Addition of a Terminal Phosphinidene Complex to a Conjugated Diene. Thermal Rearrangement of a Vinylphosphirane to a 1,4-Adduct

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Reaction of the carbene-like terminal phosphinidene complex Ph–P–$W(CO)_5$ with 1-methoxy-1,3-cyclohexadiene yields in high stereoselectivity a 1,2-addition product, phosphirane **4**. Under the reaction conditions **4** subsequently rearranges to a 1,4-adduct, phospholene **5**. The [1,3]-sigmatropic shift of the Ph–W–$W(CO)_5$ group occurs with complete inversion of the sterically crowded P-center. The stereochemistries of the products **4** and **5** have been characterized by single-crystal X-ray structures (**4**, monoclinic space group $P2_1/c$, a = 11.999 (2) Å, b = 6.720 (3) Å, c = 23.939 (2) Å, β = 99.102 (9)°, Z = 4, R = 4.62%, and R_w = 6.62%; **5**, monoclinic space group $P2_1/n$, a = 16.555 (1) Å, b = 16.860 (2) Å, c = 6.7665 (5) Å, β = 91.96 (5)°, Z = 4, R = 4.35%, and R_w = 6.26%).

Introduction

The past decade has shown a tremendous development in the synthesis of the small ring phosphorus compounds,[1] largely spurred by Mathey's seminal discovery that the thermal decomposition of the phosphanorbornadiene complex **1** yields the reactive, terminal complexed phosphinidene Ph–P–$W(CO)_5$ (**2**),[2] but also by reports of other phosphinidenes.[1a] The extensive synthetic literature provides ample evidence to suggest unencumbered singlet carbene-like behavior for **2** in numerous addition and insertion reactions but detailed mechanistic information is scarce.[1,3] In an elegant kinetic study, Mathey et al.[4] have shown that the (uncatalyzed) thermal decomposition of complex **1** is first order in **1** and does not depend on the concentration of the trapping reagent. This was taken as support for the intermediacy of the terminal phosphinidene complex **2** in the decomposition. Subsequently, we determined from competitive (CuCl catalyzed) experiments a Hammett reaction constant of –0.76 (r = 0.99) for the addition of **2** to styrenes to yield phosphiranes (eq 1). This not only supports the slightly electrophilic, carbene-like behavior of **2**[5]—carbenes[6] and alkylidenes[7] have similar ρ values—but also suggests that the addition reaction follows second-order kinetics. This seeming disparity supports the formation of intermediate **2**, which may be stabilized by the solvent, by the phthalate, and/or by olefins. From computational studies Houk and co-workers[8] concluded that the negative activation energy for the CCl_2– and CBr_2–ethylene addition is solely due to entropy effects. Likewise, the PH–ethylene addition occurs without π-complex formation.[9] In an extensive time-resolved laser flash spectroscopic investigation of the singlet arylhalocarbene–olefin addition Turro, Moss, and co-workers[10] suggested the intermediacy of a loose charge-transfer complex or contact pair in a solvent cage prior to product formation. Similar transient complexes/pairs have been formulated in electrophilic aromatic substitutions.[11] To further explore the properties of the carbene-like phosphinidene **2**, we now report on its addition reaction to a cyclic conjugated diene.

Recent studies have suggested that dibromocarbene[12] and 1,2-alkadienylidenecarbene[13] react with conjugated dienes to give both direct 1,2- and 1,4-adducts. With the possible exception of these cases, however, it is generally difficult to distinguish between primary and secondary carbene reaction products. As we will show, this is not the case with phosphinidene **2** because the reaction can be followed by ^{31}P NMR and the products can be characterized by X-ray crystallography. In an exploratory study, Marinetta and Mathey[2d] reported that conjugated dienes react with **2** to give 1,2-adducts at 55 °C. For one case, 2,3-dimethyl-1,3-butadiene, they showed that at temperatures ≥ 95 °C its vinylphosphirane converted into a phospholene, which is a formal 1,4-adduct (eq 2). No mechanistic details were provided. On the basis of kinetic evidence, Richter[14] postulated that the thermal rearrangement of (uncomplexed) 1-*tert*-butyl-2-vinylphosphirane to the corresponding phospholene occurs in sequential first order reactions with a biradical intermediate (eq 3). To examine the stability of vinylphosphiranes and to determine the mechanistic pathway for rearrangement to a phospholene, we report on the reaction of **2** with 1-methoxy-1,3-cyclohexadiene (**3**) (eq 4).

Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore FT-NMR spectrometer. Chemical shifts are 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. Product compositions were determined from

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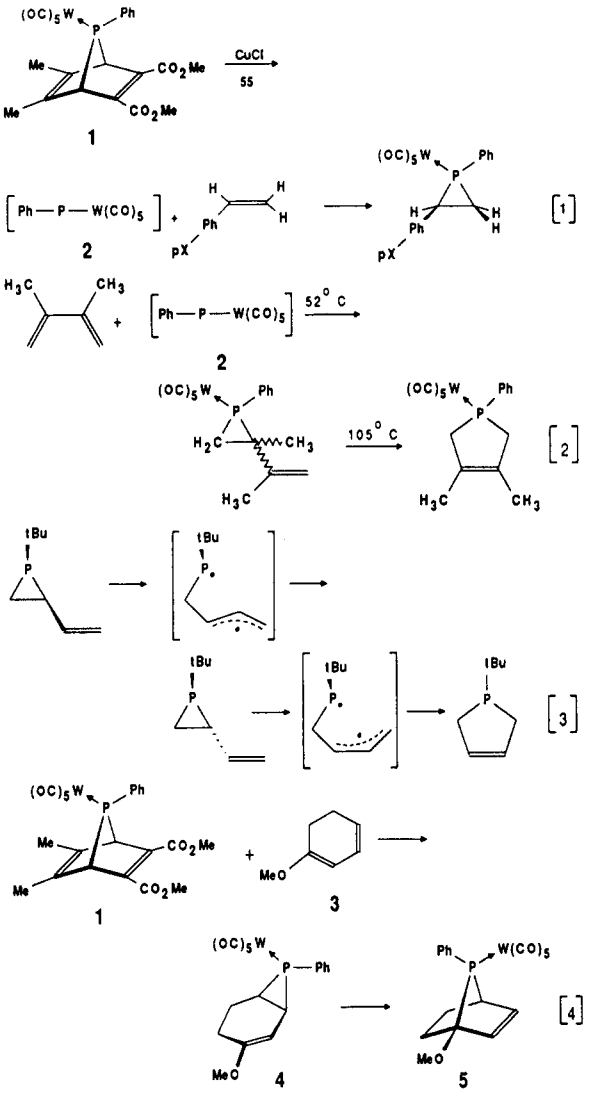

integration of ^{31}P NMR spectra. On several occasions these were compared with those from ^{1}H NMR spectra to ensure that the integrations were quantitative. In addition, separate NOE ^{31}P NMR sensitivity experiments were conducted. IR spectra were recorded on a Nicolet IR44 spectrometer. Mass spectra 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. Technical 1-methoxy-1,3-cyclohexadiene (**3**), purchased from Aldrich, contained the 1-methoxy-1,4-cyclohexadiene (**6**) isomer in a 76:24 ratio by GC-MS. Isomer **6**, also technical grade and purchased from Aldrich, contained 10% of **3** by GC-MS. 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 2a.

(3-Methoxy-7-phenyl-7-phosphabicyclo[4.1.0]hept-2-ene)pentacarbonyltungsten (4). Complex **1** (1.00 g, 1.53 mmol) and 1-methoxy-1,3-cyclohexadiene (1.30 g, 6.12 mmol) were heated at 55–60 °C in toluene with CuCl (100 mg, 1.0 mmol) for 45 min. The reaction mixture was filtered, evaporated to dryness, and chromatographed on silica with hexane–benzene (4:1) to yield 0.42 g of a 7:1 mixture of **4** and **5**. Fractional crystallization from hexane gave **4** as a colorless solid: mp 92–93 °C; ^{31}P NMR (C_6H_6) δ −131.5 ($^{1}J(^{31}P-^{183}W)$ = 261 Hz); ^{13}C NMR (C_6H_6) δ 159.7 (d, ^{3}J(C-P) = 9 Hz, C=CH), 89.4 (s, HC=C), 53.9 (s, OCH_3), 26.5 (d, ^{1}J(C-P) = 14.9 Hz, CHP), 25.7 (s, CH_2), 22.4 (s, CH_2), 21.8 (d, ^{1}J(C-P) = 15.8 Hz, CHP), 197.8 (d, ^{2}J(C-P) = 34.2 Hz, trans CO), 196.0 (s, cis CO), 129.6–131.6 (m, phenyl); ^{1}H NMR (C_6H_6) δ 4.59 (s, CH=C), 3.22 (s, OCH_3), 1.96–2.16 (m, 4 H, CH_2–CH_2), 1.73–1.88 (m, 1 H, CHP), 1.55–1.59 (m, 1 H, CHP), 6.96 (m, 5 H, phenyl); IR (KBr) μ(CO) 2074, 1910 cm^{-1}; mass spectrum (^{184}W) m/e (relative intensity) 542 (M^+, 7), 402 (M − 5CO, 46) 376 (PhPW$(CO)_3$, 25), 348 (PhPW$(CO)_2$, 100), 320 (PhPWCO, 63), 292 (PhPW, 86). Anal. Calcd for $C_{18}H_{15}O_6PW$: C, 39.86; H, 2.77. Found: C, 39.82, H, 2.79.

