Addition of a Terminal Phosphinidene Complex to Cyclohexadienes

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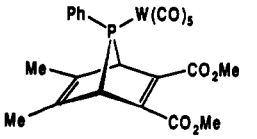
The reaction of the terminal phosphinidene complex $PhPW(CO)_5$ with cyclohexene, 1,4-cyclohexadienes, and 1,3-cyclohexadiene was investigated. In all cases a mixture of *syn*- and *anti*-phosphiranes is obtained. The *syn*-vinylphosphirane resulting from reaction with 1,3-cyclohexadiene rearranges at 110 °C to a phospholene, whereas the *anti*-isomer decomposes. The formation of *syn*- and *anti*-phosphiranes is discussed in terms of kinetic versus thermodynamic control.

Phosphiranes are readily synthesized through phosphinidene addition to olefins, largely due to Mathey and co-workers' discovery that thermal decomposition of phosphanorbornadiene complex 1 yields the reactive, terminal complexed phosphinidene $PhPW(CO)_5$ (2).[1] They



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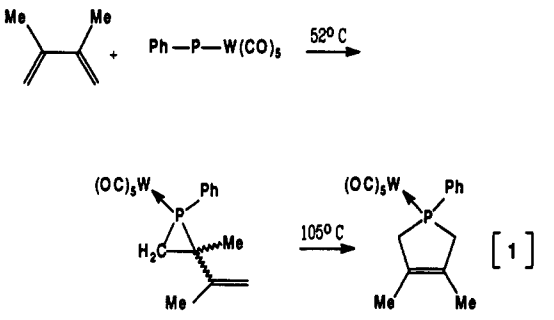
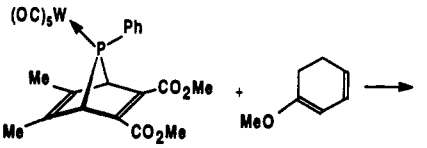
showed that the uncatalyzed decomposition of 1 is a first-order process which was taken to support the intermediacy of phosphinidene complex 2 in the reaction with trapping reagents.[2] The synthetic literature suggests unencumbered singlet carbene-like behavior for 2, but detailed mechanistic information is scarce. Recently, we determined from competitive (CuCl catalyzed) experiments a Hammett reaction constant ρ^+ of −0.76 for the addition of 2 to styrenes[3a] and a ρ^+ of −0.60 for the similar addition of $CH_3PW(CO)_5$.[3b] These constants support the slightly electrophilic, carbene-like nature of the phosphinidene complexes and suggest second-order kinetics for the olefin addition reaction.[4]

Mathey and Marinetti have reported that conjugated dienes react with 2 to give 1,2-addition products, of which the vinylphosphirane of 2,3-dimethyl-1,3-butadiene rearranges at ≥95 °C into a phospholene (a formal 1,4-adduct), but no specifics were supplied (eq 1).[1d] Recently, we have shown that 2 reacts in high stereoselectivity with 1-methoxy-1,3-cyclohexadiene to yield phosphirane 3, which under the reaction conditions (55 °C) rearranges to 4 through a concerted [1,3]-sigmatropic shift with *complete inversion of the P-center* (eq 2).[5] To investigate the particulars that contribute to this remarkable rearrangement, we decided to study the phosphinidene addition to cyclohexadienes in more detail.





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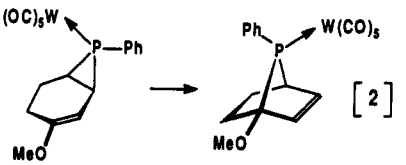

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Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore spectrometer. Chemical shifts were referenced in ppm to internal $(CH_3)_4Si$ for the ^1H and ^{13}C NMR spectra and to external 85% H_3PO_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. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. 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, and toluene, which was dried over molecular sieves. The olefins were purchased from Aldrich and were used without further purification. 1-Methoxycyclohexene was synthesized following known procedures.[7] 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.

(1) (a) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, J. *J. Chem. Soc., Chem. Commun.* **1982**, 667; (b) *J. Am. Chem. Soc.* **1982**, *104*, 4484. (c) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488; (d) *Organometallics* **1984**, *3*, 456.

