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Synthesis and X-ray crystal structure analysis of a phosphorus analogue of (1,2,3-η)-*trans*-butadienyl complexes

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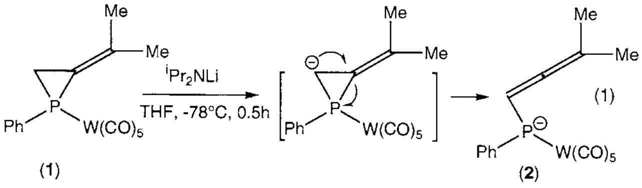
Abstract

Metalation of the 1-phenyl-2-isopropylidene–phosphirane P–W(CO)$_5$ complex (**1**) by lithium diisopropylamide occurs at the ring CH$_2$ and cleaves the ring to give the corresponding (3,3-dimethyl-allen-1-yl)phenylphosphide P–W(CO)$_5$ complex (**2**). The reaction of **2** with [CpFe(CO)$_2$I] then yields the μ-phosphido complex **3** whose heating at 110°C finally gives the (1,2,3-η)-*trans*-1-phenyl-4,4-dimethyl-1-phosphabutadienyl complex (**4**). The structure of **4** shows the *syn*-coplanar stereochemistry of the W–P–C–H unit with a short P–C bond at 1.773 Å. The methylene substituent forms an angle of 145.4° with the C–C bond of the η^3-allyl unit. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium diisopropylamide; Metallation; Ring cleavage

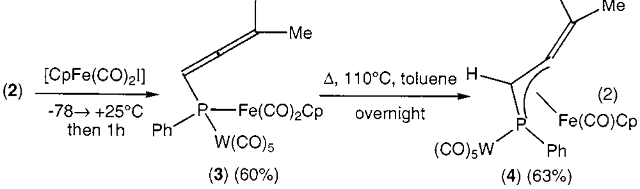
Since their discovery by Nesmeyanov [1], complexes containing the (1,2,3-η)-*trans*-butadienyl ligands have been the subject of numerous studies [2–21]. Besides, they have recently been recognized as key intermediates in the palladium-catalyzed synthesis of functional allenes [22]. From another standpoint, the obvious similarity which exists between the chemistry of low-coordinate carbon and phosphorus compounds [23] has led to the discovery of a whole range of phosphorus analogues of unsaturated hydrocarbon π-complexes [24]. In line with this type of research, we wish to describe hereafter the synthesis and X-ray crystal structure analysis of the first (1,2,3-η)-1-phosphabutadienyl transition metal complex. This work also provides a further illustration of the huge synthetic potential of the carbene-like electrophilic terminal phosphinidene complexes [25].

Our starting product, the 2-alkylidenephosphirane complex (**1**), was easily prepared by reaction of the transient terminal phosphinidene complex [PhP–W(CO)$_5$] with an excess of 1,1-dimethylallene as described by Lammertsma et al. [26]. Allylic metalation at the unsubstituted carbon of the ring by lithium diisopropylamide led to the allenylphosphide ion (**2**) (Eq. 1) whose formation could be monitored by ^{31}P-NMR spectroscopy (δ^{31}P −74.5, $^1J_{PW} = 89.1$ Hz).



(1)

Anion **2** was then allowed to react with [CpFe(CO)$_2$I] to give the μ-phosphido complex **3** [27]. The central allenic carbon of **3** resonates at 205.3 ppm on the ^{13}C-NMR spectrum. Upon prolonged heating in boiling toluene, complex **3** lost one molecule of CO and gave the (1,2,3-η)-1-phosphabutadienyl complex (**4**) [28] (Eq. 2).



(2)

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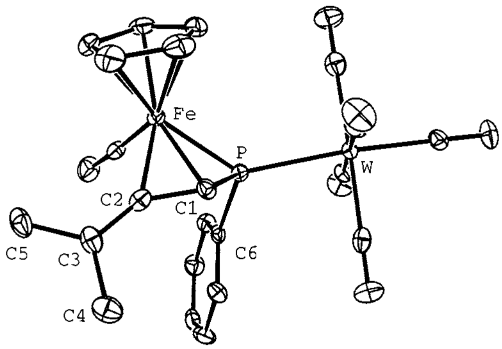

Fig. 1. Crystal Structure of **4**. Significant bond distances (Å) and angles (°). W–P 2.5159(6), P–C(1) 1.773(2), P–C(6) 1.825(2), P–Fe 2.2906(6), C(1)–C(2) 1.390(3), C(1)–Fe 2.061(2), C(2)–C(3)) 1.326(3), C(2)–Fe 2.004(2); W–P–C(1) 119.10(8), W–P–C(6) 112.53(7), W–P–Fe 133.71(3), C(1)–P–C(6) 105.6(1), C(1)–P–Fe 59.34(7), C(6)–P–Fe 111.63(7), P–C(1)–C(2) 118.6(1), P–C(1)–Fe 72.94(7), C(2)–C(1)–Fe 67.8(1), C(1)–C(2)–C(3) 145.4(2), C(1)–C(2)–Fe 72.2(1), C(3)–C(2)–Fe 142.3(2), C(2)–C(3)–C(4) 120.0(2), C(2)–C(3)–C(5) 122.9(2), C(4)–C(3)–C(5) 117.0(2).

