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Addition of a Terminal Phosphinidene Complex to Norbornadiene[‖]

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The phosphinidene complex Ph–P–W(CO)$_5$ (2), generated from the appropriate 7-phosphanorbornadiene complex 1, reacts with norbornadiene to give a mixture of (*Z*)-exo, (*Z*)-endo, (*E*)-exo, and (*E*)-endo 1,2-addition products. The ratio of these *Z*/*E* and exo/endo phosphiranes is 2 and 10, respectively. X-ray analysis shows the major isomer to be the sterically congested (*Z*)-*exo*-phosphirane 3, which crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 6.534(2)$ Å, $b = 13.663(2)$ Å, $c = 20.555(2)$ Å, $V = 1835(1)$ Å^3, and $Z = 4$; the structure was refined to $R = 0.0252$ and $R_w = 0.0272$ for 3167 reflections with $I > 2.5\sigma(I)$ and 227 paramters. The stereochemistry and reactivity of phosphinidene complex 2 toward norbornadiene and the stabilizing conjugative features in the resulting phosphiranes are discussed.

Introduction

The discovery by Mathey[1] that phosphinidenes are conveniently generated by thermal degradation of transition metal complexed 7-phosphanorbornadienes has stimulated a rapid exploration of the synthetic aspects of their carbene-like chemistry.[2] In the plethora of new compounds that has resulted, the hitherto difficult to synthesize phosphiranes stand out. These complexes are now conveniently formed by the addition to olefins of phosphinidenes that are stabilized by complexation to transition metals. However, as compared to the many detailed mechanistic studies on carbenes,[3] relatively little is known about the reactivities, selectivities, and stereochemistry of the analogues phosphinidene–olefin addition. To fill this void, we reported earlier on the Hammett reaction constant for the reaction of Ph–P–W(CO)$_5$ (2) with styrenes.[4] The determined ρ^+ value of −0.76 is similar to that of halocarbenes and indicates mild electrophilic carbene-like character for 2.[4,5] To further identify mechanistic aspects of the terminal complexed phosphinidene 2[6] we report here on its reaction with norbornadiene, which is known to be subject to competing exo-[1,2]-, endo-[1,2]-, and homo-[1,4]-chelotropic cycloadditions by various halocarbenes.[7]

Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore spectrometer. Chemical shifts are referenced in ppm to internal (CH$_3$)$_4$Si for the ^{1}H and ^{13}C NMR spectra and to external 85% H$_3$PO$_4$ for the ^{31}P NMR spectra. Downfield shifts are reported as positive. IR spectra were recorded on a Nicolet IR44 spectrometer. Mass spectra were recorded on a HP 5985 at 70 eV. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All materials were handled under an atmosphere of dry, high-purity nitrogen. Reagents and solvents were used as purchased, except for THF, which was distilled from sodium–benzophenone prior to use. Norbornadiene, 7-phenylnorbornadiene, and norbornene were purchased from Aldrich and used without further purification. Chromatographic separations were performed on silica gel columns (230–400 mesh, EM Science). The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten, 1, is described in ref 1a.

Reaction of 1 with Norbornadiene. Complex 1 (654 mg, 1 mmol) and norbornadiene (368 mg, 4 mmol) were heated at 55–60 °C in 20 mL of toluene with CuCl (60 mg, 0.6 mmol) till completion of the reaction (3 h), as followed by ^{31}P NMR. On the basis of their characteristic ^{31}P NMR chemical shifts (in toluene) of δ −99.4 (3), −59.6 (4), −116.8 (5), and −67.6 (6) four phosphirane products were identified. The main products are the *Z*-syn- and *E*-anti-isomers 3 and 4 that result from exo addition in a ratio of 2, as determined from integration of the ^{31}P resonances. The same *Z*/*E* ratio of 2 is obtained for the endo products 5 and 6. The exo/endo ratio is 10/1. The two major products were isolated after filtration of the reaction mixture, evaporated to dryness, and chromatographed over silica with hexane–benzene (4/1) as eluent to yield 0.25 g (48%) of a 2/1

