

Preparation of η^1 -1,3-dienyl, η^1 -1,2-dienyl and η^3 -cyclobutenone complexes via reactions of transition-metal carbonyl containing anions with allenic electrophiles

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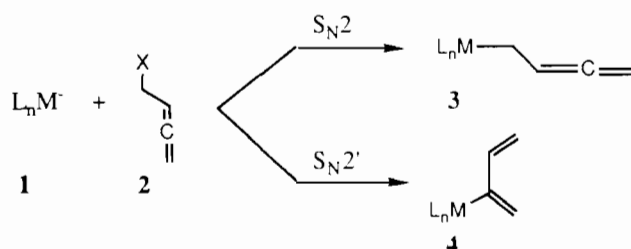
Abstract

The preparation and reaction chemistry of 1,3- and 1,2-diene and related complexes derived from metal carbonyl containing anions and allenic electrophiles are addressed. The preparation of some $\text{CpFe}(\text{CO})_2$ η^1 -diene complexes and their conversion into $\text{CpFe}(\text{CO})$ η^3 -diene complexes is presented followed by reactions of $\text{CpMo}(\text{CO})_3^-$, $\text{CpW}(\text{CO})_3^-$ and $\text{CpMo}(\text{CO})_2\text{PR}_3^-$ anions with allenic electrophiles which produce metal complexed cyclobutenones (via CO and alkene insertions from the initially formed product) and 1,2-diene complexes, respectively. Lastly, the reactions of $\text{PPh}_3(\text{CO})_3\text{Co}^-$ anions with allenic electrophiles are outlined which result in several different coordination geometries depending on the reaction conditions used.

Key words: Diene; Allene; Cycloaddition reaction; Iron complexes; Tungsten complexes; Molybdenum complexes; Carbonyl complexes; Anion complexes

Introduction

Over the last 15 years, several groups (following the pioneering leads of the Rosenblum [1d] and Wojcicki [1c] groups) have been investigating organic applications of cycloaddition reactions between transition-metal complexes containing σ bonds to unsaturated ligands and electrophiles [1]. Most of the time, the transition-metal allyl and propargyl complexes used in these studies have been prepared via reactions of transition-metal anions with the appropriate allylic or propargylic electrophile [1]. As an outgrowth of our interest in the preparation of metal allyls and propargyls for use in 3+2 cycloadditions [1a], we became interested in preparing transition-metal substituted η^1 -1,2-butadienyl (η^1 -allenic) complexes (3) and 2-transition-metal substituted-1,3-butadienes (4) so that their reaction chemistry (particularly cycloaddition chemistry) could be investigated as well.



We envisioned that complexes of the form 3 and 4 could be prepared via reactions of transition metal anions (1) with 1,2-butadienyl electrophiles (2). There are many examples of η^1 -propargyl and η^1 -allyl complex synthesis through reactions analogous to the S_N2 reaction [1] shown above and there are some examples of S_N2' attack by transition-metal anions on propargyl and pentadienyl electrophiles [2]. Recently, we reported how $\text{pyr}(\text{glyoxime})_2\text{cobalt}$ anions react with allenic electrophiles to produce cobalt substituted 1,3-dienes via the S_N2' pathway [3], and Tada and Shimizu reported an alternative preparation of these same 1,3-dienes [4]. This transition-metal substitution enhanced the reactivity of 1,3-dienes as well as the regio and stereoselectivity of subsequent cycloaddition reactions of these dienes [3, 4]. We were interested in preparing metal

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carbonyl substituted dienes, because they should offer reaction possibilities in CO insertion and alkene/allene insertion which are not possible in the pyr(glyoxime)₂cobalt series [3, 4]. In the present paper, we describe reactions of metal carbonyl containing anions with allenic electrophiles which lead to unusual diene coordination geometries.

Experimental

General

All nuclear magnetic resonance (NMR) spectra were obtained using a Varian VXR-200 FT NMR. All absorptions were expressed in parts per million relative to tetramethylsilane. Infrared (IR) spectra were obtained using a Perkin Elmer 1620 FTIR. All elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, GA. High resolution mass spectral analyses were performed by the Midwest Center for Mass Spectrometry, University of Nebraska-Lincoln. Low resolution EI mass spectra were obtained on a Hewlett Packard 5989 GC/MS system. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected.

All solvents were distilled immediately prior to use. All reactions were performed under an inert atmosphere of dry nitrogen unless stated otherwise. Alumina adsorption (80–200 mesh) for column chromatography was purchased from Fisher Scientific and deactivated with an acetone/water mixture (90/10) immediately prior to use. Flash silica gel (40 μ m) was purchased from Universal Scientific Inc.

Cyclopentadienyliron dicarbonyl dimer, cyclopentadienyl molybdenum tricarbonyl dimer, cyclopentadienyl tungsten tricarbonyl dimer and dimethyl- and diethylphenylphosphine were purchased from Strem Chemicals and used as received. Cyclopentadienyl molybdenum tricarbonyl iodide [5] and bis(triphenylphosphine) dicobalt hexacarbonyl [6] were prepared according to literature procedures. 1,2-Butadien-4-ol [7] and 2-methyl-2,3-pentadien-5-ol [7] were prepared according to literature methods.

Preparation of 4-chloro-1,2-butadiene (6)

Pyridine (8.0 ml, 98.9 mmol) in anhydrous diethyl ether (20 ml) was cooled to 0 °C in an ice bath. Thionyl chloride (7.5 ml, 0.103 mol) was then slowly added to the pyridine/diethyl ether solution. 1,2-Butadien-4-ol [7] (5.83 g, 83.2 mmol) in anhydrous diethyl ether (50 ml) was cooled to 0 °C in an ice bath. The pyridine/thionyl chloride mixture was then added at 0 °C and stirred for 10 min. This mixture was then refluxed for

2 h. After cooling to room temperature, water (50 ml) was added. This solution was stirred for 15 min. The two layers were separated and the aqueous layer extracted with diethyl ether (5 \times 25 ml). The combined organic layers were dried over magnesium sulfate and filtered. The ether was distilled off at 1 atm and **6** was isolated by distillation at 1 atm, collecting between 86 and 90 °C (lit. [8] 86–88 °C). Yield 3.38 g, 38.3 mmol (46%). ¹H NMR (CDCl₃): 5.34 (pentet, *J* = 7.3 Hz, 1H), 4.89 (dt, *J* = 7.3, 2.3 Hz, 2H), 4.06 (dt, *J* = 7.3, 2.3 Hz, 2H) [8b].

Preparation of 4-(*p*-toluenesulfonyl)-1,2-butadiene (7)

In an adaptation of a literature procedure [9], 1,2-butadien-4-ol [7] (5.82 g, 83.1 mmol) and *p*-toluenesulfonyl chloride (19.10 g, 0.100 mol) in anhydrous diethyl ether (160 ml) were cooled to –14 °C. Potassium hydroxide (40.78 g, 0.763 mol) was crushed into a powder and added in 5 g portions over 30 min. This mixture was stirred at –14 °C for 45 min. Ice water (240 ml) was added and the aqueous layer was extracted with diethyl ether (4 \times 50 ml). The combined organic layers were dried over magnesium sulfate, the solvent was removed under reduced pressure and the residue was vacuum dried. This residue was triturated with petroleum ether (80 ml) and cooled to –78 °C to cause solidification of **7**. The remaining solid was vacuum dried to yield 4-(*p*-toluenesulfonyl)-1,2-butadiene (**7**) as a waxy, white solid; m.p. 23–24 °C. Yield 13.61 g, 60.8 mmol (73%). ¹H NMR (CDCl₃): 7.76 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.17 (pentet, *J* = 7.2 Hz, 1H), 4.79 (dt, *J* = 7.2, 2.2 Hz, 2H), 4.53 (dt, *J* = 7.2, 2.2 Hz, 2H), 2.42 (s, 3H). IR (CDCl₃): 3068, 3050, 2958, 2927, 1956, 1599, 1495, 1456, 1354, 1180 cm⁻¹. Anal. Calc. for C₁₁H₁₂O₃S: C, 58.9; H, 5.4. Found: C, 58.63; H, 5.40%.

Preparation of 5-(*p*-toluenesulfonyl)-2-methyl-2,3-pentadiene (8)

In an adaptation of a literature procedure [9], 2-methyl-2,3-pentadien-5-ol [7] (3.21 g, 32.8 mmol) was dissolved in diethyl ether (100 ml) and *p*-toluenesulfonyl chloride (6.12 g, 32.1 mmol) was added and the solution was cooled to –14 °C. Finely crushed potassium hydroxide (16.4 g, 292 mmol) was added in 5 g portions. The solution was stirred at –14 °C for 2 h and ice water (50 ml) was added. The aqueous layer was extracted with ether (3 \times 100 ml) and the ether was dried with MgSO₄. After rotary evaporation, the remaining colorless oil was triturated with petroleum ether (2 \times 50 ml) and then cooled to –78 °C whereupon waxy white crystals (which melt below 25 °C) formed which were vacuum dried and stored under nitrogen

to yield **8** (5.58 g, 22.1 mmol, 68%). $^1\text{H NMR}$ (CDCl_3): 7.79 (d, $J=7.5$ Hz, 2H), 7.33 (d, $J=7.5$ Hz, 2H), 5.0 (m, 1H), 4.49 (m, 2H), 2.42 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H). IR (CDCl_3): 3067, 3049, 2986, 2944, 1971, 1794, 1648, 1599, 1495, 1452 cm^{-1} . FAB HRMS: calc. for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{S}$: 252.0820; found: 252.0831.