(2) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

(3) (a) Lammertsma, K.; Chand, P.; Yang, S.-W.; Hung, J.-T. *Organometallics* **1988**, *7*, 1875. (b) Hung, J.-T.; Lammertsma, K. *Organometallics* **1992**, *11*, 4365.

(4) These observations are similar to those reported recently for the carbene–olefin addition reaction; see: Gould, K. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. J.; Moss, R. A.; Cox, D. P.; Munial, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

(5) Lammertsma, K.; Hung, J.-T.; Chand, P.; Gray, G. M. *J. Org. Chem.* **1992**, *57*, 6557.

(6) Richter, W. J. *Chem. Ber.* **1985**, *118*, 1575.

(7) Wohl, R. A. *Synthesis* **1974**, 38.

0022-3263/93/1958-1800$04.00/0

(7-Phenyl-7-phosphabicyclo[4.1.0]hept-3-ene)pentacarbonyltungsten (5a,b). Complex 1 (1.05 g, 1.59 mmol) and 1,3-cyclohexadiene (0.50 g, 6.25 mmol) in 25 mL of benzene with CuCl (100 mg, 1.0 mmol) were heated at 55 °C for 3 h under a nitrogen atmosphere. Filtration of the reaction mixture, evaporation to dryness, and chromatography over silica with hexane–benzene (3:2) as eluent (R_f = 0.8) gave 0.62 g (76%) of a 60/40 mixture of the isomers **5a** and **5b** as based on ^{31}P NMR. The products were partly separated by fractional crystallization. Major isomer **5a**: ^{31}P NMR (C_6D_6) δ −139.9 ($^1J(^{31}P-^{183}W)$ = 251.0 Hz); ^{13}C NMR (C_6D_6) δ 18.5 (d, ^2J(P–C) = 4.3 Hz, H_2CC=), 21.4 (s, H_2CCHP), 24.3 (d, ^1J(P–C) = 15.4 Hz, PCH), 26.2 (d, ^1J(P–C) = 15.8 Hz, PCH), 122.0 (d, ^2J(P–C) = 8.5 Hz, HC=), 123.3 (s, HC=), 129.2, 130.1, and 133.1 (Ph), 196.6 (d, ^1J(P–C) = 8.1 Hz, *cis*-CO), 199.0 (d, ^1J(P–C) = 27.8 Hz, *trans*-CO); ^{1}H NMR (C_6D_6) δ 0.34 (dd, J = 8.4 and 17.9 Hz, CH_2CP), 1.21 (dt, J = 3.7 and 17.9 Hz, CH_2CP), 1.95 (dd, J = 4.8 and 8.7 Hz, CHP), 1.63 (m, CHP), 1.67–1.73 (m, 2 H, CH_2C=), 5.10 (dt, J = 4.8 and 13.0 Hz, HC=CH), 5.64 (m, HC=CH), 7.04–7.10 (m, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 512 (M^+, 12), 484 (M − CO, 5), 432 ($PhPW(CO)_5$, 18), 404 ($PhPW(CO)_4$, 50), 376 ($PhPW(CO)_3$, 22), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 57), 292 (PhPW, 95). Anal. Calcd for $C_{17}H_{13}O_5PW$: C, 39.48; H, 2.54. Found: C, 39.78; H, 2.57. Minor isomer **5b**: ^{31}P NMR (C_6D_6) δ −137.1 ($^1J(^{31}P-^{183}W)$ = 261.6 Hz); ^{13}C NMR (C_6D_6) δ 21.6 (s, H_2CC=), 20.1 (s, H_2CCHP), 23.0 (d, ^1J(P–C) = 18.0 Hz, PCH), 123.1 (s, HC=), 124.2 (s, HC=), 129.9, 131.4, and 131.8 (Ph), 197.2 and 199.5 (*cis*- and *trans*-CO); MS the same as for **5a**.

