.12 (d, $^1J_{CP}$ 94.3 Hz, C_{ipso} of 3 C_6H_5), 128.47 (d, $^3J_{CP}$ 12.0 Hz, C_{meta} of 3 C_6H_5), 131.91 (d, $^4J_{CP}$ 2.9 Hz, C_{para} of 3 C_6H_5), 133.41 (d, $^2J_{CP}$ 9.7 Hz, C_{ortho} of 3 C_6H_5), 162.37 (C_2 of imidazole), 169.50 (d, $^2J_{CP}$ 12.5 Hz, CO_2CH(CH_3)$_2$), 169.67 (d, $^3J_{CP}$ 10.8 Hz, *C*O_2CH(CH_3)$_2$). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 25.00 (Ph_3P^+-C).

Di-tert-buthyl 2-[(1-Methyl-1*H*-imidazole-2-yl)sulfanyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (3d)

Colorless crystals, m.p. 140–142°C, yield 1.17 g, 97%. IR (KBr) (ν_{max}, cm^{-1}): 1738 ($CO_2{}^tBu$), 1644 (C=C), 1431 (P—Ph), 1301 (C—O), 1118 (P—Ph), 994 (P—Ph). Analysis: calcd for $C_{34}H_{39}N_2O_4PS$ (602.7): C, 67.75; H, 6.52; N, 4.65%. Found: C, 67.7; H, 6.5; N, 4.7%. MS (*m/z*, %): 602 (M^+, 2), 489 (M^+-$C_4H_5N_2S$, 38), 377 ($C_{24}H_{26}O_2P$, 100), 333 ($C_{23}H_{26}P$,

30), 287 ($C_{20}H_{16}P$, 38), 262 (Ph_3P, 88), 183 ($C_{12}H_8P$, 87), 114 ($C_4H_6N_2S$, 30), 108 (C_6H_5P, 57).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.92 (9H, s, (CMe_3), 1.49 (9H, s, (CMe_3), 3.43 (3H, s, N—CH_3), 5.32 (1H, d, $^3J_{CP}$ 19.8 Hz, CH), 6.57 (1H, s, CH of imidazole), 7.53 (1H, s, CH of imidazole), 7.42–7.63. (15H, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 28.19 (CH_3), 28.26 (CH_3), 34.50 (N—CH_3), 42.36 (d, $^1J_{CP}$ 128.1 Hz, C—P), 60.97 (d, $^2J_{CP}$ 18.1 Hz, CH), 77.50 (O*C*Me_3), 80.81 (O*C*Me_3), 116.46 (CH of imidazole), 117.41 (CH of imidazole), 127.03 (d, $^1J_{CP}$ 92.0 Hz, C_{ipso} of 3 C_6H_5), 128.72 (d, $^3J_{CP}$ 12.3 Hz, C_{meta} of 3 C_6H_5), 132.00 (d, $^4J_{CP}$ 2.5 Hz, C_{para} of 3 C_6H_5), 133.64 (d, $^2J_{CP}$ 9.7 Hz, C_{ortho} of 3 C_6H_5), 161.90 (C_2 of imidazole), 169.20 (d, $^2J_{CP}$ 26.0 Hz, C=O), 169.3 (d, $^3J_{CP}$ 24.0 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 23.56 (Ph_3P^+-C).

2-[(1-Methyl-1*H*-imidazol-2-yl)sulfanyl]-1,4-diphenylbutane-1,4-dione (4)

Orange crystals, m.p. 136–138°C, yield 0.70 g, 98%. IR (KBr) (ν_{max}, cm^{-1}): 1675 (C=O), 1584 (C=C), 1233 (CCOC). Analysis: calcd for $C_{20}H_{18}N_2O_2S$ (350.4): C, 68.55; H, 5.18; N, 7.99%. Found: C, 68.6; H, 5.2; N, 8.0%. MS (*m/z*, %): 351 (M^++1, 8), 245 (M^+-PhCO, 22), 236 ($C_{16}H_{12}O_2$, 10), 114 ($C_4H_6N_2S$, 91), 105 (PhCO, 100), 76 (C_6H_4, 47). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 3.50 (1H, dd, $^3J_{HH(gem)}$ 17.5 Hz, $^3J_{HH(gauche)}$ 3.7 Hz, CH of CH_2CH), 3.54 (3H, s, N—CH_3), 4.02 (1H, dd, $^3J_{HH(gem)}$ 17.5 Hz, $^3J_{HH(anti)}$ 9.6 Hz, CH of CH_2CH), 6.60 (1H, d, $^3J_{HH}$ 2.2 Hz, CH of imidazole), 6.70 (1H, d, $^3J_{HH}$ 2.3 Hz, CH of imidazole), 7.01 (1H, dd, $^3J_{HH(anti)}$ 9.77 Hz, $^3J_{HH(gauche)}$ 3.6 Hz, CH), 7.38–7.44 (4 H, m, 4 CH_{meta} of 2 C_6H_5), 7.52–7.54 (2H, m, 2 CH_{para} of 2 C_6H_5), 7.90 (1H, d, $^3J_{HH}$ 7.4 Hz, CH_{ortho} of 2 C_6H_5), 8.14 (1H, d, $^3J_{HH}$ 7.6 Hz, CH_{ortho} of 2 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 35.30 (N—CH_3), 40.24 (CH_2), 55.60 (CH), 114.61 (CH of imidazole), 118.75 (CH of imidazole), 128.10 (CH_{meta} of C_6H_5), 128.65 (CH_{meta} of C_6H_5), 128.90 (CH_{ortho} of C_6H_5), 129.26 (CH_{ortho} of C_6H_5), 133.61 (CH_{para} of C_6H_5), 133.06 (CH_{para} of C_6H_5), 134.54 (C_{ipso} of C_6H_5), 135.90 (C_{ipso} of C_6H_5), 162.81 (C2 of imidazole), 195.04 and 196.27 (2 C=O).

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