2-(Cyclopentadienyliron dicarbonyl)-1,3-butadiene (**9**)

A solution of FpNa (**5**) [10] (11.32 mmol) in THF (20 ml) was added via cannula to a cooled (0 °C) solution of 4-chloro-1,2-butadiene (**6**) (0.994 g, 11.2 mmol) in THF (20 ml). The mixture was stirred at room temperature for 1.5 h and then concentrated under reduced pressure. The residue was extracted with pentane (25 × 10 ml). The combined organic extracts were filtered, concentrated under reduced pressure, and vacuum dried to yield **9** as a red–orange oil. Yield 2.03 g, 8.83 mmol (79%). $^1\text{H NMR}$ (C_6D_6): 6.74 (dd, $J=17, 10$ Hz, 1H), 6.15 (s, 1H), 5.48 (s, 1H), 5.09 (dd, $J=17, 2.3$ Hz, 1H), 4.93 (dd, $J=10, 2.3$ Hz, 1H), 4.11 (s, 5H). UV (CH_3CN): 360 (1000). Literature $^1\text{H NMR}$ values (CS_2) [11a, b]*: 6.50 (m, $J=15, 9$ Hz, 1H), 5.78 (m, 1H), 5.20 (m, 1H), 4.92 (m, $J=2.4$ Hz, 1H), 4.76 (s, 5H), 4.76 (m, 1H).

9 was also prepared using 4-(*p*-toluenesulfonyl)-1,2-butadiene (**7**) as the electrophile in the following manner. A solution of FpNa (**5**) [10] (5.66 mmol) in THF (10 ml) was added via cannula under nitrogen to a cooled (0 °C) solution of 4-(*p*-toluenesulfonyl)-1,2-butadiene (**7**) (1.25 g, 5.57 mmol) in THF (10 ml). This mixture was warmed to room temperature and stirred for 90 min. The solvent was removed under reduced pressure and the residue was extracted with pentane (25 × 10 ml). The combined extracts were filtered and the solvent was removed under reduced pressure to give **9**. Yield 1.18 g, 5.12 mmol (92%), identical by spectroscopic comparison with the material isolated above.

3-Cyclopentadienyliron dicarbonyl-2-methyl-2,4-pentadiene (**10**)

A solution of FpNa(**5**) [10] (4.02 mmol) in THF (60 ml) was transferred via cannula to a second flask containing the tosylate **8** (0.955 g, 3.8 mmol) dissolved in THF (10 ml) at 0 °C. After stirring overnight at room temperature, THF was removed under reduced pressure. The brown residue was then extracted with ether until the extracts were colorless. Concentration of the ether extracts yielded a rose colored oil. Chro-

*Two other related iron diene complexes have also been prepared by alternative routes but their reaction chemistry has not been reported [11c, d].

matography of the residue on deactivated alumina (hexane) gave the iron butadiene **10** as a yellow–orange oil. Yield 0.802 g, 3.11 mmol (82%). $^1\text{H NMR}$ (CDCl_3): 6.35 (dd, $J=17.3, 10.3$ Hz, 1H), 4.77 (s, 5H), 4.63 (dd, $J=10.3, 2.7$ Hz, 1H), 4.43 (dd, $J=17.3, 2.7$ Hz, 1H), 1.89 (s, 6H). IR (CDCl_3) 3155.6, 2983.9, 2903.4, 2850.4, 2010.1, 1954.0, 1618.2, 1458.8 cm^{-1} . Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{FeO}_2$: C, 60.50; H, 5.47. Found: C, 60.41; H, 5.91%.

Cyclopentadienyliron carbonyl- η^3 -buta-1,3-diene (**11**)

A solution of **9** (0.653 g, 2.83 mmol) in pentane (250 ml) was irradiated with a 450 W Hanovia UV lamp using a quartz filter for 1.5 h while being cooled in an ice bath. The solvent was removed under reduced pressure, and the residue was chromatographed on deactivated neutral alumina and eluted with pentane. A yellow band was collected and the solvent removed to afford **11** as a yellow oil. Yield 0.158 g, 0.779 mmol (28%). $^1\text{H NMR}$ (C_6D_6): 6.08 (s, 1H), 5.37 (s, 1H), 4.12 (s, 5H), 3.50 (dd, $J=11.9, 7.4$ Hz, 1H); 2.45 (d, $J=7.4$ Hz, 1H), 1.27 (d, $J=11.9$ Hz, 1H). IR (CDCl_3): 2968, 1958, 1706, 1465, 1381 cm^{-1} . HRMS: calc. for $\text{C}_{10}\text{H}_{10}\text{FeO}$: 202.0078; found: 202.0084.

Cyclopentadienyliron carbonyl- η^3 -2-methyl-2,4-penta-2,4-diene (**12**)

The iron butadiene **10** (0.128 g, 0.496 mmol) was dissolved in d_6 -benzene (4 ml). Immediately following the addition of 11 mg of 5% Pd/C, the reaction was photolyzed with a 150 W flood lamp for 6 h [12]. The solution was filtered through Celite, then concentrated to yield the yellow iron η^3 compound **12** as an oil. Yield 0.074 g, 0.32 mmol (65%). $^1\text{H NMR}$ (C_6D_6): 4.12 (s, 5H), 3.43 (dd, $J=12.1, 6.9$ Hz, 1H), 2.45 (d, $J=6.9$ Hz, 1H), 2.10 (s, 3H), 2.01 (s, 3H), 1.15 (d, $J=12.1, 1\text{H}$). IR (benzene): 3077, 2858.2, 1950.5, 1682, 1621.9, 1615.7 cm^{-1} . HRMS: m/z calc. for $\text{C}_{12}\text{H}_{14}\text{OFe}$: 230.0394; found: 230.0396.

Cyclopentadienylmolybdenum dicarbonyl- η^3 -2-methylene-2-cyclobuten-1-one (**17**)

$\text{CpMo}(\text{CO})_3^- \text{Na}^+$ (**13**) (4.46 mmol) was prepared according to a literature procedure [13] in THF (10 ml). The solution of **13** was added via cannula under nitrogen to a cooled (0 °C) solution of 4-(*p*-toluenesulfonyl)-1,2-butadiene (**7**) (1.00 g, 4.48 mmol) in THF (10 ml). This mixture was stirred overnight at room temperature and then concentrated under reduced pressure. The residue was extracted with pentane (25 × 10 ml). The combined extracts were filtered and the solvent removed under reduced pressure to yield **17** as a yellow

solid; m.p. 89-92 °C. Yield 1.11 g, 3.72 mmol (83%). IR (CDCl₃): 3156, 2972, 2921, 1963, 1885, 1749 cm⁻¹. ¹H NMR (CDCl₃): 5.25 (s, 5H), 4.31 (d, *J*=3.5 Hz, 1H), 3.76 (dd, *J*=15.0, 3.5 Hz, 1H), 3.11 (d, *J*=3.5 Hz, 1H), 3.08 (d, *J*=15.0 Hz, 1H), 1.72 (d, *J*=3.5 Hz, 1H). ¹³C NMR (CDCl₃): 236.3, 233.3, 197.5, 94.7 (Cp), 85.9, 77.5, 55.8, 30.6. EI MS (reported for Mo⁹⁸ isotope): 300 (25), 272 (6), 244 (24), 214 (100), 188 (34), 161 (14). **Anal.** Calc. for C₁₂H₁₀MoO₃: C, 48.32; H, 3.36. Found: C, 48.82; H, 3.66%. HRMS: calc. for C₁₂H₁₀Mo⁹⁶O₃: 297.9687; found: 297.9685.

4-Cyclopentadienyltungsten tricarbonyl-1,2-butadiene (21)

A solution of the cyclopentadienyltungsten tricarbonyl anion (20) (4.50 mmol) in THF (10 ml) [13] was added via cannula under nitrogen to a cooled (0 °C) solution of 4-(*p*-toluenesulfonyl)-1,2-butadiene (7) (1.01 g, 4.49 mmol) in THF (10 ml). The mixture was warmed to room temperature and stirred for 22 h. The solvent was then removed under reduced pressure. The residue was extracted with pentane (25 × 10 ml). The combined organic extracts were filtered, concentrated under reduced pressure and vacuum dried. The crude product was chromatographed on deactivated neutral alumina and eluted with 2/1 petroleum ether/diethyl ether to yield 21 as an orange oil. Yield 0.990 g, 2.56 mmol (57%). ¹H NMR (CDCl₃): 5.46 (m, 1H), 5.41 (s, 5H), 4.80 (dt, *J*=5.7, 2.3 Hz, 2H), 2.23 (dt, *J*=8.2, 2.3 Hz, 2H). ¹³C NMR (CDCl₃) (< δ 214): 207.9, 98.9 (Cp), 92.2, 74.9, -14.3. IR (CDCl₃): 3155, 3115, 2021, 1998, 1912, 1702, 931 cm⁻¹. HRMS: calc. for C₁₂H₁₀O₃W: 384.0109; found: 384.0127.

21 was also synthesized from 4-chloro-1,2-butadiene (6) by the following procedure. A solution of 20 (6.00 mmol), prepared as above, in THF (20 ml) was added via cannula under nitrogen to a cooled solution of 5 (0.531 g, 6.00 mmol) in THF (10 ml). This mixture was warmed to room temperature and stirred for 60 min. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether (15 × 10 ml). The combined extracts were filtered and the solvent was removed under reduced pressure to give 21, yield 0.396 g, 1.02 mmol (17%), identical by spectroscopic comparison to 21 isolated above.

