aromatics). Spectrum also contains P*Me* signal due to ca. 25% of [Rh{(*R**,*R**)-diph}(Me_2CO-d_6)$_2$]$^+$ at δ 2.24 (virtual triplet, $^2J_{PH}$ + $^4J_{PH}$ = 20.2 Hz, $^3J_{RhH}$ = 1.3 Hz).

[*SP*-4-(*R,*R**)]-(Methyl α-acetamidocinnamate)[1,2-phenylenebis(methylphenylphosphine)]rhodium(I) Hexafluorophosphate [(±)-5].** A suspension of *meso*-**4** (1.2 g) in acetone (20 mL) containing methyl α-acetamidocinnamate (0.44 g) was stirred until all of the dimer had dissolved (ca. 10 min). The addition of diethyl ether (40 mL) to the deep red solution produced the product as clumps of needles: mp 155–160 °C; yield 1.03 g (65%). Anal. Calcd for $C_{32}H_{33}F_6NO_3P_3Rh$: C, 48.7; H, 4.2; N, 1.8. Found: C, 48.9; H, 4.6; N, 1.6. ^1H and ^{31}P NMR (CD_2Cl_2): see Tables II and III.

Hydrogenation Procedure. Hydrogenation experiments were performed with use of a "Towers" atmospheric pressure microhydrogenation apparatus. The reaction vessel was charged with ca. 1 g (5 mmol) of substrate and ca. 0.03 g (0.05 mmol) of catalyst and then evacuated and flushed with argon before admission of solvent (ethanol, ca. 50 mL) and base (10 mmol if required) and exposure of the resulting solution to hydrogen. When gas uptake was complete, catalyst (−)-**1** was removed with use of Dowex 50W-X2 cation exchange resin in the acid form (200–400 mesh, 5–6 g). For experiments involving triethylamine or (−)-**2**, however, the extractive method of Riley and Shumate[3] was used. Optical yields were determined by comparison of optical rotations of product solutions after removal of catalyst with solutions of authentic specimens under the same conditions. The identity and chemical purity of the products were subsequently determined by ^1H NMR spectroscopy: isolated yields were >95%.

Identical results were obtained with use of (−)-**1** after it had been exposed to the atmosphere for 1 week. Dimer (−)-**4** performed identically to (−)-**1**.

Registry No. (−)-**1**, 100945-97-9; (±)-**1**, 101052-77-1; (−)-**2**, 100945-99-1; **3**, 60470-22-6; (−)-**4**, 100946-01-8; *meso*-**4**, 101052-79-3; (±)-**5a**, 101052-81-7; (±)-**5b**, 100946-03-0; $[RhCl(NBD)]_2$, 12257-42-0; [*S*-(*R**,*R**)]-diph, 72150-63-1; (±)-diph, 72091-01-1; [*S*-(*R**,*R**)]-dias, 57341-01-2; dppe, 1663-45-2; (*Z*)-PhCH=C(NHCOMe)CO_2H, 55065-02-6; (*Z*)-PhCH=C(NHCOMe)CO_2Me, 60676-51-9; (*Z*)-PhCH=C(NHCOPh)CO_2H, 26348-47-0; (*Z*)-PhCH=C(NHCOPh)CO_2Et, 26348-46-9; CH_2=C(NHCOMe)CO_2H, 5429-56-1; (*Z*)-EtCH=C(NHCOPh)CO_2H, 100928-37-8; Me_2C=C(NHCOPh)CO_2H, 1738-64-3; (*Z*)-*i*-PrCH=C(NHCOMe)CO_2H, 64896-30-6; (*Z*)-*i*-PrCH=C(NHCOPh)CO_2H, 64896-31-7; *N*-acetyl-(*S*)-phenylalanine, 2018-61-3; *N*-acetyl-(*S*)-phenylalanine methyl ester, 3618-96-0; *N*-benzoyl-(*S*)-phenylalanine, 2566-22-5; *N*-benzoyl-(*S*)-phenylalanine ethyl ester, 7200-18-2; *N*-acetyl-(*S*)-alanine, 97-69-8; *N*-benzoyl-(*S*)-α-aminobutyric acid, 87068-75-5; *N*-benzoyl-(*S*)-valine, 5699-79-6; *N*-acetyl-(*S*)-leucine, 1188-21-2; *N*-benzoyl-(*S*)-leucine, 1466-83-7.