(7-Phenyl-7-phosphanorborn-2-ene)pentacarbonyltungsten (6). A total of 0.50 g (0.98 mmol) of vinylphosphirane **5a** was heated with 30 mg of CuCl in 10 mL of toluene at 110 °C for 2 h. After purification, following the same procedure as described for **5a,b**, 0.32 g (64%) of a colorless solid **6** was obtained: mp 79–81 °C; ^{31}P NMR (C_6D_6) δ 66.9 (^1J(P–W) = 233.9 Hz); ^{13}C NMR (C_6D_6) δ 23.9 (s, H_2C), 44.1 (d, ^1J(P–C) = 26.0 Hz, PCH), 134.0 (d, ^2J(P–C) = 13.4 Hz, CH=CH), 128.0–133.1 (Ph); ^{1}H NMR (C_6D_6) δ 0.90 (m, endo-H, ^3J(P–H) = 18.0 Hz, CH_2), 1.32 (d, ^3J(H–H) = 8.4 Hz, exo-H, CH_2), 2.70 (s, br, HCP), 5.95 (dt, J = 2.7 and 8.3 Hz, HC=CH), 6.79–7.05 (m, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 512 (M^+, 11), 404 ($PhPW(CO)_4$, 53), 376 ($PhPW(CO)_3$, 21), 348 ($PhPW(CO)_2$, 100), 292 (PhPW, 89).

(7-Phenyl-7-phosphabicyclo[4.1.0]heptane)pentacarbonyltungsten (7a,b). Reaction of complex 1 (0.65 g, 1 mmol) with freshly distilled cyclohexene (0.50 g, 6.10 mmol) in 30 mL of benzene with CuCl (30 mg, 0.3 mmol) were heated at 60 °C for 1.5 h to yield 0.21 g (41%) of isolated material that consisted of a mixture of phosphiranes in a ratio of 1.85, as based on ^{31}P NMR, of which **7b** could be separated through fractional crystallization from hexane. Major isomer **7b**: mp 119 °C; ^{31}P NMR (C_6D_6) δ −167.4 ($^1J(^{31}P-^{183}W)$ = 251.0 Hz); ^{13}C NMR (C_6D_6) δ 21.0 (d, ^2J(P–C) = 3.8 Hz, ^1J(C–H) = 128 Hz), H_2C), 22.7 (s, ^1J(C–H) = 173 Hz, PCH), 22.8 (s, CH_2), 129.2–133.2 (Ph), 196.5 (d, ^2J(C–P) = 8.1 Hz, *cis*-CO), 198.9 (d, ^2J(C–P) = 29.3 Hz, *trans*-CO); ^{1}H NMR (C_6D_6) δ 0.34–0.41 (m, 2 H, CH_2, endo), 0.70–0.81 (m, 2 H, CH_2, exo), 1.23–1.36 (m, 2 H, ^2J(H–H) = 14.4 Hz, ^3J(H–P) = 11.9 Hz, 2 H, CH_2), 1.60–1.77 (m, 2 H, CH_2), 1.40 (t, ^3J(H–H) = 2.4 Hz, ^2J(H–P) = 0 Hz, HCP), 6.86–7.09 (m, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) of **7a,b** 514 (M^+, 8), 432 ($PhPW(CO)_5$, 18), 404 ($PhPW(CO)_4$, 54), 376 ($PhPW(CO)_3$, 16), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 58), 292 (PhPW, 86). Anal. Calcd for $C_{17}H_{15}O_5PW$; C, 39.69; H, 2.92. Found: C, 39.76; H, 2.98. Minor isomer **7a**: ^{31}P NMR (C_6D_6) δ −158.8 ($^1J(^{31}P-^{183}W)$ = 260.0 Hz); ^{13}C NMR (C_6D_6) δ 21.4 (s, H_2C), 22.3 (s, CH_2), 22.5 (s, CHP), 128.7–131.5 (Ph), 196.5 (d, ^2J(C–P) = 8.8 Hz, *cis*-CO), 197.6 (d, ^2J(C–P) = 23.5 Hz, *trans*-CO).