Cyclopentadienyl molybdenum dicarbonyl diethylphenylphosphine iodide (25b and 26b)

Cyclopentadienylmolybdenum tricarbonyl iodide (23) [5] (6.66 g, 17.9 mmol) was dissolved in toluene (50 ml). Diethylphenylphosphine (4.398 g, 26.5 mmol) was then added and the solution was refluxed for 6 h under nitrogen. The solution was filtered while hot and most

of the solvent was then removed by rotary evaporation. Hexane was added and the red-orange precipitate was washed with several portions of hexane and then recrystallized from toluene/hexane to yield 25b and 26b as a red-orange solid as a 17:1 mixture of *cis:trans* isomers [14]. Yield 5.72 g, 11.2 mmol (63%); m.p. 110-112 °C dec. ¹H NMR (C₆D₆): 7.32-7.01 (m, 5H), 4.78 (s, 5H, *cis* major isomer Cp), 4.62 (d, *J*=2.6 Hz, Cp of *trans*, minor isomer), 2.68 (apparent septet, *J*=6.7 Hz, 1H), 2.36-2.02 (m, 2H), 1.88 (apparent septet, *J*=6.7 Hz, 1H), 0.88 (apparent ddt, *J*=6.7 Hz, 6H). IR (C₆D₆): 3062, 2979, 2938, 1965, 1887, 1482, 1457, 1436 cm⁻¹. **Anal.** Calc. for C₁₇H₂₀MoO₂PI: C, 40.02; H, 3.95. Found: C, 39.99; H, 4.03%.

Cyclopentadienyl molybdenum dicarbonyl dimethylphenylphosphine iodide (25a and 26a)

Cyclopentadienylmolybdenum tricarbonyl iodide (23) [5] (3.749 g, 10.0 mmol) was dissolved in toluene (50 ml). Dimethylphenylphosphine (2.14 g, 15.0 mmol) was then added and the solution was refluxed for 5 h under nitrogen. The solution was filtered while hot and most of the solvent was then removed by rotary evaporation. Hexane was added and the red-orange precipitate was washed with several portions of hexane and then recrystallized from toluene/hexane to yield 25 and 26a as a red-orange solid as 2.5:1 mixture of *cis:trans* isomers [14]. Yield 2.135 g, 4.4 mmol (44%); m.p. 105-107 °C dec. ¹H NMR (C₆D₆): 7.32-6.95 (m, 5H), 4.62 (s, 5H, *cis* major isomer Cp), 4.53 (d, *J*=1.9 Hz, Cp of *trans*, minor isomer), 1.70 (d, *J*=10.0 Hz, 3H), 1.58 (d, *J*=10.0 Hz, 3H), 1.21 (d, *J*=10.0 Hz, H, methyls of minor isomer). IR (CDCl₃): 3153, 2982, 2916, 1965, 1877, 1472, 1436, 1424 cm⁻¹. **Anal.** Calc. for C₁₅H₁₆MoO₂PI: C, 37.37; H, 3.35. Found: C, 37.48; H, 3.39%.

4-(Cyclopentadienylmolybdenum dicarbonyl diethylphenylphosphine)-1,2-butadiene (27)

A 1% sodium amalgam was prepared in a Schlenk flask under nitrogen by dissolving sodium (0.432 g, 18.8 mmol) in mercury. THF (50 ml, degassed) was added followed by the iodide 25b and 26b (1.915 g, 3.75 mmol) and the solution was stirred overnight. The anion was then transferred by double ended needle into a THF solution (25 ml) of the tosylate 7 (0.840 g, 3.75 mmol) and the solution was allowed to stir overnight at 25 °C. The THF was removed by rotary evaporation and the remaining orange paste was washed with pentane until no more orange color was apparent in the pentane extracts. The pentane extracts were concentrated to 10 ml on the rotary evaporator and the concentrate was placed in the freezer overnight. Orange crystals formed which were isolated by vacuum filtration. Yield 1.281

g, 2.94 mmol (78%); m.p. 62–65 °C. ^1H NMR (C_6D_6): 7.40–7.29 (m, 2H), 7.18–7.00 (m, 3H), 6.17 (m, 1H), 4.98 (m, 2H), 4.52 (d, $J=1.5$ Hz, 5H), 2.52 (m, 2H), 1.81 (apparent pentet, $J=8.0$ Hz, 4H), 0.85 (apparent dt, $J=8.0$ Hz, 6H). ^{13}C NMR (C_6D_6) (< 215 ppm) 208, 139, 138, 131.4, 131.2, 129.5, 100.8, 92.5 (Cp), 74.6, 23.8 (d, $J_{\text{PC}}=29$ Hz), 8.5, 0.4 (d, $J_{\text{PC}}=10$ Hz). IR (C_6D_6): 3058, 2973, 2936, 2880, 1964, 1858, 1461, 1435, 1420 cm^{-1} . Anal. Calc. for $\text{C}_{21}\text{H}_{25}\text{MoO}_2\text{P}$: C, 57.81; H, 5.77. Found: C, 57.62; H, 5.78%.

4-(Cyclopentadienylmolybdenum dicarbonyl dimethylphenylphosphine)-1,2-butadiene (28)

A 1% sodium amalgam was prepared in a Schlenk flask under nitrogen by dissolving sodium (0.116 g, 5.0 mmol) in mercury. THF (50 ml, degassed) was added followed by the iodide **25a** and **26a** (0.528 g, 1.09 mmol) and the solution was stirred overnight. The anion was then transferred by double ended needle into a THF solution (10 ml) of the tosylate **7** (0.241 g, 1.08 mmol) and the solution was allowed to stir overnight at 25 °C. The THF was removed by rotary evaporation and the remaining orange paste was washed with pentane until no more orange color was apparent in the pentane extracts. The pentane extracts were concentrated to 5 ml on the rotary evaporator and the concentrate was placed in the freezer overnight. Orange crystals formed which were isolated by vacuum filtration. Yield 0.238 g, 0.58 mmol (54%); m.p. 60–61 °C. ^1H NMR (C_6D_6): 7.35–7.20 (m, 2H), 7.08–6.95 (m, 3H), 6.09 (m, 1H), 4.92 (m, 2H), 4.48 (d, $J=1.8$ Hz, 5H), 2.48 (m, 2H), 1.36 (d, $J=9.1$ Hz, 6H). IR (C_6D_6): 3057, 2974, 2914, 1925, 1838, 1460, 1445 cm^{-1} . Anal. Calc. for $\text{C}_{19}\text{H}_{21}\text{MoO}_2\text{P}$: C, 55.89; H, 5.18. Found: C, 55.64; H, 5.19%.

5-(Cyclopentadienylmolybdenum dicarbonyl dimethylphenylphosphine)-2-methyl-2,3-pentadiene (29)

The Mo anion was prepared as described above for the preparation of **28** and then transferred by double ended needle into a THF solution (5 ml) of the tosylate **8** (0.269 g, 1.07 mmol) and the solution was allowed to stir overnight at 25 °C. The THF was removed by rotary evaporation and the remaining orange paste was washed with pentane until no more orange color was apparent in the pentane extracts. The pentane extracts were concentrated to 5 ml on the rotary evaporator and the concentrate was placed in the freezer overnight. Orange crystals formed which were isolated by vacuum filtration. Yield 0.272 g, 0.62 mmol (58%); m.p. 68–70 °C. ^1H NMR (C_6D_6): 7.39–7.28 (m, 2H), 7.10–6.99 (m, 3H), 6.00 (m, 1H), 4.50 (m, 2H), 4.46 (d, $J=1.9$ Hz, 5H), 2.52 (dd, $J=8.9, 3.4$ Hz, 2H), 1.82 (s, 3H), 1.81

(s, 3H), 1.39 (d, $J=8.6$ Hz, 6H). IR (C_6D_6): 3059, 2977, 2912, 1930, 1856, 1445, 1435, 1422 cm^{-1} . Anal. Calc. for $\text{C}_{21}\text{H}_{25}\text{MoO}_2\text{P}$: C, 57.81; H, 5.77. Found: C, 56.85; H, 5.71%.

Preparation of ($\eta^3\text{-C}_5\text{H}_5\text{O}$)Co(CO) $_2$ (PPh $_3$) (32)

Hexacarbonylbis(triphenylphosphine) cobalt dimer [6] (1.002 g, 1.82 mmol) was reduced to the cobalt anion **30** [15] in THF (30 ml) using a sodium (0.209 g, 9.08 mmol) amalgam. The cobalt anion was transferred via cannula to a second flask cooled to -78 °C. The unsubstituted tosylate **7** (0.780 g, 3.7 mmol) dissolved in THF (10 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature gradually. Once at room temperature the reaction was stirred for 5 h. The green–orange colored solution was filtered and the solvent was removed under reduced pressure. The residue was washed with ether and the ether extracts were concentrated to an orange paste. The paste was triturated with ether and filtered. The filtrate was concentrated to give **32** as an orange solid. Yield 1.136 g, 2.48 mmol (68%); m.p. 151–152 °C dec. ^1H NMR (CDCl_3): 7.4 (m, 15H); 5.42 (dd, $J=17.1, 10.2$ Hz, 1H); 5.14 (d, $J=17.1$ Hz, 1H); 4.81 (d, $J=10.2$ Hz, 1H); 3.26 (s, 1H), 2.92 (d, $J=4.1$ Hz, 1H). IR (CDCl_3): 3061.8, 2983.1, 2901.3, 2025.1, 1972.9, 1772.4 cm^{-1} . FAB-MS (3-NBA): m/z calc. for $\text{C}_{25}\text{H}_{20}\text{O}_3\text{PCo}$, MW 458; found: 459.1 ($M+H$) (66), 402.0 (14), 374.1 (29.3), 321.0 (24.3), 279.1 (100), 154.1 (86), 107.0 (24.7). Anal. Calc. for $\text{C}_{25}\text{H}_{20}\text{O}_3\text{PCo}$: C, 65.51; H, 4.40. Found: C, 65.04; H, 5.01%.