Metal- and Alkoxide-Mediated Phosphorus–Oxygen Bond Cleavage in (η^5-Cyclopentadienyl)cobalt Phosphinite Ester Complexes

David B. Collum,* Randall T. Depue, and Jeffrey A. Klang

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

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Reaction of 2-pyridyl dimethylphosphinite (**1**) with 0.5 equiv of η^5-CpCo(CH_2=CH_2)$_2$ affords Cp_2Co_2-(μ-PMe_2)(μ-Opy) (**4**) in a 74% yield. Bridging phosphide **4** appears to arise by a formal oxidative addition across the phosphorus–oxygen bond of ligand **1**. Reaction of 4-*tert*-butylphenyl dimethylphosphinite (**6**) with CpCo(CH_2=CH_2)$_2$ affords CpCo(CH_2=CH_2)(Me_2POAr) (**7**) in a 75–80% yield. Reactions of **7** with several allylic and homoallylic potassium alkoxides afford chelated unsaturated phosphinite ester complexes. Thermodynamic, kinetic, and photostationary diastereofacial selectivities are observed but the chelate stereochemistries are not assigned.

Introduction

We have been interested in developing a technology that would enable us to effect hydroxyl-directed organometallic reactions of unsaturated alcohols under *aprotic* conditions. In principle, the powerful stereochemical determinants that have added profound importance to hydroxyl-directed epoxidations[1] and hydrogenations[2] of olefins would become available to transition-metal-mediated olefin functionalizations other than simple redox processes.[3,4] The investigations began with attempts to chelate unsaturated dimethylphosphinite esters (Me_2POR, R = alkene) to a $Mo(CO)_4$ fragment.[5] Through efforts to solve a series of technical problems, we developed the alkoxide-triggered substitution reaction illustrated in eq 1. Although this reaction appeared to be potentially useful in both organic and inorganic synthesis with no immediately apparent limitations, the transition-metal chemistry of 2-pyridyl

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(3) Main-group and oxophilic early-transition-metal alkyls undergo alkoxide-directed carbometalation of olefins under strenuous conditions: Eisch, J. J. *J. Organomet. Chem.* **1980**, *200*, 101. Prasad, J. V. N.; Pillai, C. N. *J. Organomet. Chem.* **1983**, *259*, 1.

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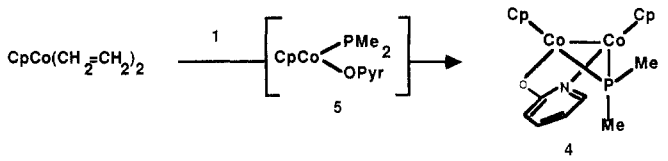
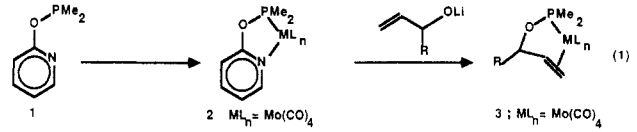
Scheme I



dimethylphosphinite (1) subsequently has proven to be more complex.



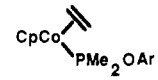
Presented herein is a reaction of ligand 1 with CpCo(CH_2=CH_2)$_2$ (Cp = η^5-cyclopentadienyl) that leads to phosphorus–oxygen bond cleavage. We also describe a means to circumvent the cleavage using more traditional ligand substitution procedures to prepare CpCo chelates of unsaturated phosphinite esters.

Results

Preparation of phosphinite ester chelates of type **3** (ML_n = CpCo) according to eq 1 were hindered by unsuccessful attempts to prepare the starting material **2** (ML_n = CpCo). Reaction of $CpCo(CO)_2$, CpCo(η^4-norbornadiene),[6] or CpCo(η^4-cyclooctadiene)[7] with ligand 1 (or the corresponding diphenyl derivative) afforded intractable materials under a variety of thermal and photochemical conditions.