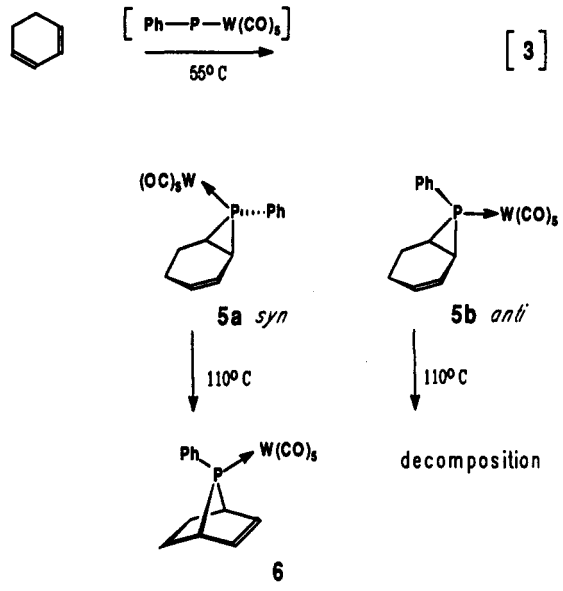
(7-Phenyl-7-phosphabicyclo[4.1.0]hept-4-ene)pentacarbonyltungsten (8a,b). Reaction of complex 1 with 1,4-cyclohexadiene (0.50 g, 6.25 mmol) similar to that described for **5a,b** yielded 0.29 g (75%) of a 35:65 mixture of **8a** and **8b**, respectively. Major isomer **8b** was separated by fractional crystallization from hexane: mp 107–8 °C; ^{31}P NMR (C_6D_6) δ −175.5 ($^1J(^{31}P-^{183}W)$ = 251.4 Hz); ^{13}C NMR (C_6D_6) δ 21.1 (d, ^2J(P–C) = 3.8 Hz, H_2C), 22.6 (d, ^1J(P–C) = 14.1 Hz, PCH), 123.2 (s, HC=), 129.3, 130.2, and 131.6 (Ph), 196.7 (d, ^2J(C–P) = 7.9 Hz, *cis*-CO), 199.0 (d, ^2J(C–P) = 29.8 Hz, *trans*-CO); ^{1}H NMR (C_6D_6) δ 1.40 (t, ^3J(H–H) = 2.1 Hz, HCP), 1.98 (dq, ^2J(H–H) = 17.5 Hz, ^3J(H–P) = 13.5 Hz, ^3J(H–H) = 2.4 Hz (to HC=), CH_2), 2.21 (dq, ^2J(H–H) = 17.5 Hz, ^3J(H–P) = 20.5 Hz, ^3J(H–H) = 2.1 Hz (to PCH), CH_2), δ 4.68 (s, HC=CH), 6.87–7.01 (m, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) of **8a,b** 512 (M^+, 13), 484 (M − CO, 5) 432 ($PhPW(CO)_5$, 20), 404 ($PhPW(CO)_4$, 51), 376 ($PhPW(CO)_3$, 20), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 58), 292 (PhPW, 96). Anal. Calcd for $C_{17}H_{13}O_5PW$: C, 39.48; H, 2.54. Found: C, 39.59; H, 2.57. Minor isomer **8a**: ^{31}P NMR (C_6D_6) δ −158.0 ($^1J(^{31}P-^{183}W)$ = 258.7 Hz); ^{13}C NMR (C_6D_6) δ 21.7 (s, H_2C), 22.2 (d, ^1J(P–C) = 11.4 Hz, PCH), 124.3 (s, HC=), 128.6–131.6 (Ph), 196.1 (d, ^2J(C–P) = 7.8 Hz, *cis*-CO), 198.0 (d, ^2J(C–P) = 29.3 Hz, *trans*-CO); ^{1}H NMR (C_6D_6) δ 0.89 (t, ^2J(H–P) = 6.5 Hz, HCP), δ 1.9–2.4 (m, CH_2), δ 5.49 (s, HC=), 6.8–7.0 (m, Ph).