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mixture of **3** and **4**. Fractional crystallization from hexane afforded isolation of the pure isomers. (*Z*)-*exo*-phosphirane **3**: mp 148–9 °C; ^{31}P NMR (C_6D_6) δ −100.7 ($^1J(^{31}P{-}^{183}W) = 248$ Hz); ^{13}C NMR (C_6D_6) δ 140.3 (d, $^3J(C{-}P) = 6.3$ Hz, $^1J(C{-}H) = 171$ Hz, $HC{=}C$), 43.0 (s, $^1J(C{-}H) = 152$ Hz, CH), 42.3 (d, $^3J(P{-}C) = 9.8$ Hz, $^1J(C{-}H) = 132$ Hz, CH_2), 31.2 (d, $^1J(P{-}C) = 17.6$ Hz, $^1J(C{-}H) = 171$ Hz, CHP), 196.4 (d, $^2J(C{-}P) = 7.4$ Hz, cis CO), 198.8 (d, $^2J(C{-}P) = 31.6$ Hz, trans CO); ^{1}H NMR (C_6D_6) δ 6.80–7.12 (m, 5H, Ph), 5.99 (s, 2H, $C{=}CH$), 2.93 (s, 2H, CH), 1.31 (s, 2H, PCH), 2.15 (d, 1H, $^2J(H{-}H) = 9.7$ Hz, CH_2(anti)), 1.05 (m, 1H, CH_2(syn)); MS (^{184}W) (*m*/*e*, relative intensity), 524, 384 (M − 5CO), 348 ($PhPW(CO)_2$, 100), 292 (PhPW). Anal. Calcd for $C_{18}H_{13}O_5PW$: C, 41.22; H, 2.48. Found: C, 41.16; H, 2.52. (*E*)-*exo*-phosphirane **4**: mp 77–9 °C; ^{31}P NMR (C_6D_6) δ −61.0 ($^1J(^{31}P{-}^{183}W) = 220.9$ Hz); ^{13}C NMR (C_6D_6) δ 141.4 (d, $^3J(C{-}P) = 6.7$ Hz, $^1J(C{-}H) = 174$ Hz, $HC{=}C$), 45.5 (d, $^2J(C{-}P) = 6.6$ Hz, $^1J(C{-}H) = 153$ Hz, CH), 41.5 (s, $^1J(C{-}H) = 135$ Hz, CH_2), 35.8 (d, $^1J(C{-}P) = 18.2$ Hz, $^1J(C{-}H) = 169$ Hz, CHP), 196.6 (d, $^2J(C{-}P) = 8.1$ Hz, cis CO), 199.6 (d, $^2J(C{-}P) = 26.7$ Hz, trans CO); ^{1}H NMR (C_6D_6) δ 6.80–7.10 (m, 5H, Ph), 6.07 (s, 2H, $C{=}CH$), 2.78 (s, 2H, CH), 1.66 (d, 2H, $^2J(P{-}H) = 10.8$ Hz, PCH), 0.56 and 0.60 (q (AB), 2H, 9.9 Hz, CH_2); MS (^{184}W) (*m*/*e*, relative intensity), 524 (M, 24), 496 (M − CO, 5), 468 (M − 2CO, 8), 440 (M − 3CO, 29), 384 (M − 5CO, 100), 348 ($PhPW(CO)_2$, 96), 292 (PhPW, 96).