Phosphorus–Oxygen Bond Cleavage. When CpCo(CH_2=CH_2)$_2$[8] was treated with 0.5 equiv of ligand 1, bridging phosphide **4** was isolated in a 74% yield as an air-sensitive, olive green crystalline solid. In the ^{1}H NMR spectrum of **4** (toluene-d_8, 30 °C), the 1:1:2 pyridyloxy/PMe_2/Cp stoichiometry was readily apparent. The two distinct Cp groups appeared as singlets at 4.56 and 4.52 ppm. The phosphide methyls appeared as discrete doublets at 1.99 ppm (J_{PH} = 11.8 Hz) and 0.61 ppm (J_{PH} = 13.5 Hz). Stepwise warming of the probe from −60 to 150 °C showed the anticipated coalescence[9] equilibrating the diastereotopic methyls at approximately 60–90 °C to a broad mound in the fast-exchange limit.[10] The Cp ligands did *not* become equivalent up to 150 °C.[9] The ^{13}C NMR spectrum lent strong support for the absence of a P–O bond since the resonances corresponding to the pyridyl carbons were not coupled to the phosphorus nucleus. Compound **4** exhibited a singlet at 111.4 ppm in its ^{31}P NMR spectrum (toluene-d_8, −80 °C)[11] and analyzed correctly for the proposed empirical formula.[12]

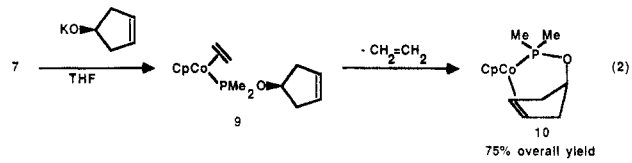
As illustrated in Scheme I, CpCo(CH_2=CH_2)$_2$ effected a facile phosphorus–oxygen bond cleavage on ligand 1. Although the reaction was consistent with the intermediacy of terminal phosphide **5**, no direct spectral evidence for **5** could be obtained.[13] Curiously, when CpCo(CH_2=CH_2)$_2$ was treated with 4-*tert*-butylphenyl dimethylphosphinite (**6**), we obtained **7** as a rust-brown crystalline solid in a 75–80% yield after recrystallization. Unlike η^1-pyridyl complex **8** presumed to be a labile intermediate en route to phosphide **4**, **7** was thermally stable to 110 °C (toluene-d_8).



7 ; Ar = 4-t-butylphenyl

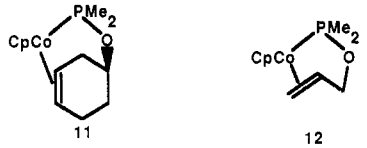
8 ; Ar = 2-pyridyl

Preparation of Unsaturated Phosphinite Ester Chelates. Compound **7** proved to be a viable starting material for the preparation of a series of phosphinite ester chelates derived from unsaturated potassium alkoxides. For example, treatment of **7** with 1.5 equiv of the potassium alkoxide of 3-cyclopenten-1-ol in THF at 25 °C for 4–5 h effected clean displacement of the phenoxy moiety to afford unchelated adduct **9** as a dark orange oil (eq 2).



Complex **9** exhibited broad multiplets at 1.15 and 2.30 ppm characteristic of a coordinated ethylene, as well as a broad singlet at 5.56 ppm attributable to the uncoordinated vinyl protons of the cyclopentene. Upon standing at room temperature in C_6D_6 for approximately 30 days or upon photolysis with a 275-W sunlamp at 25 °C for 18 h, **9** lost ethylene to provide chelate **10** in a 75% overall yield from **7**. The vinyl resonances in the ^{1}H NMR spectrum of chelate **10** appeared as a broad singlet at 3.36 ppm. The ^{31}P NMR spectrum (toluene-d_8, −80 °C)[11] showed a singlet at 145.7 ppm significantly upfield of the resonances for the unchelated derivatives (164–169 ppm).

Chelates **11** and **12** were prepared analogously in 25 and 60% respective overall yields. The corresponding chelates derived from 2-cyclopenten-1-ol, 2-cyclohexene-1-ol, and 1-phenyl-2-propen-1-ol proved too labile to isolate.