Triphenylphosphine cobalt dicarbonyl η^3 -2-methyl-2,3-pentadiene, ($\eta^3\text{-C}_6\text{H}_9$)Co(CO) $_2$ (PPh $_3$) (36)

Hexacarbonylbis(triphenylphosphine) cobalt dimer [6] (1.693 g, 2.09 mmol) was suspended in THF (60 ml) and stirred overnight over a sodium (0.402 g, 0.017 mol) amalgam. The pine green anion solution **30** [15] was transferred via cannula to a second flask at -78 °C. The allenyl tosylate **8** (1.49 g, 5.9 mmol) in THF (10 ml) was then added dropwise. The reaction mixture was allowed to warm to room temperature then THF was removed under reduced pressure to yield a green paste. The residue was extracted with ether and the ether removed by rotary evaporation to give an orange oily paste which was triturated with pentane to yield **36** as a yellow solid. Yield 1.129 g, 2.47 mmol (59%); m.p. 121–122 °C. ^1H NMR (CDCl_3): 7.44 (m, 15H), 4.02 (m, 1H), 2.68 (bd, $J=10.8$ Hz, 1H), 2.23 (dd, $J_{\text{HH}}=11.1$ Hz, $J_{\text{PH}}=8.0$ Hz, 1H), 1.97 (s, 3H), 1.88 (s, 3H). IR (CDCl_3): 3060.8, 2978.4, 2908.7, 2850.2, 1994.0, 1938.0 cm^{-1} . LRMS (FAB) for $\text{C}_{26}\text{H}_{24}\text{CoO}_2\text{P}$: found 430.1 (39.3) ($M-\text{CO}$), 402.1 (100) ($M-2\text{CO}$), 279.1

(33.3), 154.1 (86.6). Anal. Calc. for $C_{26}H_{24}CoO_2P$: C, 68.13; H, 5.28. Found: C, 68.06; H, 5.33%.

Alternatively, the cobalt η^3 -butadiene 36 can be prepared from dicobalt octacarbonyl using the following procedure [16]. Dicobalt octacarbonyl (0.35 g, 1.02 mmol) was stirred over a sodium (0.128 g, 5.5 mmol) amalgam under a N_2 atmosphere for 3 h. The silver colored anion was transferred via cannula to a second flame dried flask at 0 °C. PPh_3 (0.539 g, 2.05 mmol) in THF (5 ml) was added dropwise followed immediately by tosylate 8 (0.515 g, 2.04 mmol) in THF (5 ml). The reaction mixture was slowly warmed to room temperature. The reaction was allowed to stir overnight at room temperature. The tan salts were separated from the red liquid by filtration. The salts were washed with ether until the extracts were colorless. The combined extracts were concentrated to a red solid (0.978 g) which was chromatographed on deactivated alumina (30% ether in pentane) to give the Co η^3 compound 36, yield 0.511 g, 1.11 mmol (55%), identical by spectroscopic comparison to the material isolated above.

Preparation of $(\eta^1-C_7H_9O)Co(CO)_3(PPh_3)$ (37)

The octacarbonyl dicobalt dimer (0.56 g, 1.63 mmol) was reduced to the corresponding anion in THF (30 ml) using a sodium (0.25 g, 0.01 mmol) amalgam. After 3 h, the silver colored anion was transferred to another flask at -20 °C via cannula. Next, the flask was purged with CO, and then PPh_3 (0.860 g, 3.3 mmol) in THF (5 ml) was added dropwise followed immediately by the tosylate 8 (0.7644 g, 2.9 mmol) in THF (5 ml) [16]. The reaction mixture was allowed to gradually warm to room temperature and stir overnight. THF was removed under reduced pressure and then the residue was extracted with ether. The orange paste was chromatographed on silica (60:40, ether:hexane) to yield the CO inserted Co butadiene 37 as a yellow solid. Yield 0.287 g, 0.56 mmol (19.3%); m.p. 83-84 °C. 1H NMR (C_6D_6): 7.5 (m, 5H), 6.95 (m, 10H), 6.45 (dd, $J=18.3, 10.7$ Hz, 1H), 5.62 (d, $J=18.3$ Hz, 1H), 5.23 (d, $J=10.7$ Hz, 1H), 1.93 (s, 3H), 1.46 (s, 3H). IR (C_6D_6): 3075.0, 1967.1, 1902.8, 1863.0, 1658.8, 1622.6, 1612.0, 1460.0, 1334.0 cm^{-1} . Anal. Calc. for $C_{28}H_{24}O_4PCo$: C, 65.38; H, 4.70; Found: C, 65.26; H, 4.78%. FAB-MS (3-NBA): m/z calc. for $C_{28}H_{25}O_4PCo$ ($M+H$): 515.0822; (HRFAB) $M+H$ found: 515.0805.

Conversion of 36 to 37

The cobalt η^3 compound 36 (0.212 g, 0.46 mmol) was dissolved in benzene (4 ml) and CO(g) was bubbled through the reaction solution for 6 h. Removal of benzene under reduced pressure yielded the CO inserted Co butadiene 37, yield 0.230 g, 0.45 mmol (97%),

identical by spectroscopic comparison to the material isolated above.

Conversion of the CO inserted butadiene 37 to the η^3 Co compound 36

The CO inserted butadiene 37 (0.054 g, 0.105 mmol) was dissolved in THF (10 ml) and the solution was heated at reflux for 2 h after being degassed. The solvent was removed under vacuum to provide the η^3 Co compound 36 as the only product, yield 0.043 g, 0.094 mmol (89%), identical by spectroscopic comparison to the material isolated above.

6,6-Dicarboethoxy-2-methyl-2,3-hexadiene (39)

Diethyl malonate (0.66 ml, 4.34 mmol) was added at 0 °C to sodium hydride (0.203 g, 60% suspension in mineral oil, 5.07 mmol) in THF (20 ml). After stirring for 15 min at 0 °C, the stabilized anion was added dropwise to the Co η^3 compound 36 (0.203 g, 0.44 mmol) dissolved in THF (10 ml). The solution was then refluxed for 4 h under N_2 . The solvent was removed and the resulting oily paste was chromatographed on silica (10% ether/pentane) to yield 39 as a colorless oil. Yield 0.034 g, 0.14 mmol (32%). 1H NMR ($CDCl_3$): 4.98 (m, 1H), 4.17 (q, $J=7.2$ Hz, 4H), 3.43 (t, $J=7.3$ Hz, 1H), 2.53 (apparent t, $J=7.3$ Hz, 2H), 1.63 (s, 3H), 1.62 (s, 3H), 1.25 (t, $J=7.2$ Hz, 6H). IR ($CDCl_3$): 3155.8, 2984.2, 1793.4, 1727.0, 1472.9, 1382.2 cm^{-1} . FAB-HRMS calc. for $C_{13}H_{20}O_4Na$ ($M+Na$)⁺: 263.1259; found: 263.1263.

X-ray experimental

Crystallographic characterization of 25b, 32 and 36

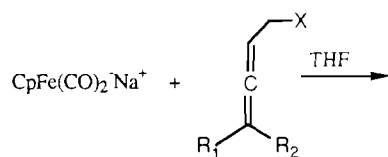
Crystal data are collected in Tables 1-9. Samples of all three crystals were affixed to glass fibers and photographically characterized. For the Mo complex 25b, preliminary photographic characterization revealed 2/ m Laue symmetry and systematic absences in the data indicated either of the space groups $C2/c$ or Cc . The centrosymmetric alternative was initially preferred by the E-statistics and subsequently verified by the results of refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were treated as idealized, updated isotropic contributions. For the Co η^3 - C_6H_9 complex 36, 2/ m Laue symmetry was found and the space group was unambiguously assigned as $P2_1/c$. For the Co η^3 - C_5H_5O complex 32, $\bar{1}$ symmetry was found and the centrosymmetric alternative space group $P\bar{1}$ was assumed correct in the absence of contraindications. For the Co complexes, all non-hydrogen atoms were anisotropically refined and hydrogen atoms were treated as idealized

contributions. All crystals showed negligible intensity variations around the diffraction vector and corrections for absorption were ignored. All computations used SHELXTL (4.2) software (G. Sheldrick, Siemens XRD, Madison, WI).

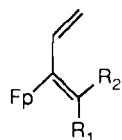
Results and discussion

Preparation and reaction chemistry of $\text{CpFe}(\text{CO})_2(\text{diene})$ complexes

The cyclopentadienyl iron dicarbonyl ($\text{CpFe}(\text{CO})_2$) diene complex (**9**) was prepared by three different routes by Giering and co-workers during the 1970s [11a, b]. Unfortunately, none of these routes resulted in the preparation of **9** cleanly and the highest overall yield was 30%. Diels–Alder chemistry of **9** was reported in 1985 [17], however, this chemistry was somewhat limited by the thermal instability (dec. at 110 °C) of **9**. We thought diene complexes like **9** could be prepared cleanly and in high yield by reaction of the $\text{CpFe}(\text{CO})_2^-$ anion (**5**) [10] with allenic electrophiles. In order to test this idea, we first prepared known allenic alcohols [7], 1,2-butadien-4-ol and 2-methyl-2,3-pentadien-5-ol and converted them into the corresponding chlorides or tosylates (**6–8**). Both unsubstituted allenic electrophiles **6** and **7** as well as the more sterically encumbered **8** reacted cleanly with the anion **5** in a $\text{S}_{\text{N}}2'$ fashion to produce the 1,3-diene complexes **9** and **10** in excellent yield albeit as somewhat air and thermally sensitive yellow–orange oils. One way to extend the thermal stability as well as reaction chemistry of these diene complexes would be to prepare chiral $\text{CpFe}(\text{CO})(\text{PR}_3)$ diene complexes from **9** and **10** which like the chiral iron acyls ($\text{CpFe}(\text{CO})(\text{PR}_3)(\text{C}(\text{O})\text{R})$) [18] should have high thermal stability and interesting reaction chemistry. In principle, $\text{CpFe}(\text{CO})(\text{PR}_3)$ diene complexes could be synthesized by a low temperature photolysis of **9** or **10** in the presence of PR_3 [12, 19]. We have tried