(1-Methoxy-7-phenyl-7-phosphanorbornene-2)pentacarbonyltungsten (5). The same reaction after 3 h yielded 0.51 g (62%) of **5** as a colorless solid: mp 99–100 °C (pentane); ^{31}P NMR (C_6H_6) δ 65.7 ($^{1}J(^{31}P-^{183}W)$ = 238 Hz); ^{13}C NMR (C_6H_6) δ 135.8 (d, ^{2}J(C-P) = 24.3 Hz, CH=C), 133.7 (d, ^{2}J(C-P) = 24.9 Hz, CH=C), 96.7 (d, ^{1}J(C-P) = 39.0 Hz, C-OCH_3), 54.9 (d, ^{1}J-(C-P) = 6.9 Hz, OCH_3), 42.3 (d, ^{1}J(C-P) = 25.7 Hz, CHP), 27.1 (d, ^{2}J(C-P) = 13.5, CH_2), 25.5 (s, CH_2), 199.2 (d, ^{2}J(C-P) = 24.5 Hz, trans CO), 197.1 (s, cis CO), 129.0–129.6–131.1 (m, C-phenyl); ^{1}H NMR (C_6H_6) δ 6.15 (t, J(H-H) = 5.4 Hz, ^{3}J(H-P) = 6.8 Hz, CH=C), 5.94 (dd, J(H-H) = 5.4 Hz, ^{3}J(H-P) = 12.3 Hz, CH=C), 3.30 (s, OCH_3), 2.61 (s, CHP), 1.52–1.64 (m, 2 H, CH_2), 1.29 (m, 1 H, CH_2), 1.04 (m, 1 H, CH_2), 6.92–7.05 (m, 5 H, phenyl); IR (KBr) μ(CO) 2070, 1910 cm^{-1}; MS (^{184}W) m/e (25), 348 (PhPW-$(CO)_5$, 100), 292 (PhPW, 87). Anal. Calcd for $C_{18}H_{15}O_6PW$: C, 39.86; H, 2.77. Found: C, 39.95; H, 2.80.

Following the reaction of **1** with **3** by ^{31}P NMR showed after 12 h a yield of **5** (relative to **4**) of 98% at 45 °C and of 77% at 25 °C. Immediate analysis (ca. 15 min) of a filtered aliquot from a reaction at 55 °C gave only (>95%) products **4** and **5** in a ratio of 11:1. The olefins **3** and **4** do not isomerize under the reaction conditions. An isolated and purified sample for **4** rearranged under the reaction conditions (with and without catalyst) in 2 h at 55 °C to **5** with 50% conversion as monitored by integration of both the ^{31}P and methoxy ^{1}H NMR chemical shifts; a small fraction of (*O*-methyl phenylphosphinite)pentacarbonyltungsten (**7**) was also obtained.

Reaction of a 4-fold excess of 1-methoxy-1,4-cyclohexadiene (**6**, containing 10% **3**) with complex **1** yielded **4** and **5** as major reaction products, 5% of **7**, and 5% of presumably a phosphirane, **8**. Product **7** has been reported to result from the insertion of **2** in methanol[2a] and therefore is the likely product of either a contaminant (5% by GCMS) in technical grade **6** or of a complex disproportionation process.[2d] Product **8** could not be characterized other than by its ^{31}P NMR chemical shift of δ −144.7 ppm (in toluene), which is a typical value for a phosphirane. Speculatively, this could be a phosphirane resulting from **6**. Reaction of **6** with **1** in a 1:1 ratio yielded **4**, **5**, **7**, **8**, and unidentifiable products, which did not contain a phosphirane ring according to ^{31}P NMR analysis.