Reaction of 1 with Norbornene. The reaction was executed as described for norbornadiene. A combined isolation yield of phosphiranes **11** and **12** of 52% resulted. The major product is (*Z*)-*exo*-phosphirane **11**: mp 142 °C (hexane); ^{31}P NMR (C_6D_6) δ −176.7 ($^1J(^{31}P{-}^{183}W) = 251.5$ Hz); ^{13}C NMR (C_6D_6) δ 30.3 (d, $^3J(C{-}P) = 6.9$ Hz, $^1J(C{-}H) = 134$ Hz, CH_2CH_2), 37.2 (s, $^1J(C{-}H) = 149$ Hz, CH), 28.5 (d, $^1J(C{-}P) = 11.2$ Hz, $^1J(C{-}H) = 172$ Hz, CHP), 32.5 (d, $^1J(C{-}P) = 15.5$ Hz, $^1J(C{-}H) = 133$ Hz, CH_2 bridge), 131.7 ($J(C{-}P) = 10.6$ Hz, Ph), 129.6 and 128.7 ($J = 9.0$ Hz, Ph), 196.5 (d, $^2J(C{-}P) = 7.7$ Hz, cis CO), 198.5 (d, $^2J(C{-}P) = 32.1$ Hz, trans CO); ^{1}H NMR (C_6D_6) δ 1.16 (s, 2H, PCH), 2.44 (s, 2H, CH), 0.65 (dt, 1H, $^2J(H{-}H) = 11.0$ Hz, $^4J(H{-}H) = 1.8$ Hz, CH_2(syn)), 1.93 (d, $^2J(H{-}H) = 11.0$ Hz, 1H, CH_2(anti)), 1.18 (d, $^2J(H{-}H) = 7.5$ Hz, 2H, CH_2(exo)), 0.83 (dd, $^2J(H{-}H) = 7.5$ Hz, $^4J(H{-}H) = 1.8$ Hz, 2H, CH_2(endo)); MS (^{184}W) (*m*/*e*, relative intensity) (mixture of **11** and **12**) 526 (M, 14), 470 (M − 2CO, 3), 432 ($PhPW(CO)_5$, 16), 404 ($PhPW(CO)_4$, 51), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 49), 292 (PhPW, 68). Anal. Calcd for $C_{18}H_{15}O_5PW$: C, 41.06; H, 2.85. Found: C, 41.11; H, 2.86. The minor isomer **12**: ^{31}P NMR (C_6D_6) δ −155.7 ($^1J(^{31}P{-}^{183}W) = 253.7$ Hz); ^{13}C NMR (C_6D_6) δ 30.7 (d, $^3J(C{-}P) = 8.5$ Hz, $^1J(C{-}H) = 130$ Hz, CH_2CH_2), 39.4 (d, $^2J(C{-}P) = 6.0$ Hz, $^1J(C{-}H) = 148$ Hz, CH), 33.2 (d, $^1J(C{-}P) = 14.4$ Hz, $^1J(C{-}H) = 173$ Hz, CHP), 31.7 (s, $^1J(C{-}H) = 131$ Hz, CH_2 bridge), 129.6–131.8 (Ph), 195.7 (d, $^2J(C{-}P) = 6.9$ Hz, cis CO), 199.0 (d, $^2J(C{-}P) = 29.7$ Hz, trans CO); ^{1}H NMR (C_6D_6) δ 1.54 (d, $^2J(H{-}H) = 10.1$ Hz, 2H, PCH), 2.30 (s, 2H, CH), 0.35 (dd, 1H, $^2J(H{-}H) = 11.2$ Hz, $^4J(H{-}H) = 2.0$ Hz, CH_2(syn)), 0.09 (d, $^2J(H{-}H) = 11.2$ Hz, 1H, CH_2(anti)), 1.17 (d, $^2J(H{-}H) = 7.5$ Hz, 2H, CH_2(exo)), 0.89 (dd, $^2J(H{-}H) = 7.5$ Hz, $^4J(H{-}H) = 2.0$ Hz, 2H, CH_2(endo)).

Reaction of 1 with 7-Phenylnorbornadiene. The reaction was executed as that described for norbornadiene. An isolated yield of phosphiranes of 0.29 g (32%) was obtained after chromatography over silica using a 4/1 mixture of hexane and benzene as eluent. The major product is (*Z*)-*exo*-phosphirane **9**: $R_f = 0.46$; mp 85 °C; ^{31}P NMR (C_6D_6) δ −96.7 ($^1J(^{31}P{-}^{183}W) = 250.9$ Hz); ^{13}C NMR (C_6D_6) δ 137.0 (d, $^3J(C{-}P) = 6.0$ Hz, $HC{=}C$), 46.9 (s, CH), 56.0 (d, $^3J(P{-}C) = 12.9$ Hz, CH bridge), 32.2 (d, $^1J(P{-}C) = 17.2$ Hz, CHP), 126.4–130.8 (Ph), 196.2 (d, $^2J(C{-}P) = 7.0$ Hz, cis CO), 198.6 (d, $^2J(C{-}P) = 32.2$ Hz, trans CO); ^{1}H NMR (C_6D_6) δ 6.88–7.14 (m, 5H, Ph), 5.82 (s, 2H, $C{=}CH$), 3.35 (s, 2H, CH), 1.50 (s, 2H, PCH), 4.13 (s, 1H, CH bridge); MS (^{184}W) (*m*/*e*, relative intensity) 600 (M, 10), 572 (M − CO, 7), 544 (M − 2CO, 8), 516 (M − 3CO, 39), 488 (M − 4CO), 460 (M − 5CO, 91), 348 ($PhPW(CO)_2$, 99), 320 (PhPWCO, 72), 292 (PhPW, 100). Anal. Calcd for $C_{24}H_{17}O_5PW$: C, 48.01; H, 2.83. Found: C, 48.09; H, 2.92. (*E*)-*exo*-phosphirane **10**: $R_f = 0.48$; mp 203 °C; ^{31}P NMR (C_6D_6) δ −56.2 ($^1J(^{31}P{-}^{183}W) = 248.3$ Hz); ^{13}C NMR (C_6D_6) δ 137.6 (d, $^3J(C{-}P) = 6.9$ Hz, $HC{=}C$), 49.5 (d, $^2J(C{-}P) = 6.7$ Hz, CH), 54.1 (s, CH bridge), 37.1 (d, $^1J(P{-}C) = 19.0$ Hz, CHP), 126.0–130.0 (Ph), 196.6 (d, $^2J(C{-}P) = 9.7$ Hz, cis CO), 198.9 (d, $^2J(C{-}P) = 31.6$ Hz, trans CO); ^{1}H NMR (C_6D_6) δ 6.52–7.22 (m, 5H, Ph), 5.84 (s, 2H, $C{=}CH$), 3.08 (s, 2H, CH), 1.80 (d, $^2J(P{-}H) = 10.5$ Hz, 2H, PCH), 2.72 (s, 1H, CH bridge).