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(7) Lewis, J.; Parkins, A. W. *J. Chem. Soc. A* **1967**, 1150.

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(9) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 746. Casey, C. P.; Bullock, R. M. *Organometallics* **1984**, *3*, 1100. Grobe, V. J. *Z. Anorg. Allg. Chem.* **1968**, *361*, 32. Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L. *Inorg. Chem.* **1984**, *23*, 1779. Harley, D. A.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 383.

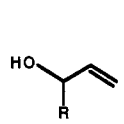
(10) When ^{1}H NMR spectra of **4** were recorded in toluene-d_8 at 30 °C temperature increments between −60 and 150 °C, considerable temperature dependencies of the two Cp and the downfield diastereotopic methyl resonance were observed. For example, upon warming throughout the temperature range, the two Cp resonances at 4.61 and 4.39 ppm at −60 °C crossed at approximately 105 °C and ended at 4.49 and 4.55 ppm, respectively, at 150 °C. In a process independent of the methyl group coalescence, the diastereotopic downfield methyl resonance moved from 1.75 ppm at −60 °C to 2.00 ppm at 30 °C (the beginning of coalescence broadening); the upfield methyl showed little temperature dependence. The averaged methyl peaks continued to shift to 1.35 ppm upon warming to 150 °C. These phenomena could not be explained but were found to occur exclusively in aromatic solvents.

(11) It was often necessary to record ^{31}P NMR spectra at low temperatures in toluene-d_8 to minimize the effects of quadrupolar broadening. See: Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 3265 and references cited therein.

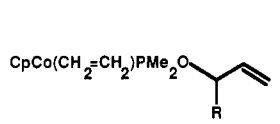
(12) Treatment of CpCo(CH_2=CH_2)$_2$ with 1.0 equiv of 1 afforded a thermally sensitive forest green oil that exhibited singlets at 172.3 and 156.5 ppm (1:5 ratio) in the crude ^{31}P NMR spectrum (toluene-d_8, H_3PO_4 standard). Although the major pyridyl resonances in the ^{13}C NMR spectrum exhibited no phosphorus–carbon coupling, indicating that P–O bond cleavage had occurred, numerous purification efforts failed to provide analytically pure material for unambiguous characterization. Treatment of the crude forest green oil with CpCo(CH_2=CH_2)$_2$ in benzene-d_6 afforded bridging phosphide **4**.

(13) The intermediacy of **5** is less than secure and is provided as a mechanistic mnemonic. A referee's suggestion that the cleavage may be a dinuclear mechanism has been highlighted by our mechanistic studies of related reactions mediated by group 7 dinuclear systems.[21]

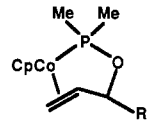
Previously, we had reacted molybdenum chelate **2** (eq 1) with alkoxides containing pre-existing stereocenters to obtain information on the steric and electronic biases that determine the diastereofacial selectivity of chelation.[5] Similar efforts on the CpCo fragment yielded interesting, yet inconclusive results. For example, treatment of **7** with the potassium salts of alcohols **13–15** afforded uncyclized monoethylene complexes **16–18** (respectively) contaminated with small amounts of the corresponding chelates **19–21**. Upon standing at 25 °C for 4 days, the unchelated



13; R = Me
14; R = Bn
15; R = i-Pr



16; R = Me
17; R = Bn
18; R = i-Pr



19; R = Me
20; R = Bn
21; R = i-Pr

forms cyclized to give what appeared to be pairs of stereoisomers of **19–21** resulting from coordination to the two diastereotopic faces of the olefins. In each case, the major isomers exhibited a ^{31}P NMR resonance 4–5 ppm downfield of the minor isomers as well as ^{1}H NMR data that were qualitatively and quantitatively consistent with this formulation. For discussion purposes, we will refer to the major isomers by postscript **a** and minor isomers by postscript **b**. The observed isomeric ratios as determined by ^{31}P NMR were as follows: **19a:19b** = 5:1; **20a:20b** = 11:1; **21a:21b** = 16:1. If the isomer mixtures were left standing in C_6D_6 at 25 °C and monitored *exclusively* by ^{31}P NMR, each sample appeared to smoothly equilibrate in approximately 30 days to distributions favoring the **b** isomer in ≥97% selectivity; after presumed equilibration[14] the isomers that predominated under kinetic conditions (the **a** isomers) could not be detected (≤3%) in the ^{31}P NMR spectra. Sunlamp irradiation of either the thermodynamic or kinetic isomer mixtures in C_6D_6 afforded approximate 1:1 photostationary mixtures in each of the three cases.