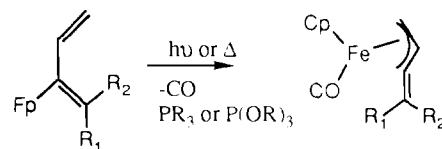


- 5** **6** $\text{R}_1=\text{R}_2=\text{H}$, $\text{X}=\text{Cl}$
7 $\text{R}_1=\text{R}_2=\text{H}$, $\text{X}=\text{OTs}$
8 $\text{R}_1=\text{R}_2=\text{Me}$, $\text{X}=\text{OTs}$



- 9** $\text{R}_1=\text{R}_2=\text{H}$, 92% from **7**, 79% from **6**
10 $\text{R}_1=\text{R}_2=\text{Me}$, 82%

this route as well as thermal conditions in attempts to do phosphine/phosphite substitution reactions on **9** and **10** but we have found that intramolecular alkene complexation rather than intermolecular phosphine/phosphite coordination produced the only isolated products **11** and **12**.



9 or **10**

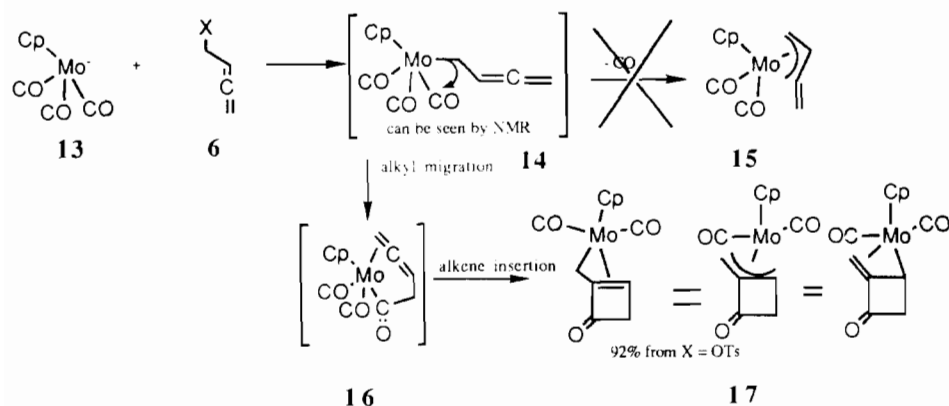
11 $\text{R}_1=\text{R}_2=\text{H}$, 28%
12 $\text{R}_1=\text{R}_2=\text{Me}$, 65%

The η^3 -butadiene complexes produced (**11** and **12**) are interesting coordination geometries of which there are relatively few known examples [20]. The η^3 -butadiene structures are implicated by the appearance of only one metal carbonyl absorption in the IR for **11** (1958 cm^{-1}) and **12** (1951 cm^{-1}) as well as by their ^1H NMR spectra which show the three protons in the π -allyl portion at chemical shifts (1–3.5 ppm) much upfield from the corresponding protons in **9** or **10** and in a range typical of other η^3 -butadiene complexes [20].

Reactions of $\text{CpMo}(\text{CO})_2\text{L}$ anions ($\text{L}=\text{CO}$, PR_3) and the $\text{CpW}(\text{CO})_3$ anion with allenic electrophiles. Synthesis of complexed cyclobutenones and 4-transition-metal substituted 1,2-dienes

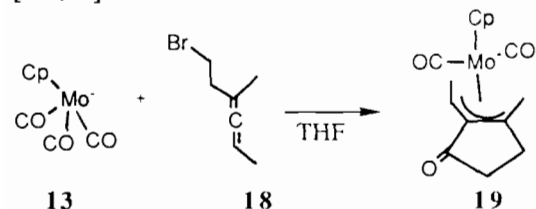
Recall from the 'Introduction' that one of the reactions we hoped to discover initially was a transition-metal anion $\text{S}_{\text{N}}2$ attack on allenic electrophiles. The 'softer' $\text{CpMo}(\text{CO})_3$ [13] and $\text{CpW}(\text{CO})_3$ [13] anions were used for reactions with **5** and **6** because a general trend of 'soft' nucleophiles reacting with α -allenic electrophiles in $\text{S}_{\text{N}}2$ reactions and 'hard' nucleophiles reacting with them in $\text{S}_{\text{N}}2'$ reactions has been observed previously [21]. Reaction of the $\text{CpMo}(\text{CO})_3$ anion (**13**) [13] with tosylate **7** initially produces **14** which can be observed by ^1H NMR (C_6D_6): 5.60 (m, 1H), 4.83 (dt, $J=6.7, 2.6$ Hz, 2H), 4.52 (s, 5H), 2.22 (dt, $J=7.4, 2.6$ Hz, 2H). However, **14** rapidly undergoes further reaction at 25 °C to produce an air stable yellow complex. Initially we thought CO loss from **14** to produce a η^3 -butadiene complex (**15**) might be a facile process but the isolated complex did not have spectroscopic data consistent with that reported for other η^3 -butadiene complexes [20] or **11** and **12** reported above.

We now believe based on mass spectral, ^1H and ^{13}C NMR, and IR data that the product of this reaction is a complexed cyclobutenone (**17**) (see Scheme 1). The ^1H NMR chemical shifts are consistent with those expected for a molybdenum π -allyl of this type [22]. The IR contains a CO absorption at 1749 cm^{-1} in

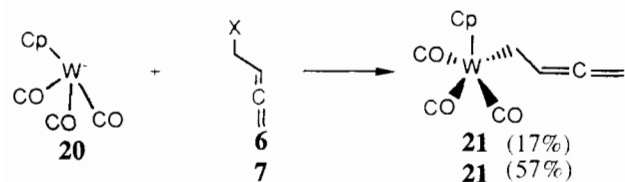


Scheme 1.

addition to the metal carbonyls. This absorption is at too high a wavenumber to be a metal acyl but is consistent with a cyclobutanone carbonyl [23]. Additionally, the ^{13}C spectrum contains a carbonyl at 198 ppm in addition to the metal carbonyls and this would be in the range expected for an α,β -unsaturated ketone carbonyl [24]. We could account for the formation of **17** via a CO insertion to form **16** followed by an alkene insertion to form **17**. There is ample precedent for a σ -acyl π -alkene complex like **16** in related cyclopentadienyl molybdenum, tungsten and iron chemistry [22, 25]. Additionally, Roustan and co-workers showed in the early 1970s that the homologues with an additional methylene underwent both CO insertion and alkene insertion to provide complexed cyclopentenones (**19**) [22c, d].

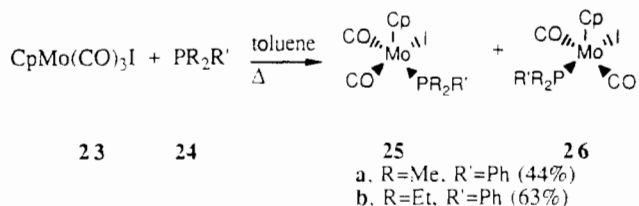


In order to slow down or stop the CO insertion which ultimately led to cyclobutenone production, we used the softer CpW(CO)_3 (**20**) [13] and $\text{CpMo(CO)}_2(\text{L})$ (**22**) anions [26]. The reaction of tungsten anion (**20**) with allenyl chloride **6** or tosylate **7** does indeed produce the desired 4-transition-metal substituted 1,2-butadiene complex (**21**) as a somewhat thermally unstable orange oil. The η^1 bonding mode for the allenic portion was



implicated by the observation of three metal carbonyl absorptions, typical allene proton absorptions in the

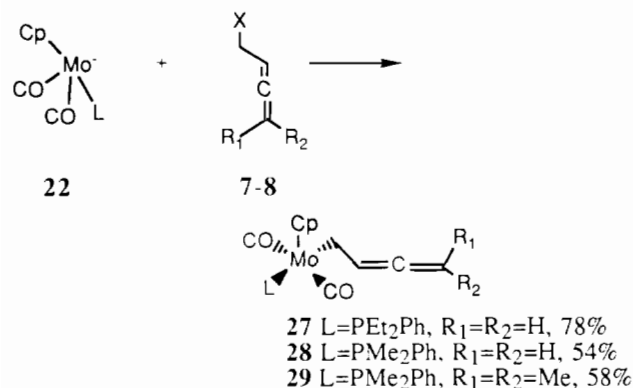
4.8–5.5 ppm range and an upfield shift for the methylene protons compared to their absorbance in the tosylate **7** or chloride **6**. The cyclopentadienyl molybdenum dicarbonyl triphenylphosphine anion (**22**, $\text{L}=\text{PPh}_3$) (generated by Na(Hg) reduction of the known iodide) [14] was then tried in a reaction with **7**. Unfortunately, an inseparable mixture (2:1) of what appeared by ^1H NMR to be the desired η^1 compound (C_6D_6 : 7.82–6.98 (m, 15H), 6.18 (m, 1H), 4.95 (m, 2H), 4.61 (s, 5H), 2.52 (d, $J=7.2$ Hz, 2H)) and an η^3 -butadiene which may or may not also contain phosphine was isolated. The cyclopentadienyl molybdenum dicarbonyl dialkylphenylphosphine anions were then investigated with the expectation that CO loss and CO insertion should be slowed even further. Iodides **25** and **26** were prepared by a procedure analogous to that reported by Manning [14] and **25a** and **26a** were formed as a 2.5:1 mixture of *cis:trans* isomers whereas **25a** and **26b** were formed almost exclusively as the *cis* isomer (17:1, *cis:trans*). The minor *trans* isomer was identified in each case by a characteristic J_{PH} of 2 Hz seen in the cyclopentadienyl



resonance. Complex **25b** was characterized by X-ray diffraction which confirmed the *cis* geometry and the crystal and data acquisition parameters and atomic coordinates are located in Tables 1 and 2. The molecular structure of **25b** is shown in Fig. 1. The *cis* I–Mo–P, I–Mo–C(1), C(1)–Mo–C(2) and P–Mo–C(2) angles of 79.6, 77.3, 76.2 and 77.0° and *trans* P–Mo–C(1) and I–Mo–C(2) angles of 121.6 and 127.4° are similar to those found in related piano stool CpMo complexes

[14, 27]. Bond lengths and angles for **25b** are summarized in Tables 3 and 4.