Table I. Crystal Data

compd	$C_{18}H_{13}O_5PW$, MW 524.13, $F_{000} = 1000$
cryst	colorless prism, 0.08 × 0.08 × 0.43 mm
	orthorhombic $P2_12_12_1$
	$a = 6.534(2)$, $b = 13.663(2)$, $c = 20.555(2)$ Å
	$V = 1835(1)$ Å^3, $Z = 4$, $D_c = 1.90$ g/cm^3
data	Mo Kα ($\lambda = 0.710\,73$ Å), $T = 296(1)$ K
	scan = θ–2θ, rate = 1–4°/min
	width = $(0.6 + 0.34 \tan\theta)°$, $2\theta_{max} = 60°$, $h,k,\pm l$
	4043 collected, 3462 unique
corrns	*Lp*, extinction (7×10^{-8})
	empirical absorption (0.92–1.00 for $\mu = 65.4$ cm^{-1})
soln	Patterson/diff Fourier
refinement	full-matrix least squares
	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ minimized, $w = 4F_o^2/\sigma^2(F_o^2)$
	non-H atoms anisotropic
	H atoms calcd, riding bonded C atom
	$B_{iso}(H) = 1.5B_{iso}$(bonded C)
	3167 reflns with $F_o^2 > 2.5\sigma(F_o^2)$, 227 params
	$R = 0.0252$, $R_w = 0.0272$, R(all) = 0.0497
	goodness of fit = 1.16, max shift/error = 0.01
	max $\Delta\rho = 0.94(15)$ e/Å^3

X-ray Structure Determination of 3. Diffraction data from a well-formed single crystal, mounted on a glass fiber with epoxy cement, were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation. Least-squares refinement of 25 well-centered reflections yielded precision lattice constants. Three reflections were measured periodically during data collection to monitor crystal decay. The data were processed using the Enraf-Nonius SDP software on a VAX/VMS. Intensities were corrected for Lorentz and polarization effects; a linear decay correction and an empirical absorption correction were also applied. Variances were assigned on the basis of standard counting statistics, with the addition of an instrumental uncertainty term $0.02F_o^2$. The structure was solved by standard Patterson and difference Fourier techniques and refined by weighted full-matrix least squares. The final model contains anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions riding their attached carbon atoms. The final difference Fourier map contained maximum $\Delta\rho$ values near the W atom, with no peaks interpretable as extra atoms. Details of the data collection, structure solution, and refinement are summarized in Table I (R_{all} is the standard residual factor including "unobserved" intensities with $F_o^2 < 2.5\sigma(F_o^2)$). Selected bond distances and angles are presented in Table II, and positional parameters are given in Table III.

Discussion

The terminal complexed phosphinidene **2**, generated in situ from **1**, reacts with norbornadiene to give the four phosphiranes **3–6** in a ratio of 20/10/2/1, as determined from integration of the phosphirane ^{31}P NMR resonances. A similar ratio was obtained by executing the reaction at 115 °C in the absence of the CuCl catalyst or heating the mixture overnight, which strongly suggests the observed phosphiranes to be primary reaction products. The *Z*/*E* product ratio (**3**/**4** and **5**/**6**) is 2, and the exo/endo product ratio is 10. No evidence was obtained for the formation of homo-[1,4]-addition products, which are common in halocarbene additions. The organization of the discussion is to address first the phosphirane product characterization followed by an examination of their properties.