The apparent kinetic, thermodynamic, and photostationary stereocontrol was interesting since the trends appeared to be rational and curiously complementary with respect to the steric demands of the alkyl substituent. Unfortunately, the situation proved to be far less tractable than the ^{31}P NMR analysis indicated. Although the kinetic cyclizations afforded isomer mixtures that were relatively free of impurities in the ^{1}H NMR spectra, both the thermal and photostationary isomerizations suffered considerably from formation of significant decomposition products. The decomposition products were undetectable by ^{31}P NMR but were readily observed both visually as insoluble solids and as additional broad resonances in the ^{1}H NMR spectra. Overall, the labilities of the six isomers prevented us from obtaining diffractable crystals for stereochemical assignment and thus restricted any interpretation of the isomer ratios.

Discussion

Clearly, catalyst destruction is easily argued to be a central issue in homogeneous catalysis.[15] It is not surprising, therefore, that the well-documented phosphorus–carbon bond cleavages mediated by transition metals have received serious attention in recent years.[16,17] In contrast, the analogous phosphorus–oxygen bond cleavages have been reported only very rarely.[18] Although this may arise, in part, from the very high (>80 kcal/mol) phosphorus–oxygen bond disruption enthalpy,[19] it may also be that the products are typically intractable. In either case, the cleavage of ligand **1** by $CpCo(CH_2{=}CH_2)_2$ represents, in the very least, a notably clean example of a transition-metal-mediated bond scission that has resisted thorough documentation.

On first inspection, the cleavage appeared to be simply a nucleophilic displacement of the pseudohalide hydroxypyridyl moiety by the electron-rich CpCo fragment.[20] However, since the simple aryl phosphinite ester complex **7** proved to be robust, the pyridyl moiety in ligand **1** may have served a more complex role in the cleavage. We have recently studied in detail seemingly related P–O bond cleavages in electron-deficient (and therefore less nucleophilic) group 7 $M_2(CO)_8(\eta^2\text{-}Me_2POpy)$ complexes. We defer further mechanistic discussions to the forthcoming paper.[21]

Experimental Section

General Information. Routine ^{1}H NMR spectra were recorded on a Varian CFT-20 (80 MHz) spectrometer. ^{1}H NMR spectra were obtained on a Brucker WP 300 and JEOL FX90Q spectrometers. ^{13}C and ^{31}P NMR spectra were taken on a JEOL FX90Q spectrometer operating at 22.49 and 36.23 MHz, respectively. $CpCo(CH_2{=}CH_2)_2$,[8] 3-cyclohexen-1-ol,[22] chlorodimethylphosphine,[23] and ligand **1**[5] were prepared as described previously. Other alcohols were commercially available (Aldrich) or were made by addition of vinylmagnesium bromide to the corresponding aldehyde and distilled prior to use. Benzene, benzene-d_6, toluene, toluene-d_8, pentane, hexane, THF and diethyl ether were distilled *in vacuo* from sodium benzophenone ketyl/1% tetraglyme using standard vacuum line techniques. All other reagents were handled using standard protocols. All organometallic compounds were manipulated using standard vacuum line and glovebox techniques.