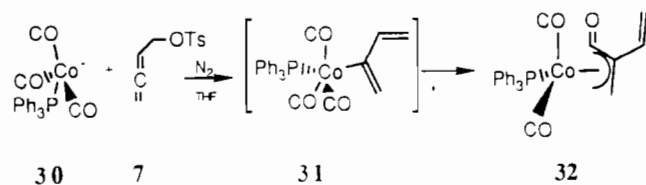
Iodides **25** and **26** were easily reduced to the anions **22** using Na(Hg) [26] and each anion reacted with allenic electrophiles (**7**, **8**) to produce η^1 -allenic complexes (**27–29**) as air-stable orange solids in good yield.



Only one isomer was isolated in all three cases and we are confident that all have the *trans* piano stool arrangement shown since we see the characteristic 1–2 Hz splitting of the Cp resonance in the ¹H NMR which has been observed in many related complexes when the phosphorus is between the 2 COs and *trans* to the R group [14, 22e]. This *trans* orientation is presumably favored here due to the bulk of the allene and phosphine.

Reactions of the cobalt (CO)₃(PPh₃) anion (**30**) with allenic electrophiles

The reactions of the (PPh₃)(CO)₃Co anion (**30**) with allenic electrophiles as a route to new diene complexes (possibly CO inserted) looked promising since the corresponding alkyl and acyl complexes are reportedly quite stable [15, 16, 28]. The cobalt (CO)₃(PPh₃) anion (**30**) (generated by Na(Hg) reduction [15] of the known dimer [6]) reacted with the allenic tosylate **7** to produce the η^3 - α,β -unsaturated carbonyl complex (**32**) as an air-stable orange solid in 68% yield. The position where the CO has been inserted implies that this anion (**30**) attacked **7** in an S_N2' fashion to produce **31** which subsequently underwent CO insertion and alkene coordination. Heck and Breslow reported a similar



α,β -unsaturated complex from the reaction of the anion **30** with acryloyl chloride [29]. The protons on carbon No. 1 of the diene are significantly shielded as expected by comparison to other related cobalt η^3 -allyl complexes

TABLE 1. Crystallographic data for C₁₇H₂₀IMoO₂P (**25b**)

Crystal parameters	
Formula	C ₁₇ H ₂₀ IMoO ₂ P
Formula weight	510.1
Crystal system	monoclinic
Space group	C2/c
a (Å)	34.807(9)
b (Å)	7.589(2)
c (Å)	15.596(5)
α (°)	
β (°)	113.38(2)
γ (°)	
V (Å ³)	3781.4(17)
Z	8
Crystal dimensions (mm)	0.20 × 0.35 × 0.35
Crystal color	red
D _{calc} (g cm ⁻³)	1.792
μ (Mo K α) (cm ⁻¹)	23.80
Temperature (K)	296
T(max.)/T(min.)	893/802
Data collection	
Diffractometer	Siemens P4
Monochromator	graphite
Radiation, λ (Å)	Mo K α , 0.71073
2 θ Scan range (°)	4–55
Data collected (h, k, l)	±44, +9, +20
Reflections collected	3990
Independent reflections	3850
Independent observed reflections	2392 (n = 5)
F _o ≥ n σ (F _o)	
Standard reflections	3 std/197 rflns
Variation in standards (%)	< 1
Refinement	
R(F) (%)	3.96
R _w (F) (%)	4.81
Δ/σ (max.)	0.02
Δ/ρ (e Å ⁻³)	0.72
N _o /N _v	12.0
GOF	1.00

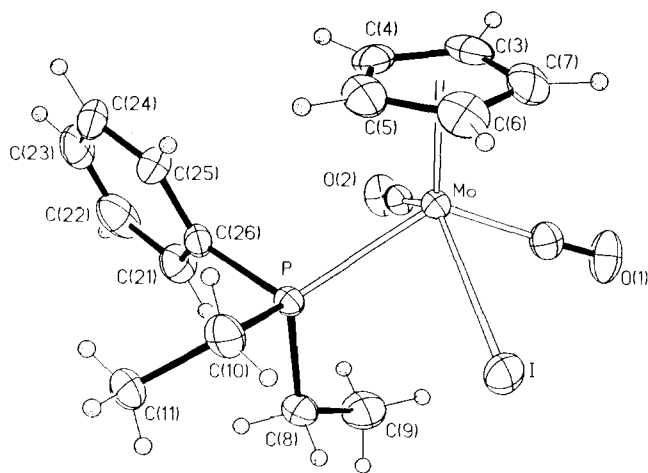
[30]. The proton *syn* to cobalt on carbon No. 1 is not coupled to the *anti* proton but it is coupled to phosphorus [30]. The protons on the non-complexed double bond exhibit the expected monosubstituted alkene absorptions. The IR shows two metal carbonyls in addition to another carbonyl absorption at 1772 cm⁻¹. Confirmation of the proposed structure of **32** was obtained via X-ray diffraction. The crystal and data acquisition parameters for **32** are summarized in Table 5. The atomic coordinates are presented in Table 6 and selected bond angles and distances are presented in Table 7. Figure 2 provides a view of the molecular structure of **32**.

Several comments on the structure are in order. The non-complexed double bond is *syn* to the C=O rather than the CH₂ of the η^3 -allyl ligand. The Co–C(3) bond distance (1.911(3)) is considerably shorter than the

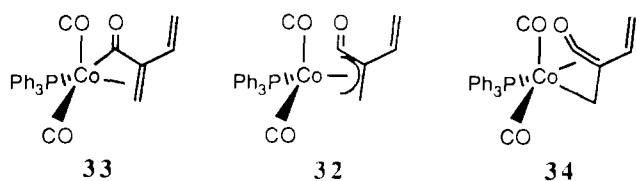
TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **25b**

	x	y	z	U_{eq}^a
Mo	1670(1)	2477(1)	419(1)	30(1)
I	1792(1)	-782(1)	-367(1)	60(1)
P	1087(1)	674(2)	528(1)	33(1)
O(1)	1667(2)	3721(9)	-1478(4)	74(3)
O(2)	920(2)	5036(7)	-380(4)	53(2)
C(1)	1667(2)	3224(11)	-804(6)	47(3)
C(2)	1195(2)	4043(9)	-77(5)	39(3)
C(3)	2091(3)	4681(12)	1261(6)	60(4)
C(4)	1893(2)	3941(12)	1798(5)	54(3)
C(5)	2056(3)	2241(14)	2063(5)	64(4)
C(6)	2340(2)	1897(13)	1639(6)	63(4)
C(7)	2361(2)	3403(13)	1145(6)	62(4)
C(8)	693(2)	-214(11)	-559(5)	51(3)
C(9)	574(3)	936(14)	-1419(6)	74(4)
C(10)	1242(3)	-1318(10)	1267(6)	55(4)
C(11)	889(3)	-2292(11)	1386(6)	64(4)
C(21)	393(2)	2534(11)	592(6)	56(3)
C(22)	194(3)	3532(13)	1042(10)	83(6)
C(23)	396(4)	3910(14)	1972(10)	89(7)
C(24)	799(4)	3252(13)	2474(7)	77(5)
C(25)	993(3)	2281(12)	2039(5)	59(4)
C(26)	795(2)	1891(10)	1090(5)	41(3)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fig. 1. Molecular structure of **25b**.

Co-C(5) bond (2.112(4)) consistent with a tautomer of structure **33** however, the short C(3)-O(3) bond (1.185(3)) and the high wavenumber acyl CO absorption (1772 cm^{-1}) (cobalt $(\text{PR}_3)(\text{CO})_3$ acyls typically absorb at $1650\text{--}1730\text{ cm}^{-1}$ [28]) indicate a significant amount of ketene character (**34**).