Table II. Selected Bond Distances (Å) and Angles (deg) for 3

(a) Bond Distances

W–P	2.514(1)	C(12)–C(13)	1.520(8)
W–C(7)	1.975(7)	C(12)–C(17)	1.552(8)
W–C(8)	2.039(7)	C(13)–C(14)	1.527(8)
W–C(10)	2.017(6)	C(14)–C(15)	1.520(9)
P–C(1)	1.819(6)	C(14)–C(18)	1.53(1)
P–C(12)	1.838(6)	C(15)–C(16)	1.30(1)
P–C(13)	1.838(6)	C(16)–C(17)	1.52(1)
O(8)–C(8)	1.133(7)	C(17)–C(18)	1.51(1)
O(10)–C(10)	1.131(6)		

(b) Bond Angles

P–W–C(7)	177.9(2)	P–C(12)–C(17)	122.0(4)
P–W–C(8)	92.1(2)	C(13)–C(12)–C(17)	104.1(6)
P–W–C(10)	93.6(2)	P–C(13)–C(12)	65.6(3)
C(7)–W–C(8)	89.0(2)	P–C(13)–C(14)	122.1(4)
C(7)–W–C(10)	88.1(3)	C(12)–C(13)–C(14)	102.0(5)
C(8)–W–C(10)	90.8(2)	C(13)–C(14)–C(15)	105.1(5)
W–P–C(1)	114.8(2)	C(13)–C(14)–C(18)	102.8(5)
W–P–C(12)	135.3(2)	C(15)–C(14)–C(18)	100.0(7)
W–P–C(13)	138.2(2)	C(14)–C(15)–C(16)	106.3(8)
C(1)–P–C(12)	101.8(3)	C(15)–C(16)–C(17)	108.8(8)
C(1)–P–C(13)	100.2(3)	C(12)–C(17)–C(16)	101.5(6)
C(12)–P–C(13)	48.8(3)	C(12)–C(17)–C(18)	101.4(5)
W–C(8)–O(8)	178.9(6)	C(16)–C(17)–C(18)	100.2(7)
W–C(10)–O(10)	178.8(6)	C(14)–C(18)–C(17)	93.4(5)
P–C(12)–C(13)	65.6(3)		

Table III. Atomic Coordinates and Equilibrium Thermal Parameters (Å²) for 3

atom	x	y	z	B_{eq}[a]
W	0.24245(4)	0.09603(1)	0.10926(1)	2.831(3)
P	0.1240(3)	−0.0530(1)	0.17032(7)	2.19(3)
O(7)	0.3937(9)	0.2768(3)	0.0293(2)	7.5(1)
O(8)	−0.1806(7)	0.2052(3)	0.1305(2)	5.9(1)
O(9)	0.6593(7)	−0.0126(4)	0.0801(2)	6.4(1)
O(10)	0.4290(8)	0.1971(4)	0.2335(2)	7.1(1)
O(11)	0.0953(8)	0.0054(4)	−0.0245(2)	6.4(1)
C(1)	0.1676(9)	−0.1685(4)	0.1287(2)	3.1(1)
C(2)	0.020(1)	−0.2081(4)	0.0882(3)	4.5(1)
C(3)	0.056(1)	−0.2950(4)	0.0552(3)	5.1(2)
C(4)	0.239(10)	−0.3409(4)	0.0605(2)	4.7(1)
C(5)	0.392(1)	−0.3019(5)	0.0988(3)	4.8(1)
C(6)	0.357(1)	−0.2151(5)	0.1330(3)	4.4(1)
C(7)	0.338(1)	0.2101(5)	0.0585(3)	4.5(1)
C(8)	−0.0300(9)	0.1656(4)	0.1234(3)	3.8(1)
C(9)	0.510(1)	0.0265(4)	0.0917(3)	4.2(1)
C(10)	0.360(1)	0.1602(4)	0.1893(3)	4.2(1)
C(11)	0.140(1)	0.0369(4)	0.0245(3)	4.1(1)
C(12)	0.123(1)	−0.0915(4)	0.2560(3)	4.2(1)
C(13)	−0.0875(9)	−0.0881(4)	0.2245(3)	4.1(1)
C(14)	−0.199(1)	−0.0137(4)	0.2670(3)	5.7(2)
C(15)	−0.223(1)	−0.0633(5)	0.3327(3)	7.1(2)
C(16)	−0.041(1)	−0.0674(5)	0.3580(3)	7.5(2)
C(17)	0.108(1)	−0.0166(5)	0.3126(3)	6.2(2)
C(18)	−0.031(1)	0.0603(5)	0.2833(3)	6.5(2)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