(4,5-Dimethyl-7-phenyl-7-phosphabicyclo[4.1.0]hept-4-ene)pentacarbonyltungsten (9a,b). Reaction of complex 1 with 1,2-dimethyl-1,4-cyclohexadiene (0.43 g, 4.0 mmol) and 100 mg of CuCl yielded in a similar manner 0.19 g (35%) of a 15:85 mixture of **9a** and **9b**, respectively. Major isomer **9b** was separated by crystallization in hexane: mp 108–9 °C (hexane); ^{31}P NMR (C_6D_6) δ −178.4 (^1J(P–W) = 261.3 Hz); ^{13}C NMR (C_6D_6) δ 18.5 (s, H_2C), 24.3 (d, ^1J(P–C) = 13.9 Hz, PCH), 28.1 (s, CH_3), 122.5 (s, C=), 129.3–131.1 (Ph), 196.7 (d, ^1J(P–W) = 7.9 Hz, *cis*-CO), 199.0 (d, ^1J(P–W) = 29.8 Hz, *trans*-CO); ^{1}H NMR (C_6D_6) δ 0.83 (s, CH_3), 1.57 (s, br, HCP), 1.88 (dd, ^2J(H–H) = 17.0 Hz and ^3J(H–P) = 12.5 Hz, CH_2 (eq)), 2.24 (t, ^2J(H–H) = 17.0 Hz, ^3J(H–P) = 17.0 Hz, CH_2 (ax.)); mass spectrum (^{184}W) *m/e* (relative intensity) 540 (M^+, 8), 432 ($PhPW(CO)_5$, 26), 404 ($PhPW(CO)_4$, 63), 376 ($PhPW(CO)_3$, 20), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 57), 292 (PhPW, 73). Anal. Calcd for $C_{19}H_{17}O_5PW$; C, 42.22; H, 3.15. Found: C, 42.29; H, 3.16. Minor isomer **9a**: ^{31}P NMR (C_6D_6) δ −156.6, could not be isolated for spectroscopic analysis.

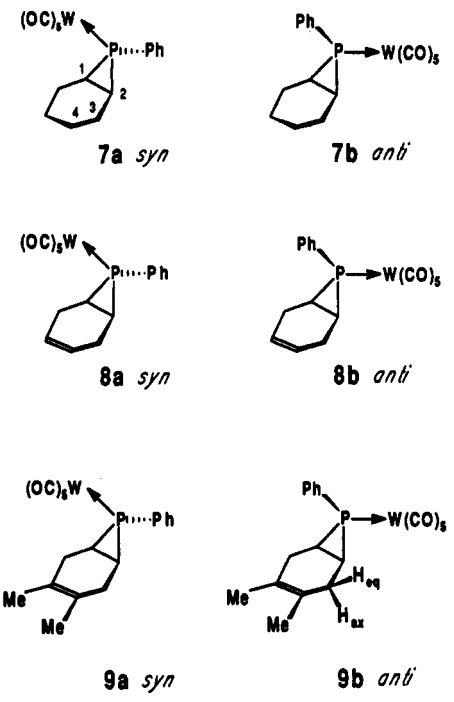
(*O*-Methyl phenylphosphinite)pentacarbonyltungsten (10). Reaction of complex 1 (1 mmol) with 1-methoxycyclohexene (0.45 g, 4 mmol) in 30 mL of toluene with CuCl (100 mg, 1.0 mmol) for 3 h at 110 °C under a nitrogen atmosphere yielded 0.28 g (61%) of **10**: mp 81–82 °C; ^{31}P NMR (C_6D_6) δ 107.0 (^1J(P–W) = 278.2 Hz); ^{13}C NMR (C_6D_6) δ 59.2 (d, ^2J(P–C) = 14.2 Hz, ^1J(C–H) = 147.6 OCH_3), 195.9 (d, ^2J(C–P) = 6.8 Hz, *cis*-CO), 200.0 (d, ^2J(P–W) = 26.9 Hz, *trans*-CO); ^{1}H NMR (C_6D_6) δ 2.76 (d, ^3J(P–H) = 12.6 Hz, OCH_3), 7.24 (d, ^1J(H–P) = 346.7 Hz,), 6.98–7.20 (m, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 462 (M^+, 15), 322 (M − 5CO, 100).