TABLE 3. Bond lengths (\AA) for **25b**

Mo-I	2.866(1)	Mo-P	2.510(2)
Mo-C(1)	1.986(10)	Mo-C(2)	1.931(7)
Mo-C(3)	2.267(8)	Mo-C(4)	2.267(8)
Mo-C(5)	2.381(7)	Mo-C(6)	2.393(7)
Mo-C(7)	2.323(8)	P-C(8)	1.833(7)
P-C(10)	1.847(8)	P-C(26)	1.832(9)
O(1)-C(1)	1.129(12)	O(2)-C(2)	1.162(9)
C(3)-C(4)	1.396(14)	C(3)-C(7)	1.412(14)
C(4)-C(5)	1.403(13)	C(5)-C(6)	1.415(14)
C(6)-C(7)	1.397(14)	C(8)-C(9)	1.514(12)
C(10)-C(11)	1.506(14)	C(21)-C(22)	1.390(17)
C(21)-C(26)	1.393(10)	C(22)-C(23)	1.367(18)
C(23)-C(24)	1.399(16)	C(24)-C(25)	1.351(17)
C(25)-C(26)	1.394(10)		

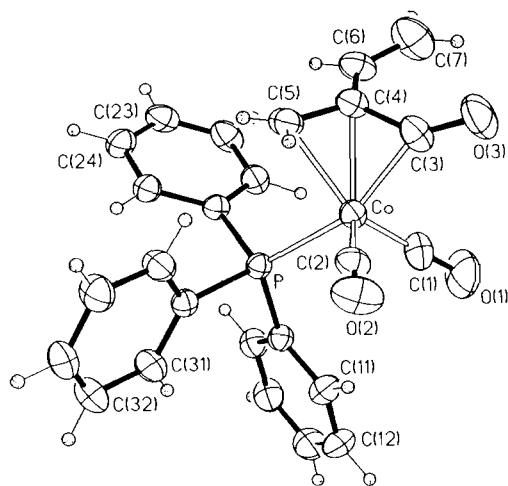
TABLE 4. Bond angles ($^\circ$) for **25b**

I-Mo-P	79.6(1)	I-Mo-C(1)	77.3(2)
P-Mo-C(1)	121.6(2)	I-Mo-C(2)	127.4(2)
P-Mo-C(2)	77.0(2)	C(1)-Mo-C(2)	76.2(3)
I-Mo-C(3)	135.5(3)	P-Mo-C(3)	135.8(3)
C(1)-Mo-C(3)	95.9(3)	C(2)-Mo-C(3)	91.8(3)
I-Mo-C(4)	140.9(2)	P-Mo-C(4)	100.6(2)
C(1)-Mo-C(4)	129.9(3)	C(2)-Mo-C(4)	89.7(3)
C(3)-Mo-C(4)	35.9(4)	I-Mo-C(5)	106.3(3)
P-Mo-C(5)	90.7(2)	C(1)-Mo-C(5)	147.3(3)
C(2)-Mo-C(5)	120.3(3)	C(3)-Mo-C(5)	58.2(3)
C(4)-Mo-C(5)	35.0(3)	I-Mo-C(6)	85.3(2)
P-Mo-C(6)	113.9(2)	C(1)-Mo-C(6)	116.7(3)
C(2)-Mo-C(6)	147.2(3)	C(3)-Mo-C(6)	58.3(3)
C(4)-Mo-C(6)	58.5(3)	C(5)-Mo-C(6)	34.5(3)
I-Mo-C(7)	99.7(3)	P-Mo-C(7)	147.2(2)
C(1)-Mo-C(7)	89.6(3)	C(2)-Mo-C(7)	124.4(3)
C(3)-Mo-C(7)	35.8(4)	C(4)-Mo-C(7)	59.4(3)
C(5)-Mo-C(7)	57.8(3)	C(6)-Mo-C(7)	34.4(3)
Mo-P-C(8)	117.8(3)	Mo-P-C(10)	116.4(3)
C(8)-P-C(10)	101.7(4)	Mo-P-C(26)	112.0(2)
C(8)-P-C(26)	105.9(4)	C(10)-P-C(26)	101.2(4)
Mo-C(1)-O(1)	177.0(7)	Mo-C(2)-O(2)	177.3(7)
Mo-C(3)-C(4)	72.1(5)	Mo-C(3)-C(7)	74.3(5)
C(4)-C(3)-C(7)	108.2(8)	Mo-C(4)-C(3)	72.1(5)
Mo-C(4)-C(5)	77.0(5)	C(3)-C(4)-C(5)	108.0(8)
Mo-C(5)-C(4)	68.0(4)	Mo-C(5)-C(6)	73.2(4)
C(4)-C(5)-C(6)	107.9(9)	Mo-C(6)-C(5)	72.3(4)
Mo-C(6)-C(7)	70.1(4)	C(5)-C(6)-C(7)	107.9(9)
Mo-C(7)-C(3)	69.9(4)	Mo-C(7)-C(6)	75.5(5)
C(3)-C(7)-C(6)	107.9(9)	P-C(8)-C(9)	116.7(6)
P-C(10)-C(11)	115.4(5)	C(22)-C(21)-C(26)	120.1(8)
C(21)-C(22)-C(23)	120.1(9)	C(22)-C(23)-C(24)	119.8(13)
C(23)-C(24)-C(25)	120.3(10)	C(24)-C(25)-C(26)	120.9(8)
P-C(26)-C(21)	122.4(6)	P-C(26)-C(25)	118.8(6)
C(21)-C(26)-C(25)	118.7(8)		

Reaction of the cobalt anion **30** with the more highly substituted allenic electrophile **8** followed a slightly different pathway. In the absence of CO, the cobalt anion **30** (generated by reduction of the known dimer [6] or generated *in situ* from the $\text{Co}(\text{CO})_4$ anion and PPh_3 [16]) reacted with **8** to produce the η^3 -pentadiene complex **36** in 59 and 55% yields, respectively, as an

TABLE 5. Crystallographic data for (η^3 -C₆H₉)Co(CO)₂(PPh₃) (**36**) and (η^3 -C₃H₅O)Co(CO)₂(PPh₃) (**32**)

	36	32
<i>Crystal parameters</i>		
Formula	C ₂₆ H ₂₄ CoO ₂ P	C ₂₅ H ₂₀ CoO ₃ P
Formula weight	458.4	459.3
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
<i>a</i> (Å)	16.791(6)	9.332(5)
<i>b</i> (Å)	9.048(2)	10.612(6)
<i>c</i> (Å)	16.169(6)	12.094(6)
α (°)		110.46(4)
β (°)	107.14(3)	100.97(4)
γ (°)		90.51(5)
<i>V</i> (Å ³)	2347.5(12)	1097.9(11)
<i>Z</i>	4	2
Crystal dimensions (mm)	0.22 × 0.32 × 0.54	0.40 × 0.40 × 0.44
Crystal color	yellow	orange
<i>D</i> _{calc} (g cm ⁻³)	1.297	1.389
μ (Mo K α) (cm ⁻¹)	8.18	8.78
Temperature (K)	296	296
<i>Data collection</i>		
Diffractometer		Siemens P4
Monochromator		graphite
Radiation, λ (Å)		Mo K α , 0.71073
2 θ Scan range (°)	4–50	4–50
Data collected (<i>h, k, l</i>)	±19, +10, +19	±11, +12, +14
Reflections collected	4295	4099
Independent reflections	4132	3900
Independent observed reflections $F_o \geq n\sigma(F_o)$ (<i>n</i> = 5)	2566	3033
Standard reflections	3 std/197 rflns	3 std/197 rflns
Variation in standards (%)	<1	<1
<i>Refinement</i>		
<i>R</i> (<i>F</i>) (%)	3.98	3.07
<i>R</i> _w (<i>F</i>) (%)	4.80	4.28
Δ/σ (max.)	0.001	0.001
Δ/ρ (e Å ⁻³)	0.35	0.30
<i>N</i> _O / <i>N</i> _V	9.5	11.2
<i>GOF</i>	0.98	1.04

Fig. 2. Molecular structure of the cobalt complex **32**.TABLE 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for **32**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Co	2825.5(3)	7540.4(3)	4875.6(3)	41(1)
P	1820.8(6)	6582.2(6)	2886.3(6)	36(1)
O(1)	3039(4)	10318(2)	5014(3)	109(2)
O(2)	5788(2)	6679(3)	4974(2)	79(1)
O(3)	3406(3)	8915(3)	7515(2)	90(1)
C(1)	2917(4)	9219(3)	4933(3)	63(1)
C(2)	4616(3)	6982(3)	4902(2)	50(1)
C(3)	2812(3)	8142(3)	6558(3)	57(1)
C(4)	1496(3)	7285(3)	5971(2)	49(1)
C(5)	1748(3)	6002(3)	5222(3)	54(1)
C(6)	50(3)	7804(3)	6066(3)	61(1)
C(7)	−201(4)	8861(4)	6915(4)	92(2)
C(11)	3259(3)	8310(3)	2103(3)	55(1)
C(12)	3406(4)	9038(3)	1377(3)	70(2)
C(13)	2240(4)	9084(3)	512(3)	73(2)
C(14)	937(4)	8403(3)	356(3)	61(1)
C(15)	775(3)	7660(3)	1070(2)	50(1)
C(16)	1930(3)	7601(2)	1954(2)	41(1)
C(21)	−1044(3)	7117(3)	3017(3)	51(1)
C(22)	−2525(3)	6802(3)	2877(3)	61(1)
C(23)	−3097(3)	5485(3)	2340(3)	60(1)
C(24)	−2215(3)	4478(3)	1919(3)	56(1)
C(25)	−733(3)	4787(3)	2047(2)	47(1)
C(26)	−137(3)	6114(3)	2601(2)	39(1)
C(31)	2806(3)	4732(3)	913(2)	50(1)
C(32)	3414(3)	3558(3)	345(3)	61(1)
C(33)	3771(3)	2651(3)	909(3)	59(1)
C(34)	3536(4)	2920(3)	2047(3)	62(1)
C(35)	2959(3)	4104(3)	2632(3)	52(1)
C(36)	2578(3)	5026(2)	2068(2)	38(1)