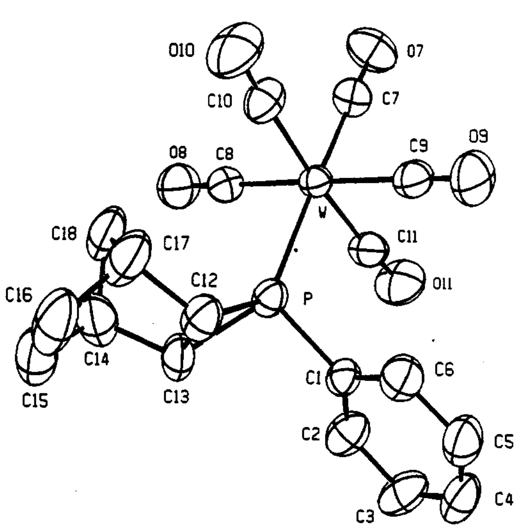
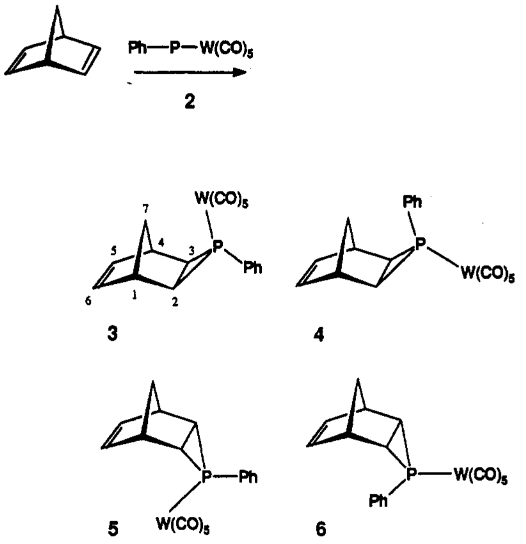
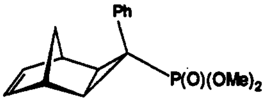


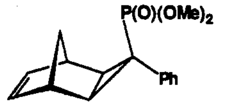
Figure 1. ORTEP drawing with atom-labeling scheme of the molecular structure of (*Z*)-*exo*-3.



The assignment of the major product 3 is largely based on its single-crystal X-ray structure, which is shown in Figure 1. Not surprisingly, this sterically congested system with the $W(CO)_5$ group directed toward the bridging methylene group enhances the chemical nonequivalence of its hydrogens (H_7) resulting in ^1H NMR chemical shifts of δ 1.05 and 2.15 ppm. The endo protons of the phosphirane ring ($H_{2,3}$) and the bridgehead protons ($H_{1,4}$) appear as singlet resonances at δ 1.31 and 2.92 ppm, respectively. Assignment of *E*-exo-isomer 4 is based on the similar chemical shifts of 0.56 and 0.60 ppm for the two methylene hydrogens H_7 (AB system), which are both in the shielding sphere of the *P*-phenyl group. The methylene chemical shifts of both 3 and 4 compare well with the similar dimethyl (3-phenyltricyclo[3.2.1.0^{2,4}]-octenyl-3)phosphonate systems 7 and 8 studied by Callot and Benezra.[8] The phosphirane hydrogens ($H_{2,3}$) of 4 are more deshielded (δ 1.66) than in 3; because of the trans *P*-phenyl group these hydrogens display a significant $^2J_{P-H}$ of 10.8 Hz—this strong coupling is absent in *Z*-isomer 3.



7



8

Integration of the ^{31}P NMR resonances at δ −116.8 and −67.6 gives a ratio of 2, similar to the 3/4 ratio, which suggests these isomers to be the *endo*-phosphiranes 5 and 6, respectively. However, their formation occurs in quantities too small to allow independent characterization.

Support for these assignments comes from the addition reaction of 2 with 7-phenylnorbornadiene which was monitored by ^{31}P NMR for comparison. Integration of the ^{31}P NMR resonances of the major products indicates that *exo*-phosphirane 9 (δ −96.7 ppm; $^1J(^{31}P-^{183}W) = 250.9$ Hz) and its isomer 10 (δ −56.2 ppm; $^1J(^{31}P-^{183}W) = 248.3$ Hz) are formed in a ratio of 2:1. This reaction also gives

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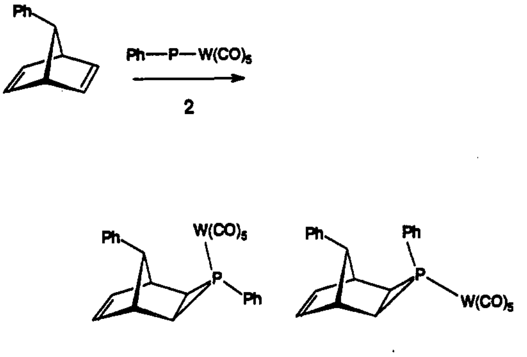
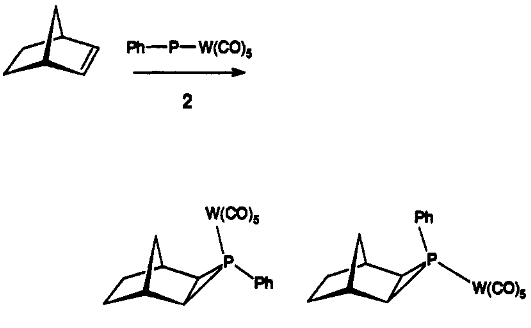
[8] Callot, H. J.; Benezra, C. *Can. J. Chem.* 1972, *50*, 1078.