Results

In this section we discuss the product assignments based on NMR chemical shift data. The *syn*-phosphiranes (labeled **a**) are defined as having the $PW(CO)_5$ group over the hydrocarbon ring, and conversely the anti-isomers (labeled **b**) have the PPh group over the ring. We assign the syn-isomer to the major product (**5a**) of the phosphinidene addition reaction to 1,3-cyclohexadiene because it is the only compound to undergo a rearrangement (vide infra) to a phosphanorbornene **6** (eq 3) similar to the reaction observed earlier for the 1-methoxy-substituted derivative.[5] In the latter case the product assignments could be confirmed by single-crystal X-ray structure determinations of both the phosphirane and 7-phosphanorbornene products. The assignments of the *syn*-(**7a,8a**) and *anti*-phosphirane (**7b,8b**) isomers resulting from cyclohexene (**7**) and 1,4-cyclohexadiene (**8**) are largely based on the ^{1}H NMR chemical shifts of the hydrogens at C4. The difference in chemical shift ($\Delta\delta$) for the olefinic hydrogens between the *syn*- and *anti*-phosphirane isomers **8** amounts to a large 0.81 ppm. The very shielded hydrogens at δ 4.68 ppm are assigned to anti-isomer **8b**, which is based on the assumed strong shielding effect of the bridging *P*-phenyl group. The situation for the phosphirane isomers of cyclohexadiene is the same even though the minor isomer **7b** could not be isolated in high enough purity to obtain its ^{1}H NMR spectrum unambig-



uously. However, the P-phenyl group is likely also the reason for the very shielded chemical shifts of δ 0.34–0.41 and δ 0.70–0.81 ppm for the C4 methylene hydrogens of **7b**, which is therefore likewise assigned to have the anti-conformation. Additionally, the ^3J(H–P) coupling constants are larger for the anti-isomers in accordance with literature data.[8]

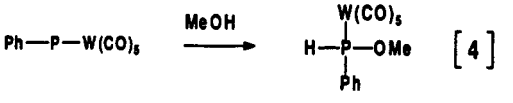


Discussion

Reactivities–Selectivities. Phosphanorbornadiene **1** reacts at 55 °C with cyclohexene and the 1,4- and 1,3-cyclohexadienes to give *syn*-/*anti*-phosphirane product ratios of 0.54, 0.54, and 1.5, respectively. The corresponding relative olefin reactivities, as determined by competition reactions, are 1:2.1:14.6. Whereas the *anti*-phosphirane is the major isomer in the olefin addition, the much faster reaction with the conjugated diene yields mainly the syn-isomer. The preference for anti-product formation in the olefin addition reactions may be explained by two arguments. (a) Sterically, the $W(CO)_5$ group is considered to be the bulkier substituent of phosphinidene **2**, which therefore prefers an olefin approach with its transition-metal group anti to the hydrocarbon ring. The *syn*-/*anti*-phosphirane product ratio of only 0.18 obtained in the reaction of **2** with 1,2-dimethyl-1,4-cyclohexadiene (to yield **9a,b**) seems to support the notion that subtle steric factors influence the product distribution. (b) Electronically, the anti-isomer is also favored by secondary orbital interactions, an argument which has been used earlier by Moss to rationalize product distributions in carbene additions to substituted olefins.[9] The same reasoning should apply to phosphinidene **2**, which due to its slightly electrophilic character ($\rho^+ = -0.76$ similar to the Hammett reaction constants of carbenes) induces some positive charge in the hydrocarbon ring, thereby enhancing a stabilizing charge-transfer interaction with the *P*-phenyl group.

Reaction of **2** with 1,2-dimethyl-1,4-cyclohexadiene occurs at the least substituted double bond (**9a,b**) in contrast to halocarbene–olefin addition reactions.[10] However, the unsaturated isopropylidene carbene, which is isolobal with phosphinidene **2**, was shown by Stang and co-workers to also prefer addition to less substituted double bonds.[11] This was explained by the authors on electronic grounds, but in the case of **2** steric factors may also contribute.

