Synthesis of a Vinylphosphine Substituted Cobalt Lactonyl Complex and Insertion of CO into the Lactonyl Ring: Crystal Structures of $[Co\{PPh_2CPh{=}CPhCOC(O)CPhCPh\}(CO)_2]$ and $[Co\{PPh_2CPh{=}CPhCC(O)OC(O)CPhCPh\}(CO)_2]$

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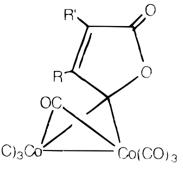
*Summary: Two new cobalt complexes, $[Co\{PPh_2CPh{=}CPhCOC(O)CPhCPh\}(CO)_2]$ (**4**) and $[Co\{PPh_2CPh{=}CPhCC(O)OC(O)CPhCPh\}(CO)_2]$ (**5**), have been synthesized and spectroscopically and structurally characterized. Complex **4** is the major product of the condensation reaction of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ with diphenylacetylene under carbon monoxide pressure, while **5** is obtained from the reaction of **4** with sodium naphthalenide followed by $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl]$. The X-ray structures of **4** and **5** reveal the cobalt atoms to be respectively chelated by lactonyl and cyclic anhydride substituted vinylphosphines, so that **5** is formally derived from **4** by insertion of CO into the lactonyl ring.*

Introduction

The reactions of alkynes with transition metal carbonyl complexes to give cyclic carbonyl-containing organic molecules, such as cyclopentadienones, cycloheptatrienones, quinones, and lactones, are well documented.[1] The organic molecules may be obtained free or coordinated to a transition metal in a complex. Cobalt carbonyl complexes are among the most active in reactions of this type, and for example, the reaction of an alkyne with $[Co_2(CO)_8]$ followed by treatment with CO at high temperature and pressure affords the lactonyl complex **1**.[2] In a similar manner compounds such as **2** containing a coordinated quarternized phosphole ring can be prepared by the reaction of alkynes with a phosphido-bridged cobalt carbonyl complex.[3]



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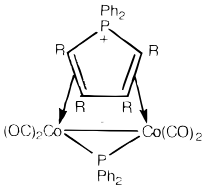

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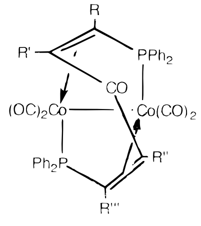

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More often, however, the coupling reaction of alkynes with phosphido-bridged species results in complexes containing metallocyclic rings incorporating up to nine atoms (for example complex **3**).[4,5]

We now report that the reaction of diphenylacetylene with $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$[6] under carbon monoxide pressure results in coupling of phosphido, alkyne, and CO fragments to yield a mononuclear cobalt complex $[Co\{PPh_2CPh{=}CPhCOC(O)CPhCPh\}(CO)_2]$ (**4**) (Scheme 1). Insertion of CO into the lactonyl ring of the chelating substituted vinylphosphine ligand in **4** to give $[Co\{PPh_2CPh{=}CPhCC(O)OC(O)CPhCPh\}(CO)_2]$ (**5**), which contains an acid anhydride ring, can be achieved by reaction of **4** with sodium naphthalenide followed by $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl]$.

Results and Discussion

Reaction of 4 equiv of diphenylacetylene with a freshly prepared sample of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ in a sealed vessel under an atmosphere of carbon monoxide at 80 atm and 385 K gave complex **4** in *ca.* 50% yield. Also isolated from the reaction in lower yield were $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$, $[Co_2\{\mu\text{-}PPh_2CPhCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$, and $[Co_2\{\mu\text{-}PPh_2CPhCPh\}(\mu\text{-}PPh_2)(CO)_4]$, all of which have been characterized previously.[6,7] Spectroscopic data for complex **4** include three absorptions in the carbonyl region of the infrared spectrum [ν_{CO} (CH_2Cl_2) 2032 s, 1984 s, 1741 m], a singlet resonance at δ −63.8 in the $^{31}P\{^1H\}$ NMR, and separate resonances corresponding to the vinyl, lactonyl, and phenyl carbon atoms of the chelating ligand in the $^{13}C\{^1H\}$ NMR spectrum (see Experimental Section). This spectroscopic information is not sufficient, however, to determine the precise structure of **4**. Crystallization of **4** by slow diffusion of

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[1] See: *Organic Syntheses with Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968, 1987; Vols. 1 and 2. *New Syntheses with Carbon Monoxide*; Farbe, J., Ed.; Springer: Berlin, 1980. *Carbonylation*; Colquhoun, H. M., Thompson, D. J., Twigg, M. V., Eds.; Plenum: New York, 1991.