X-ray Structure Determination of 4 and 5. Diffraction data of single crystals of **4** and **5**, mounted on glass fibers with epoxy cement, were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Ni-filtered Cu Kα radiation. Standard peak search and automatic indexing routines followed by least-squares fits of 25 centered reflections (2θ) gave the cell constants for both crystals. Three reflections were measured periodically to monitor decay, and linear decay corrections were applied. The data were processed using the Enraf-Nonius MolEN software on VAX/VMS computers. Variances were assigned to the *I*s on the basis of counting statistics with the addition of an instrumental uncertainty term. Lorentz, polarization, and analytical absorption corrections were made to the *I*s and σ^2 for each complex. The structures were solved by the heavy atom method (Patterson, followed by difference Fourier methods) and refined by full-matrix least-squares techniques with anisotropic non-hydrogen atoms and riding hydrogens in calculated positions with (nonrefined) isotropic thermal parameters based upon those of the attached atoms. Data with $I > 3\sigma(I)$ were used in the refinements ($R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{0.5}$, and the goodness of fits = $[\sum w(||F_o| - 1/k|F_c||)^2/v]^{0.5}$). In the final refinement no parameter varied by more than 0.03 of its standard deviation. The final difference Fourier map had no interpretable peaks with maximum $\Delta\rho$ values near the W atoms. Details of the data collection and structure solution procedures are summarized in Table I (supplementary material).

Results and Discussion

Reaction of **1** with 1-methoxy-1,3-cyclohexadiene (**3**) at 55 °C in toluene with CuCl as a catalyst yields the bicyclic

vinylphosphirane 4 and the tricyclic phospholene 5 in varying amounts as determined by ^{31}P NMR spectroscopy. Both products have been isolated, and their single-crystal X-ray structures have been determined. The 4:5 product ratio is dependent upon the reaction time. Under normal reaction conditions (55 °C, 3 h) only the 1,4-adduct 5 is isolated, but when reaction commences, the main product (by ^{31}P NMR) is 4. This would suggest that no direct 1,4-addition of the phosphinidene complex 1 to diene 3 occurs. Indeed, 4, isolated after short reaction times, purified, and heated at 55 °C in toluene with (and without) catalyst, rearranges exclusively to 5. These reactions reveal several important aspects.

1,2-Addition. The initial product from reaction of 1 with 1-methoxy-1,3-cyclohexadiene is the phosphirane 4. Whereas two isomers may be formed from the addition to the cis olefin, the phosphirane with the $W(CO)_5$ group over the cyclohexane ring is the major product (i.e., syn ≥ 95% by ^{31}P NMR). Because the $W(CO)_5$ group is larger than a phenyl group, it appears that the formation of 4 is kinetically controlled. Because no increase in the formation of the anti conformer is observed during reaction and subsequent rearrangement of 5 (vide infra), we conclude that under the reaction conditions (a) there is no equilibrium between the syn and anti isomers of 4 and (b) the chelotropic reaction of 2 with 3 to yield phosphirane 4 is not reversible. Such a retro-chelotropic reaction has been implied in the transfer of 2 from a double bond to a triple bond, i.e., the transfer of 2 from a phosphirane to an acetylene to yield a phosphirane.[2d] We observed no transfer of 2 from 4 to cyclohexene.

An interesting feature of structure 4 is the anti-parallel conformation of its cyclohexene ring and *P*-phenyl group. Even the methoxy group is in plane with the olefin. Secondary orbital interactions between the phenyl group of 2 and the methoxy-substituted vinyl group of 3 are expected to favor a syn-addition product,[15] which is contrary to observations. The high stereoselectivity of the phosphinidene addition then suggests that the phosphirane product formation is determined early on the reaction path. Speculative explanations are that (a) the anti conformation maximizes the conjugative interaction between the *P*-phenyl and diene groups and (b) the interaction between these groups is electrostatically repulsive in the syn approach.