9 10

two minor (likely endo) products with ^{31}P resonances at δ −125.1 and −110.3 ppm.

The ^{31}P chemical shifts of the phosphinidene [1,2]-cycloaddition products of unsubstituted and 7-phenyl-substituted norbornadiene (i.e.: *Z*-exo δ −99.4 (**3**) and −96.7 (**9**); *E*-exo −59.6 (**4**) and −56.2 (**10**); *Z*-endo −116.8 (**5**); *E*-endo −67.6 ppm (**6**)) are strikingly different (a) from the generally much more shielded resonances (δ −130 to −175 ppm) found for $W(CO)_5$-complexed phosphiranes[2,4,6] and (b) in particular from those of the related *exo*-phosphiranes **11** (δ −176.7 ppm, major *Z*-isomer) and **12** (δ −155.7 ppm) that result from the reaction of **2** with norbornene. This strong deshielding effect (Δδ = 77 and 96 ppm for *exo*-**3** and **4**, respectively, relative to the corresponding phosphiranes **11** and **12**) is attributed to negative hyperconjugation[9] between the phosphorus and the remote double bond, which causes P-electron withdrawal with a concomitant short C═C bond (in **3**) of only 1.30(1) Å. The *exo*-phosphiranes benefit most from this extended δ,π-conjugation, and particularly the *Z*-isomer (**3**) due to its W configuration (C═C, C_2P, Ph), which thereby indirectly supports the phosphirane product assignments.



11 12

How do the phosphinidene and carbene additions to norbornadiene compare? A summary of **2** and several halocarbene additions is given in Table IV. Experimental difficulties have caused significant degrees of uncertainties in the halocarbene data[7] of which we use the latest reported by the Jefford group in 1985;[7a] the variation in their halocarbene data (Table IV) was largely due to variations in reaction conditions and difficulties in (primary) product identifications. From their reported data[7a] on the reactions of the halocarbenes CF_2, CCl_2, and CBr_2 with norbornadiene (with 50–60% conversion), we calculate an average exo/endo ratio of 11.4 and varying (exo- + endo-[1,2])/homo-[1,4] ratios of 1.8, 8.1, and 9.2, respectively (Table IV). These data suggest that the bulkier carbenes give smaller amounts of [1,4]-homoadducts, i.e., CF_2 36% and CBr_2 10% (based on relative yields). If steric aspects are indeed a controlling factor for [1,4]-homoaddition, then its absence in reactions with the more bulky phosphinidene **2** is not surprising. The similar magnitude in exo/endo ratios for the three halocarbenes and phosphinidene **2** suggests an electronically dictated pathway for chelotropic [1,2]-addition leading to the sterically more congested exo adducts. This is not unreasonable in light of the higher electron density at the exo face of norbornadiene and the slightly electrophilic character of both phosphinidene **2** and the halocarbenes.

An intriguing question, which is spurred by the bulkiness of the $W(CO)_5$-complexed phenylphosphinidene **2**, is whether the formation of the major isomer (*Z-exo*-**3**) is dictated by electronic (kinetic) and/or steric (thermodynamic) factors. Inspection of the nonbonded distances in the crystal structure of **3** might suggest that the contact between the $W(CO)_5$ group and the CH_2 bridge is not exceptionally tight. For example, the nonbonded distances between one of the methylene hydrogens and the two closest W-carbonyl groups are 2.734(6) and 2.659(7) Å for H(18B)–C(8) and H(18B)–C(10), respectively; no hydrogen bonding is present, since the H(18B)–carbonyl oxygen distances are >3 Å. The H–C separations are similar to the nonbonded distances of this methylene hydrogen to the three atoms of the phosphirane ring; i.e., the H(18B)–C(12), H(18B)–C(13), and H(18B)–P distances are 2.592(6), 2.585(7), and 2.591(2) Å, respectively. Thus, methylene hydrogen H(18B) is boxed in with two methylene carbons below and two carbonyl carbons above, even though the H–C contacts must be considered normal, since H(18A)–C(15) = 2.581(7) Å and H(18A)–C(16) = 2.586(6) Å. Nevertheless, these four hard contacts between bridgehead hydrogen H(18B) with the trapezoidal box of carbons likely impact the conformational flexibility of **3** by hindering rotation around the P–W bond.[10]

The steric repulsions in isomeric *E-exo*-**4** can only be estimated by interchanging the *P*-phenyl and $W(CO)_5$ groups. Thus, projecting the phenyl C(1) along the P–W vector of **3** using the 1.819-Å P–C(1) bond distance gives an estimated H(18B)–C(1′) separation in **4** of 2.8 Å. It follows that a clear distinction in the formation of **3** and **4** on steric grounds is not evident, although *Z-exo*-**3** appears to be the more congested isomer. We next consider the influence of electronic factors.