On the ^{13}C-NMR spectrum, the former central allenic carbon is shifted upfield to 157.4 ppm. This same carbon resonates at 174.8 ppm in the CpMo(CO)$_2$ complex of (1,2,3-η)-*trans*-butadienyl [17]. The P–CH unit shows no $^{1}J_{CP}$ coupling and a high $^{2}J_{HP}$ coupling of 28.6 Hz. According to our previous work on η^3-1-phosphaallyl complexes [29], these data correspond to a *syn*-coplanar stereochemistry for the W–P–C–H unit. Finally, the *C*Me$_2$ carbon is shifted to low fields from 98.1 in **3** to 122.7 ppm in **4**. The terminal =CH$_2$ carbon appears at 102.5 ppm in the CpMo(CO)$_2$ complex of (1,2,3-η)-*trans*-butadienyl [17]. The X-ray crystal structure analysis of **4** agrees with the spectral findings (Fig. 1). Both the *trans* disposition of the (1,2,3-η)-1-phosphabutadienyl ligand and the *syn* coplanar stereochemistry of the W–P–C–H unit are confirmed. The overall geometry of the η^3-phosphaallyl moiety is very similar to that already reported in the literature [30]. Indeed, the P–C(1) (1.773 Å), C(1)–C(2) (1.390 Å) and P–C(1)–C(2) (118.6°) distances and angle are almost identical to those previously found. The C(2)–C(3) bond is a well localized double bond at 1.326(3) Å. The opening of the C(1)–C(2)–C(3) angle up to 145.4° fits the 139° angle reported for the η^3-butadienyl-molybdenum complex [17]. Finally, this work lends further support to the phosphorus–carbon analogy and opens the field of η^3-1-phosphabutadienyl complexes for investigation.

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[27] Complex **3** was purified by chromatography on silica gel (E. Merck) with hexane–dichloromethane 10:1 as the eluent. ^{31}P-NMR (C$_6$D$_6$): δ – 10.2, $^{1}J_{PW} = 209$ Hz, ^{1}H-NMR (C$_6$D$_6$): δ 1.71 (dd. $^{5}J_{HH} = 3.1$, $^{5}J_{HP} = 5.5$ Hz, 3H, Me), 1.77 (dd. $^{5}J_{HH} = 3.1$, $^{5}J_{HP} = 5.4$ Hz, 3H, Me), 4.02 (d, $^{3}J_{HP} = 0.7$ Hz, 5H, Cp), 5.92 (dq, $^{5}J_{HH} = 3.1$, $^{2}J_{HP} = 10.4$ Hz, 1H, CH–P), 7.2, 7.7 (2m, 5H, Ph); ^{13}C-NMR (C$_6$D$_6$): δ 20.31 (d, $^{4}J_{CP} = 3.6$ Hz, Me), 20.83 (s, br, Me), 87.09 (s, Cp), 95.26 (d, $^{1}J_{CP} = 20.3$ Hz, P–*C*H), 98.11 (d, $^{3}J_{CP} = 10.7$ Hz, *C*Me$_2$), 146.82 (d, $^{1}J_{CP} = 11.9$ Hz, *ipso* *C*(Ph)), 199.72 (d, $^{2}J_{CP} = 5.8$ Hz, *cis*-W(CO)$_5$), 201.80 (d, $^{2}J_{CP} = 16.5$ Hz. *trans*-W(CO)$_5$), 205.35 (s, =C=), 213.64 (d, $^{2}J_{CP} = 16.5$ Hz, Fe(CO)$_2$), 214.13 (d, $^{2}J_{CP} = 15.6$ Hz, Fe(CO)$_2$); Mass (70 eV, ^{184}W) m/z 676 (M, 2%), 480 (M – 7CO, 100%).

[28] Complex **4** was purified by chromatography on silica gel (E. Merck) with hexane–dichloromethane 24:1 as the eluent. ^{31}P-NMR (C$_6$D$_6$): δ – 3.6, $^{1}J_{PW} = 228$ Hz-, ^{1}H-NMR (C$_6$D$_6$): δ 1.65 (s, 3H, Me), 2.05 (s, 3H, Me), 3.14 (d, $^{2}J_{HP} = 28.6$ Hz, 1H, C*H*–P), 4.32 (s, 5H, Cp), 6.81–7.19 (m, 5H, Ph); ^{13}C-NMR (C$_6$D$_6$): δ 23.17 (s, Me), 27.72 (s, Me), 31.14 (s. P–*C*H), 83.64 (s, Cp), 122.67 (d, $^{3}J_{CP} = 6.0$ Hz, *C*Me$_2$)), 141.77 (d, $^{1}J_{CP} = 18.5$

Hz, *ipso* *C*(Ph)), 157.42 (d, $^2J_{CP} = 6.8$ Hz, *C*=CMe$_2$), 198.00 (d, $^2J_{CP} = 7.5$ Hz, *cis*-W(CO)$_5$), 200.19 (d, $^2J_{CP} = 22.9$ Hz, *trans*-W(CO$_5$), 214.81 (d, $^2J_{CP} = 9.8$ Hz, Fe(CO)); Mass (70 eV, ^{184}W) *m*/*z* 648 (M, 15%), 480 (M − 6CO, 100%).

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