From 1,2- to 1,4-Adduct. The rearrangement of the vinylphosphirane 4 to the phospholene 5 is stereospecific as illustrated by the X-ray structures. That is, *complete inversion at the P-center* occurs during reaction and as a result the $W(CO)_5$ group is located over the C=C bond in both products 4 and 5. The 4 → 5 rearrangement represents a *symmetry-allowed [1,3]-sigmatropic shift* and hence is most likely a concerted process. This conclusion contrasts Richter's postulate[14] for a two-step (biradical) thermal rearrangement of the uncomplexed, but related 1-*tert*-butyl-2-vinylphosphirane. If the present rearrangement were to occur via a biradical intermediate at least some loss of stereospecificity in the formation of 5 would be expected. Consequently, a [1,3]-sigmatropic shift with inversion at a sterically very crowded P-center appears favored energetically over a pathway that involves cleavage of a single P–C bond in the transition metal complexed phosphirane. In light of the "weak" P–C bond, with an estimated bond dissociation energy of 63 kcal/mol,[16] the ease of this sterically demanding [1,3]-sigmatropic shift is remarkable and could be of synthetic value.

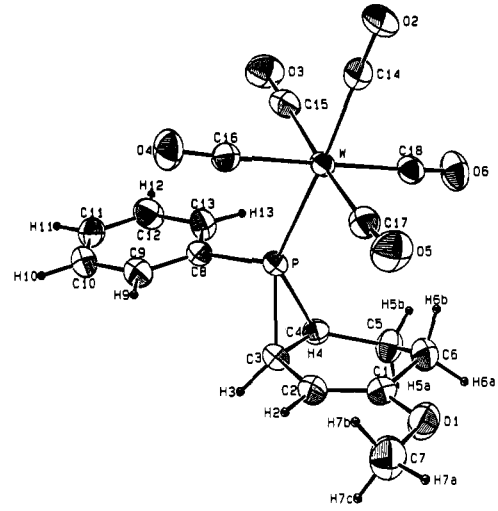

Figure 1. Molecular structure of 4.

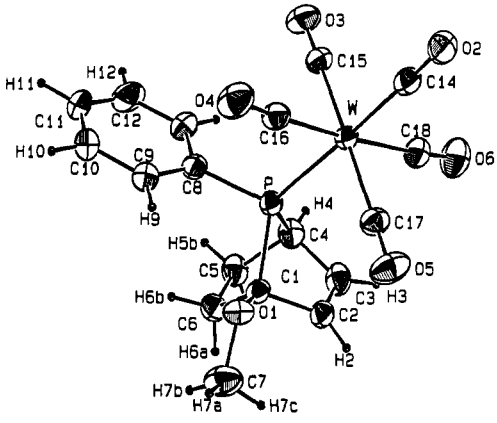

Figure 2. Molecular structure of 5.

Reactivities. The Hammett reaction constant for Ph–P–$W(CO)_5$ of –0.76 indicates a slight electrophilic behavior for phosphinidene 2. Therefore, the reactivity of a conjugated diene is expected to be enhanced by substitution with an electron-donating OCH_3 group. In fact, moderate addition of 2 to 1-methoxy-1,3-cyclohexadiene (3) to yield phosphirane 4 occurs even at 25 °C. It is also clear that the conjugated diene 3 is more reactive toward addition of the phosphinidene than the isolated double bonds in 6 are. Hence, the methoxy group enhances the rate of the chelotropic phosphinidene addition reaction.

The methoxy group has also a rate enhancing effect on the [1,3]-sigmatropic shift of vinylphosphirane to give phospholene, which occurs at ≤55 °C for the 4 → 5 reaction. For comparison, the rearrangement of the unsubstituted vinylphosphirane, which results from reaction of 2 with 2,3-dimethyl-1,3-butadiene to give a phospholene (eq 2), requires a much higher temperature of ca. 105 °C.[2d] Moreover, as noted above, Richter has provided evidence to suggest that the rearrangement of an uncomplexed and unsubstituted vinylphosphirane to a phospholene (as described in eq 3) occurs via a biradical intermediate.

Structures. Vinylphosphirane 4 and phospholene 5 are fully characterized by their X-ray structures (Tables 2–5 in the supplementary material and Figures 1 and 2) and their ^1H, ^{13}C, and ^{31}P NMR spectroscopic data. The conformational assignments of the P-substituents in 4 and 5 could not have been made unequivocally without single-crystal X-ray structure determinations. We discuss some of the structural highlights below.

The phosphirane ring in 4 (Figure 1) has a small CPC bond angle of only 48.2° with a short C3–C4 bond distance

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of 1.497 (8) Å. The short C2–C3 bond (1.469 (9) Å) suggests an electronic interaction between the phosphirane ring and its neighboring C=C bond. The two P–C bonds of the phosphirane are 1.816 (6) and 1.851 (5) Å long with the P–C3 bond being the longest for hyperconjugative reasons, which is in line with the observed [1,3]-sigmatropic shift. Homolytic cleavage of the weaker P–C3 bond to yield a biradical intermediate is highly unlikely because such a species would yield either only an *anti*-phospholene with retention of configuration, when P–C fusion is faster than P-inversion or a mixture of *syn*- and *anti*-**5** (as well as *syn*-**4**), when P-inversion is faster than P–C fusion.