The surprising observation that both the exo and endo

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[9] (a) Quin, L. D.; Caster, K. C.; Kisalus, J. C.; Mesch, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 7021. The negative hyperconjugative discussed in this reference relates to the ^{31}P NMR chemical shifts of 7-phosphanorbornanes and 7-phosphanorbornenes. The present systems represent extensions to these earlier studies. (b) Cowley, A. H.; Norman, N. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, Verkade J. G., Quin, L. D., Eds.; Deerfield Beach, VCH Publishers: Florida, 1987; Chapter 17, p 621.

[10] For a discussion on P–M bond lengths in phosphinidene complexes, see: (a) Cowley A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81. (b) Gonbeau, D.; Pfister-Guillouzo, G.; Marinetti, A.; Mathey, F. *Inorg. Chem.* **1985**, *24*, 4133. (c) Lee, J.-G.; Boggs, J. E.; Cowley, A. H. *Polyhedron* **1986**, *5*, 1027.

[11] Kostikov, R. R.; Molchanov, A. P.; Golovanova, G. V.; Zenkevich, I. G. *J. Org. Chem. USSR (Engl. Transl.)* **1977**, *13*, 1712. Moss, R. A.; Mallon, C. B. *J. Am. Chem. Soc.* **1975**, *97*, 344. Seyferth, D.; Mui, J. Y. P.; Damrauer, R. *J. Am. Chem. Soc.* **1968**, *90*, 6182.

[12] The carbene selectivity index m_{CXY} is defined as the least-squares slope of $\log(k_i/k_{isobutane})_{CXY}$ vs $\log(k_i/k_{isobutane})_{CCl_2}$, where i is a standard set of alkenes, and is an attempt to quantitatively interrelate selectivities of carbenes. Of the carbenes shown, CF_2 is considered highly selective. For an extensive discussion, see: Moss R. A. *Acc. Chem. Res.* **1980**, *13*, 58. Moss, R. A.; Guo, W.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1982**, *23*, 15.

Table IV. Phosphinidene and Halocarbene Reactivities toward Norbornadiene

carbene	[1,2]-exo/endo	[1,2]-/homo-[1,4]	Hammett ρ[e]	carbene selectivity index (m_{CXY})[g]
Ph–P–W(CO)$_5$	10	∞	–0.76[f]	
CBr$_2$	12.8[a] (2.0[b])	9.2[a] (∞[b])	–0.44	0.65
CCl$_2$	6.4[a] (4.0[b])	8.1[a] (6.7,[b] 8.0[d])	–0.62	1.00
CClF	(1.8,[b] 2.9[c])	(6.1,[b] 5.7[c])		1.28
CF$_2$	15[a] (1.2,[b] 5[c])	1.8[a] (0.9,[b] 1.9[c])	–0.57	1.48

[a] Reference 7a. [b] Reference 7h. [c] Reference 7f. [d] Reference 7g. [e] Reference 11. [f] Reference 4. [g] Reference 12.

addition of norbornadiene occurs with the same (*Z*)-/(*E*)-phosphirane ratio of 2:1 may suggest that not only the exo/endo but also the *Z*/*E* ratio is determined by electronic factors. We[4] and earlier Mathey[1,2] have observed that the major product resulting from the addition of **2** to simple cis-disubstituted alkenes is generally the *E*-isomer (i.e., P–W(CO)$_5$ trans to the alkene substituents), which seems to contrast with the present result. However, we have recently shown unequivocally that the *Z*-isomer is the major (kinetic) product from the [1,2]-addition of **2** to conjugated *cis*-dienes;[6] its formation was argued to be a consequence of electronic repulsion between the diene and the *P*-phenyl group. Speculatively, a similar electronic interaction between the norbornadiene CH$_2$ bridge (second C=C group) and the *P*-phenyl group may dictate the favored *Z*-exo(endo) addition to norbornadiene to yield phosphiranes **3** and **5**.

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Supplementary Material Available: Listings of positional parameters, bond distances and angles, and anisotropic thermal parameters for **3** (5 pages). See any current masthead page for ordering information.

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