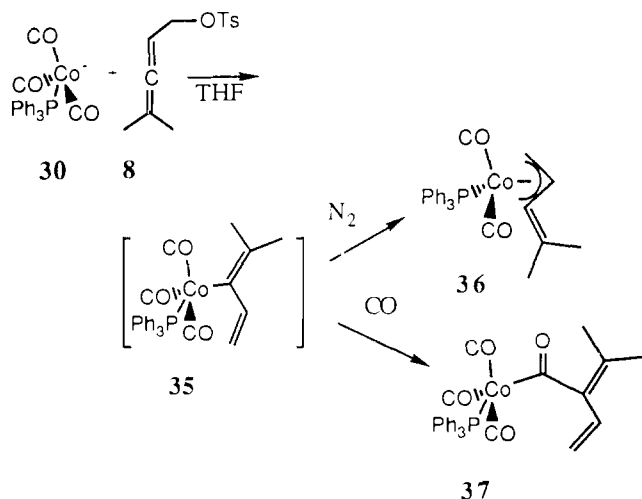
^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

TABLE 7. Selected bond angles and distances for **32**

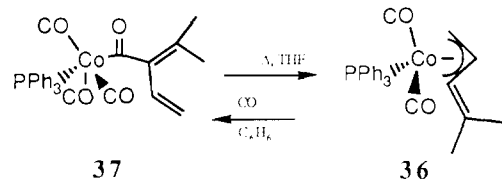
Bond angles (°)			
P–Co–C(1)	96.8(1)	O(3)–C(3)–C(4)	141.3(3)
P–Co–C(2)	100.7(1)	C(3)–C(4)–C(5)	112.8(3)
P–Co–C(3)	154.8(1)	C(3)–C(4)–C(6)	121.2(3)
P–Co–C(4)	113.4(1)	C(5)–C(4)–C(6)	125.6(2)
P–Co–C(5)	90.4(1)	Co–C(1)–O(1)	176.5(3)
C(1)–Co–C(2)	108.0(1)	Co–C(2)–O(2)	176.4(2)
Bond distances (Å)			
Co–P	2.262(2)	C(1)–O(1)	1.139(4)
Co–C(1)	1.759(4)	C(2)–O(2)	1.139(4)
Co–C(2)	1.776(3)	C(3)–O(3)	1.185(3)
Co–C(3)	1.911(3)	C(3)–C(4)	1.427(4)
Co–C(4)	2.059(4)	C(4)–C(5)	1.398(4)
Co–C(5)	2.112(4)	C(4)–C(6)	1.472(4)

air-stable yellow solid. Under 1 atm of CO, **30** reacted with **8** to yield the thermally sensitive diene **37** (19%). Both **36** and **37** presumably arise via the intermediacy of **35**. In the absence of CO, the steric hindrance of the methyls apparently prohibits migratory insertion for **35** similar to what we observed in the production of

32, so CO loss and alkene coordination yield **36**. CO insertion from **35** yields **37**. Complexes **36** and **37** are



easily interconverted. Simply heating **37** provided **36** in high yield (89%) whereas bubbling CO through a solution of **36** cleanly generated **37** (97%).



IR and ^1H NMR spectroscopic data support the structure **36**. Two metal carbonyls and no acyl in the IR and the expected shielded allyl protons seen in other cobalt η^3 -allyl complexes were observed with the allyl proton *syn* to the cobalt also showing coupling to phosphorus [30]. Likewise, **37** exhibited three metal carbonyl bands in addition to a metal acyl absorption at 1659 cm^{-1} [28]. The ^1H NMR of **37** showed the expected non-complexed alkene and methyl absorptions. The structure of complex **36** was confirmed by X-ray diffraction. Crystal and data acquisition parameters and atomic coordinates are found in Tables 5 and 8. Selected bond distances and angles for **36** are presented in Table 9. The molecular structure of **36** is presented in Fig. 3.

As expected, the bulk of the η^3 -butadiene ligand is away from the PPh_3 ligand. The C(5)–C(6) bond ($1.305(6)\text{ \AA}$) is significantly shorter than a typical C=C bond ($1.337(6)\text{ \AA}$) [31] indicating there is still significant sp character at C(5). The Co–C(5) bond length ($1.986(4)\text{ \AA}$) is significantly shorter than the Co–C(3) bond ($2.119(4)\text{ \AA}$) which is also consistent with significant sp character at C(5) as is the C(4)–C(5)–C(6) bond angle of $146.3(4)^\circ$.

TABLE 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **36**

	x	y	z	U_{eq}^a
Co	3049.1(3)	1706.9(6)	9893.3(3)	36(1)
P	2312.8(6)	-129(1)	9154.6(6)	32(1)
O(1)	1740(3)	3864(4)	9280(3)	111(2)
O(2)	4405(3)	2319(5)	9164(3)	106(2)
C(1)	2254(3)	2988(5)	9519(3)	62(2)
C(2)	3875(3)	2034(5)	9438(3)	56(2)
C(3)	3643(3)	264(5)	10922(3)	55(2)
C(4)	3247(3)	1449(5)	11176(3)	47(2)
C(5)	3489(3)	2861(5)	10977(3)	41(2)
C(6)	3785(3)	4151(5)	11277(3)	49(2)
C(7)	3872(3)	5412(5)	10717(4)	74(2)
C(8)	4074(4)	4429(7)	12239(3)	90(3)
C(11)	2397(3)	-2560(6)	8107(3)	71(2)
C(12)	2795(3)	-3677(7)	7810(4)	89(3)
C(13)	3648(3)	-3825(6)	8131(3)	73(2)
C(14)	4092(3)	-2877(5)	8733(3)	57(2)
C(15)	3696(2)	-1769(5)	9051(3)	45(1)
C(16)	2842(2)	-1593(4)	8738(2)	37(1)
C(21)	689(3)	-79(5)	7958(3)	56(2)
C(22)	113(3)	380(7)	7188(4)	80(2)
C(23)	357(4)	1285(7)	6630(4)	87(3)
C(24)	1161(4)	1762(6)	6827(3)	82(2)
C(25)	1727(3)	1335(5)	7589(3)	60(2)
C(26)	1503(2)	413(4)	8170(3)	38(1)
C(31)	1823(3)	-2602(5)	9964(3)	53(2)
C(32)	1426(3)	-3248(6)	10507(3)	73(2)
C(33)	945(3)	-2423(7)	10881(3)	74(2)
C(34)	858(3)	-936(7)	10722(3)	70(2)
C(35)	1260(3)	-284(5)	10192(3)	56(2)
C(36)	1742(2)	-1105(4)	9796(2)	37(1)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 9. Selected bond distances and angles for **36**

Bond distances (\AA)			
Co–P	2.201(1)	C(1)–O(1)	1.150(6)
Co–C(1)	1.737(5)	C(2)–O(2)	1.135(7)
Co–C(2)	1.776(6)	C(3)–C(4)	1.387(7)
Co–C(3)	2.119(4)	C(4)–C(5)	1.406(6)
Co–C(4)	2.015(4)	C(5)–C(6)	1.305(6)
Co–C(5)	1.986(4)		
Bond angles ($^\circ$)			
P–Co–C(1)	93.6(1)	C(3)–C(4)–C(5)	116.0(4)
P–Co–C(2)	106.4(2)	C(4)–C(5)–C(6)	146.3(4)
C(1)–Co–C(2)	111.0(2)	C(5)–C(6)–C(7)	123.6(4)
P–Co–C(4)	111.5(1)	C(5)–C(6)–C(8)	120.3(4)
C(1)–Co–C(4)	108.2(2)	Co–C(1)–O(1)	178.3(4)
C(2)–Co–C(4)	122.3(2)	Co–C(2)–O(2)	176.3(5)

Complex **36** is the only one of the cobalt complexes with which we have attempted much reaction chemistry to date. **36** was surprisingly inert to Ph_2CuLi and decomposed to give no isolable organic or organometallic products when treated with Grignard reagents. **36** did react with the stabilized diethyl malonate anion **38** to

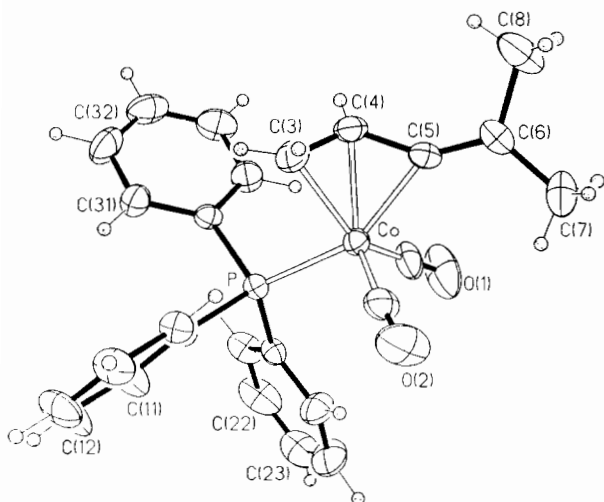
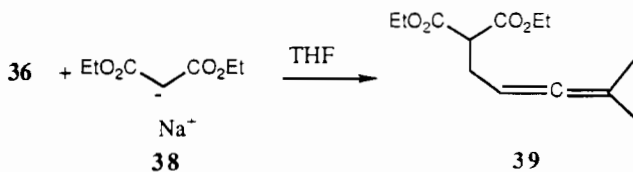


Fig. 3. Molecular structure of **36**.

produce the substituted allene **39** (attack at the least hindered carbon of the η^3 -allyl) albeit in somewhat disappointing yield (32%). Perhaps complex **36** will require NO^+ for CO ligand exchange to facilitate nucleophilic attack on the η^3 -pentadiene.



In summary, we have demonstrated that metal carbonyl containing anions will react with allenic electrophiles to produce a wide array of new diene containing coordination compounds. Our future efforts in this area will be aimed at exploring reaction chemistry of these new coordination geometries.

Supplementary material

Tables of anisotropic displacement coefficients, H atom coordinates and isotropic displacement coefficients and structure factor tables for **25b** and all of the above plus complete tables of bond distances and angles for **32** and **36** are available from the authors upon request.

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