The observed tricyclic phospholene **5** has longer bridging P–C bonds of 1.876 (6) and 1.879 (7) Å with a larger CPC angle of 79.6 (3)° than found in the bicyclic phosphirane structure **4**. As expected for the different P-hybridizations, structure **5** has the smaller phenyl–P–$W(CO)_5$ angle of 112.7° vs 118.6° in **4**, although steric effects can not be excluded. However, if these are present, they apparently do not influence the direction (or twisting) of the P-ligands; the C1–P–C4 and phenyl–P–$W(CO)_5$ planes are orthogonal. The structural parameters of **5** are similar to those of the Cr analogue of **1**,[17] which has similar bridging P–C bonds of 1.877 and 1.878 Å with a CPC angle of 79.0°.

The ^{31}P NMR chemical shifts of δ −131.2 ppm for **4** and δ +65.7 ppm for **5** are strikingly different. The former value is typical for phosphiranes while the latter compares well with P-bridged structures.[1,18]

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Conclusions. The reaction of the carbene-like terminal phosphinidene complex Ph–P–$W(CO)_5$ with the activated cyclic diene **3** yields as primary product the bicyclic phosphirane **4** in high stereoselectivity. It is suggested that this selectivity is determined early on the reaction path and results from repulsive interactions between the *P*-phenyl and diene groups. Tricyclic phospholene **5** is not a primary (1,4-addition) product from diene **3**, but rather a secondary reaction product resulting from a [1,3]-sigmatropic shift in phosphirane **4** with complete inversion of the stereochemistry of the sterically crowded P-center.

The overall reaction involves a transfer of the phosphinidene complex **2** from the tricyclic diene reagent **1** to yield a structurally similar tricyclic olefin.

The stepwise 1,4-addition of the complexed phosphinidene to a cisoid 1,3-diene differs from recently reported direct 1,4-additions of both carbenes and alkadienylidene carbenes.

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Supplementary Material Available: Listings of bond distances and angles for coordinates of hydrogen atoms, least-squares planes, and anisotropic thermal parameters **4** and **5** (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

One-Step Spiroannulation Using 1,2-Bis(methylene)cycloalkane–Magnesium Reagents

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A one-step method for the synthesis of a wide variety of spirocyclic systems has been developed based on the reactions of bis-electrophiles with a series of new 1,3-diene–magnesium reagents, the magnesium complexes of 1,2-bis(methylene)cycloalkanes. The direct metalation of 1,2-bis(methylene)cycloalkanes with highly reactive magnesium in THF at ambient temperature generates the corresponding diene–magnesium reagents in high yields. Reactions of the diene–magnesium reagents with 1,*n*-dibromoalkanes produce a large number of spirocarbocycles containing an exocyclic double bond. The ring sizes of the accessible spiro compounds can be any combinations of four- to seven-membered rings. In most cases, the initially alkylated intermediates can be trapped by protonation, giving the corresponding bromo olefins. Significantly, treatment of the diene–magnesium reagents with bromoalkyl nitriles leads to a one-step synthesis of keto-functionalized spirocycles. The initial adduct is believed to be a Grignard reagent containing a cyano group. When a bromo nitrile containing a cyclic moiety is used as the bis-electrophile, the approach provides a direct access to dispiroenones.

Introduction

Halide-free organomagnesium compounds prepared from the direct metalation of conjugated dienes with activated magnesium represent an important advance in organomagnesium chemistry.[1] From the viewpoint of nucleophilic reactivity, these diene–magnesium reagents can be regarded as magnesium 1,3-diene dianions which allow for the formation of two bonds with electrophilic substrates in one synthetic operation. Depending upon the nature of various electrophiles, both 1,2- and 1,4-additions to the original dienes have been observed.[2,3] When two electrophilic centers reside in one substrate, the overall process provides an easy access to cyclic molecules.

However, since the first report by Ramsden[4a] in 1968, the studies on the chemistry of diene–magnesium com-

(1) For a recent review, see Dzhemilev, U. M.; Ibragimov, A. G.; Tolstikov, G. A. *J. Organomet. Chem.* **1991**, *406*, 1.

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