$Cp_2Co_2(\mu\text{-}PMe_2)(\mu\text{-}Opy)$ (4). A dark brown solution of $CpCo(CH_2{=}CH_2)_2$ (501 mg, 2.78 mmol) in THF (15 mL) at −78 °C was treated with 2-pyridyl dimethylphosphinite (**1**; 0.203 mL, 1.39 mmol) and then held at 0 °C for 2 h and 25 °C for an additional 1 h. The forest green solution was concentrated in vacuo, and the resulting gum was extracted with 25 mL of diethyl ether. The ethereal extracts were concentrated to approximately 10 mL, layered with hexane (15–20 mL), and, upon completion of the mixing of the layers, slowly cooled to −78 °C. Dinuclear **4** was isolated as a deep green crystalline solid (416 mg, 74% after two crops): mp 155–157 °C dec; ^{1}H NMR (toluene-d_8, 30 °C) δ 7.78 (m, 1 H), 6.36 (m, 1 H), 5.88 (m, 1 H), 5.59 (m, 1 H), 4.57 (s, 5 H), 4.52 (s, 5 H), 2.00 (d, J_{PH} = 11.9 Hz, 3 H), 0.62 (br d, J_{PH} = 13.5 Hz, 3 H); $^{31}P\{^{1}H\}$ NMR (toluene-d_8, −80 °C)[11] δ 111.4 (s); $^{13}C\{^{1}H\}$ NMR (toluene-d_8, 0 °C) δ 177.9 (s), 153.4 (s), 134.3 (s), 115.5 (s), 109.5 (s) 79.2 (s), 78.8 (s), 18.9 (d, J_{PC} = 21.5 Hz), 10.0 (d, J_{PC} = 8.0 Hz); IR (C_6D_6) 1600 (m), 1480 (vs), 1265 (m),

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1110 (m), 1010 (m), 940 (m), 765 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{20}Co_2NOP$: C, 50.38; H, 4.82; Co, 29.50; N, 3.36; P, 7.84. Found: C, 50.64; H, 5.00; Co, 29.23; N, 3.47; P, 7.68.

4-*tert*-Butylphenyl Dimethylphosphinite (6). To a solution of 4-*tert*-butylphenol (31.64 g, 0.211 mol) in methylene chloride (200 mL) at 0 °C under argon was added dimethylchlorophosphine[23] (16.8 mL, 0.200 mol) followed by slow addition of triethylamine (29.4 mL, 0.211 mol) over 30 min. After the mixture stirred at 0 °C for 1.0 h and 25 °C for 2 h, the white suspension was filtered and the resulting colorless filtrate was concentrated in vacuo. Distillation through a 15-cm vigreaux column (58–62 °C, 10^{-2} mm) afforded **6** (28.1 g, 67% yield) as a pyrophoric colorless oil: ^1H NMR (C_6D_6) δ 7.14–7.16 (m, 4 H), 1.20 (s, 9 H), 1.18 (d, J_{PH} = 6.2 Hz, 6 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 120.5 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 155.5 (d, J_{PC} = 6.6 Hz), 144.7 (s), 126.6 (s), 118.6 (d, J_{PC} = 11.0 Hz), 34.2 (s), 31.7 (s), 20.3 (d, J_{PC} = 20.9 Hz); IR (C_6D_6) 1590 (m), 1500 (s), 1225 (vs), 940 (m), 865 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{19}OP$: C, 68.77; H, 8.97; P, 14.47. Found: C, 68.55; H, 9.11; P, 14.73.

η^5-CpCo(CH_2=CH_2)(η^1-$Me_2POC_6H_4$-*t*-Bu) (7). To a dark brown solution of CpCo(CH_2=CH_2) (1.80 g, 10.0 mmol) in hexane (50 mL) at −20 °C was added ligand **6** (2.20 mL, 10.0 mmol). The reaction vessel was allowed to first warm to 0 °C with stirring for 3 h and then to 25 °C with stirring for 1.0 h. The brown solution was concentrated to approximately 15 mL and filtered. Recrystallization by slowly cooling the filtrate to −78 °C afforded 2.74 g of **7** (76% yield) as a brown crystalline solid: mp 63–65 °C; ^1H NMR (C_6D_6) δ 7.25 (s, 4 H), 4.38 (s, 5 H), 2.45 (m, 2 H), 1.37 (m, 2 H), 1.24 (s, 9 H), 1.08 (d, J_{PH} = 6.7 Hz, 6 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −30 °C)[11] δ 173.2 (s); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 152.7 (d, J_{PC} = 4.9 Hz), 146.0 (s), 126.0 (s), 122.0 (d, J_{PC} = 4.9 Hz), 82.7 (d, J_{PC} = 2.4 Hz), 34.5 (s), 31.9 (s), 24.0 (d, J_{PC} = 3.7 Hz), 21.1 (d, J_{PC} = 26.9 Hz); IR (C_6D_6) 1500 (vs), 1225 (vs), 935 (vs), 865 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{28}CoOP$: C, 62.98; H, 7.79; P, 8.55. Found: C, 62.88; H, 7.59; P, 8.33.