The main phosphirane product from the addition reaction to 1,3-cyclohexadiene is *syn*-phosphirane **5a**. This result can be explained by the electrostatic repulsion between the *P*-phenyl and the conjugated diene, both being π groups. Indeed, adding a strong electron donor like a methoxy group enhances the *syn*/*anti* ratio from 1.5 to ca. 20 as we have shown in earlier work.[5] However, competing kinetic and thermodynamic stabilities may underlie this syn/anti product ratio difference with (nonconjugated) olefins. For example, the phosphinidene addition reaction with 1-methoxy-1,3-cyclohexadiene occurs so fast that only relatively low temperatures (<50 °C) and short reaction times (<30 min) enable the isolation of a phosphirane product from a mixture that already contains a significant amount of rearranged product (see next section). It is of interest to note that no phosphinidene addition occurs with 1-methoxycyclohexene, which despite the activating H_3CO group only yields the decomposition product **10**, which also has been reported to result from the insertion of **2** into methanol (eq 4).[1a]



Rearrangement from a [1,2]- to a [1,4]-Adduct. Vinylphosphirane **5a** rearranges at 110 °C exclusively to phospholene **6**. This process occurs with high stereoselectivity as both reactant and product have the $PW(CO)_5$ group directed toward the double bond. This means that *the rearrangement occurs with complete inversion of configuration at the P-center* in an identical fashion as

(8) Verkade, J. G.; Quin, L. D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; VCH: Deerfield Beach, 1987.

(9) Moss, R. A.; Mamantov, A. *J. Am. Chem. Soc.* **1970**, *92*, 6951.
(10) Sims, J. J.; Honwad, V. K. *J. Org. Chem.* **1969**, *34*, 496.
(11) (a) Stang, P. J.; Madsen, J. R.; Mangum, M. G.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1802. (b) Stang, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 5949.

we have observed earlier for 1-methoxy-1,3-cyclohexadiene.[5] Two observations are made. First, in the present case (**5a** → **6**) *only syn-isomer* ***5a*** *rearranges* while, in sharp contrast, *anti*-phosphirane isomer **5b** *undergoes slow decomposition* under the same reaction conditions. This observation strongly supports a concerted mechanism for phospholene product formation (**5a** → **6**) as postulated before for the methoxy derivative.[5] In the case of a biradical mechanism (i.e., sequential P–C bond breakage and bond formation) some interconversion between **5a** and **5b** would be expected. This observation also strongly suggests that *syn*-phosphirane **5a** is a kinetic product, while its *anti*-isomer **5b** is the thermodynamically favored phosphirane. This argument is supported by the phosphinidene addition reaction with the more reactive 1-methoxy-1,3-cyclohexadiene, which occurs so fast that only relatively low temperatures (<50 °C) and short reaction times (<30 min) enable the isolation of only a *syn*-phosphirane [1,2]-adduct from a mixture that already contains a significant amount of rearranged [1,4]-adduct (see below).

The differentiation in properties of **5a** and **5b** suggests the presence of concerted and biradical processes. Whereas **5b** decomposes, (suggesting P–C bond clevage with subsequent radical reactions), Richter[6] has reported that ($W(CO)_5$ uncomplexed) *tert*-butylvinylphosphirane rearranges to a phospholene via a biradical intermediate. Consequently, only the kinetic product **5a** can rearrange to the thermodynamically favored phospholene **6**. This rearrangement is enhanced by the electron-donating methoxy group (eq 2) and takes place at ≤55 °C. Combining these observations suggests that the electronic interaction between the vinyl group and the phosphirane ring is related to the P-configuration. Indeed, several reports have focused on the stabilizing hyperconjugative effect between a phosphorus lone pair and olefinic units in uncomplexed phospha-bridged cycloalkenes.[12] The present study fully supports the notion that the function of the $W(CO)_5$ group is only a stabilizing one through complexation with the phosphorus lone pair, while the characteristic properties of the phosphinidene, phosphiranes, and phospholenes are maintained.

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(12) (a) Quin, L. D.; Caster, K. C.; Kisalus, J. C.; Mesch, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 7021. (b) Quin, L. D.; Mesch, K. A. *J. Chem. Soc., Chem. Commun.* **1980**, 995. (c) Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, 319.