Representative Procedure for the Preparation of Phosphinite Ester Chelates. Chelate 10. To a suspension of oil-free potassium hydride (181 mg, 4.51 mmol) in tetrahydrofuran (5.0 mL) at 25 °C was added 3-cyclopenten-1-ol (0.375 mL, 4.46 mmol). After the visible H_2 evolution subsided and the vessel was cooled to 0 °C, additional THF (20 mL) was added by vacuum transfer, and complex **7** (1.09 g, 3.01 mmol) was added as a solid by side arm. After being stirred for 1–2 h at 0 °C and 5 h at 25 °C, the reaction was concentrated in vacuo, and the resulting brown gum was extracted two times with 15 mL of hexane. The hexane layers were concentrated to afford unchelated ethylene complex **9** as an orange oil contaminated with approximately 10% of chelate **10**: ^1H NMR of **9** (C_6D_6, the resonances corresponding to **10** are excluded) δ 5.56 (s, 2 H), 4.52 (s, 5 H), 4.30 (m, 1 H), 2.05–2.65 (m, 6 H), 1.15 (m, 2 H), 0.88 (d, J_{PH} = 6.9 Hz, 6 H). If the hexane extracts described above were photolyzed with a 275-W sunlamp (5-cm displacement from the sample, 15–20 h, forced air cooling) and then filtered and concentrated, recrystallization of the resulting gum from pentane (5–10 mL) at −78 °C afforded a 75% yield of **10** as a burnt orange microcrystalline solid: mp 75–77 °C, ^1H NMR (C_6D_6) δ 4.42 (s, 5 H), 4.16 (m, 1 H), 3.36 (s, 2 H), 1.87 (m, 4 H), 1.19 (d, J_{PH} = 7.7 Hz, 6 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 145.7 (s); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 82.2 (s), 76.8 (s), 40.0 (d, J_{PC} = 11.0 Hz), 35.5 (d, J_{PC} = 9.8 Hz), 27.0 (d, J_{PC} = 28.1 Hz); IR (C_6D_6) 1075 (s), 1025 (vs), 965 (s), 930 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{18}CoOP$: C, 53.64; H, 6.68; P, 11.37. Found: C, 53.75; H, 6.77; P, 11.55.

Chelate 11. With use of the representative procedure described above, **11** was prepared from 3-cyclohexen-1-ol in 25% overall yield: mp 78–80 °C; ^1H NMR (C_6D_6) δ 4.40 (d, J_{PH} = 0.9 Hz, 5 H), 4.12 (m, 1 H), 2.95–3.0 (m, 2 H), 1.8–2.55 (m, 4 H), 1.31 (d, J_{PH} = 6.5 Hz, 3 H), 1.15 (d, J_{PH} = 10.1 Hz, 3 H), 0.80–1.10 (m, 2 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 155.5 (s); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 82.3 (d, J_{PC} = 2.7 Hz), 72.8 (s), 33.6 (d, J_{PC} = 17.5 Hz), 32.4 (d, J_{PC} = 4.1 Hz), 31.2 (d, J_{PC} = 33.6 Hz), 29.8 (s), 28.2 (d, J_{PC} = 28.2 Hz), 25.2 (d, J_{PC} = 8.1 Hz), 24.5 (d, J_{PC} = 14.8 Hz); IR (C_6D_6) 1065 (s), 1035 (s), 975 (vs), 930 (s), 890 (s), 870 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{20}CoOP$: C, 55.33; H, 7.14; P, 10.98. Found: C, 55.08; H, 6.97; P, 10.70. The unchelated intermediate obtained prior to photolysis exhibited the following: $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 164.4 (s).

Chelate 12. With use of the representative procedure described above, **12** was prepared from 2-propen-1-ol in 60% overall yield: mp 51–53 °C; ^1H NMR (90 MHz, C_6D_6) δ 4.52 (d, J_{PH} = 0.7 Hz, 5 H), 3.40–4.10 (m, 3 H), 2.08 (d, J_{HH} = 7.9 Hz, 1 H), 1.13 (d, J_{PH} = 8.5 Hz, 3 H), 1.13 (d, J_{PH} = 7.6 Hz, 3 H), 0.84 (m, 1 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −70 °C)[11] δ 186.3 (s); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 81.2 (d, J_{PC} = 2.6 Hz), 73.1 (d, J_{PC} = 6.7 Hz), 47.2 (s), 24.9 (d, J_{PC} = 21.5 Hz), 22.1 (d, J_{PC} = 29.6 Hz), 18.2 (d, J_{PC} = 6.7 Hz); IR (C_6D_6) 1005 (s), 965 (vs), 935 (s), 880 (s), 755 (s), 695 (vs) cm^{-1}. Anal. Calcd for $C_{12}H_{16}CoOP$: C, 49.60; H, 6.66; P, 12.79. Found: C, 49.33; H, 6.48; P, 12.57. The unchelated intermediate obtained prior to photolysis exhibited the following: ^1H NMR (C_6D_6) δ 5.55–6.05 (m, 1 H), 5.17 (d, 18 Hz, 1 H), 4.99 (d, 12 Hz, 1 H), 4.50 (s, 5 H), 4.45 (m, 2 H), 2.34 (m, 2 H), 1.18 (m, 2 H), 0.90 (d, J_{PH} = 7.1 Hz, 6 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −70 °C)[11] δ 169.3 (s).

Chelates 19a and 19b. As described in the representative procedure (see above), treatment of **7** with the potassium salt of 3-butene-2-ol (**13**) afforded a mixture of products containing material tentatively attributed to the unchelated complex **16** [$^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 167.0 (s)] and small amounts of chelates **19a** and **19b** (5:1 ratio, respectively; approximately 20%). The spectral data was tentatively assigned as follows. Isomer **19a**: ^1H NMR (C_6D_6) δ 4.51 (s, 5 H), 3.96 (dt, J = 27, 6 Hz, 1 H), 3.22 (m, 1 H), 2.06 (m, 1 H), 1.33 (d, J_{PH} = 6.3 Hz, 3 H), 1.19 (d, J_{PH} = 7.4 Hz, 3 H), 1.13 (d, J_{HH} = 8.3 Hz, 3 H), 0.70 (m, 1 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 181.6 (s). Isomer **19b**: ^1H NMR (C_6D_6) δ 4.60 (s, 5 H), 4.3 (m, 1 H), 3.43 (m, 1 H), 1.92 (m, 1 H), 1.37 (d, J_{HH} = 6.0 Hz, 3 H), 1.16 (d, J_{PH} = 7.9 Hz, 6 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 177.9 (s). Photolysis of the crude reaction product (with monitoring by ^{31}P NMR) afforded an approximate 1:1 mixture of the two isomers designated as **19a** and **19b**. After the 1:1 mixture was left for 30 days at 25 °C or for 35 h at 55 °C, only isomer **19b** was visible. The photolysis of **19b** regenerated the photostationary 1:1 mixture of **19a** and **19b**.

Chelates 20a and 20b. With use of the procedures similar to those described above, complex **7** was treated with the potassium salt of 1-phenyl-3-butene-2-ol (**14**) affording a mixture of the unchelated form **17** and the chelates designated as **20a** and **20b**: $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 183.3 (s, **20a**), 179.2 (s, **20b**), 168.9 (s, **17**). The kinetic, thermodynamic, and photostationary ratios of **20a**:**20b** were found to be 11:1, 1:>30, and 1:1, respectively.

Chelates 21a and 21b. With use of the procedures similar to those described above, complex **7** was treated with the potassium salt of 4-methyl-3-pentene-1-ol (**15**) affording a mixture of the unchelated form **18** and the chelates designated as **21a** and **21b**: $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C)[11] δ 181.6 (s, **21a**), 177.1 (s, **21b**), 166.8 (s, **18**). The kinetic, thermodynamic, and photostationary ratios of **21a**:**21b** were found to be 16:1, 1:>30, and 1:1, respectively.

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