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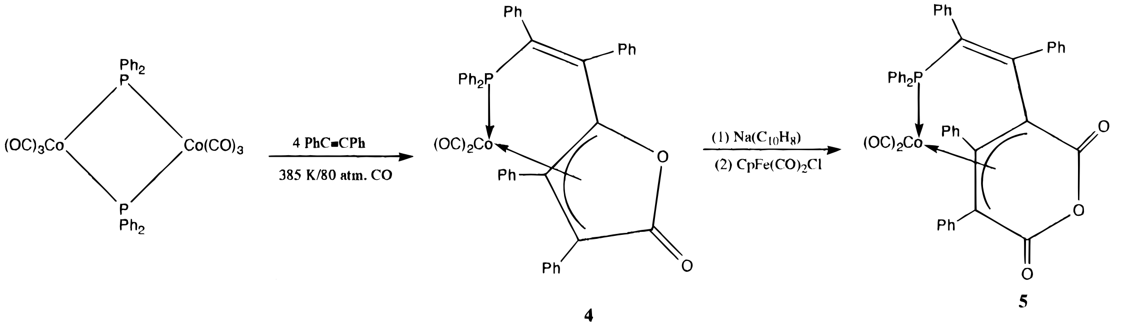
Scheme 1. Synthesis of the Lactonyl Complex 4 and Insertion of CO into the Lactonyl Ring of 4 To Give 5



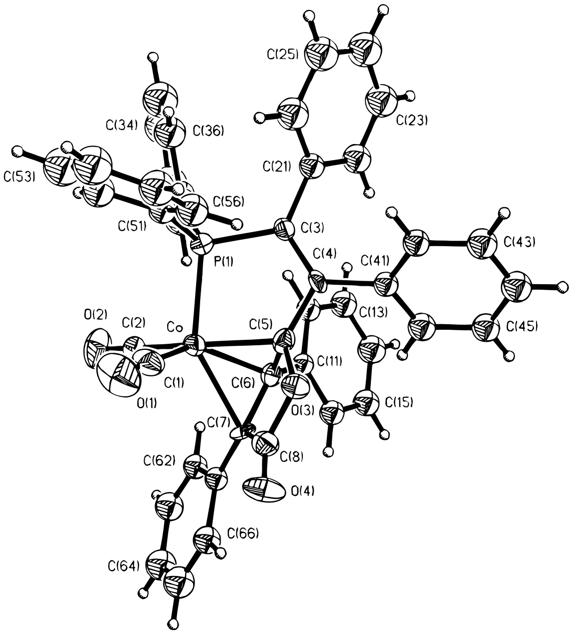


Figure 1. Molecular structure of [Co{$PPh_2CPh{=}CPhCOC(O)CPhCPh$}$(CO)_2$] (**4**) including the atom-numbering scheme.

pentane into a dichloromethane solution of **4** at room temperature generated orange single crystals suitable for *X*-ray structural analysis. The molecular structure of complex **4** is shown in Figure 1. Selected bond distances and angles are listed in Table 1, and atomic coordinates are given in the Supporting Information.

The structure consists of a single cobalt atom, coordinated by two terminal carbonyl ligands and a 5-electron donor chelating ligand consisting of a lactonyl ring substituted at C(5) by a vinylphosphine group. The lactonyl portion of the ligand is η^3-coordinated *via* C(5)C(6)C(7) to the cobalt with the carbon–cobalt distances being very similar [Co–C(5) 2.002(14), Co–C(6) 1.976(14), Co–C(7) 2.172(13) Å]. The vinylphosphine arm of the lactonyl group, $Ph_2PCPh{=}CPh$, extends round so as to coordinate *via* the phosphino group to the cobalt atom [Co–P(1) 2.190(4) Å]. Mononuclear cobalt carbonyl complexes containing η^3-lactonyl groups, [Co{$RCH_2COC(O)CR^1CR^2$}$(CO)_3$] (R = H, CO_2Et, CN, CH_2CH_2OH; R^1, R^2 = H, Et, *t*-Bu, CMe_2OH), have been previously prepared by different methods and characterized on the basis of spectroscopic data.[8]

Insertion of CO into the lactonyl portion of the chelating ligand in **4** to give complex **5**, in which the lactonyl group has been converted to a cyclic anhydride group, can be achieved in two steps. Addition of 2 equiv of sodium naphthalenide to **4** in THF at room temperature, followed by treatment with [(η^5-C_5H_5)$Fe(CO)_2Cl$], results in the formation of **5** in moderate yield.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 4

Co–P(1)	2.190(4)	Co–C(1)	1.855(15)
Co–C(2)	1.832(17)	Co–C(5)	2.002(14)
Co–C(6)	1.976(14)	Co–C(7)	2.172(13)
P(1)–C(3)	1.830(14)	P(1)–C(31)	1.817(15)
P(1)–C(51)	1.846(12)	C(1)–O(1)	1.094(18)
C(2)–O(2)	1.123(21)	C(3)–C(4)	1.351(21)
C(3)–C(21)	1.492(16)	C(4)–C(5)	1.470(16)
C(4)–C(41)	1.469(19)	C(5)–C(6)	1.466(16)
C(5)–O(3)	1.452(15)	C(6)–C(7)	1.474(14)
C(6)–C(11)	1.483(14)	C(7)–C(8)	1.499(18)
C(7)–C(61)	1.453(16)	C(8)–O(3)	1.423(15)
C(8)–O(4)	1.184(16)	C–C(phenyl)	1.328(23)–1.448(24)

P(1)–Co–C(1)	99.3(5)	P(1)–Co–C(2)	98.9(5)
C(1)–Co–C(2)	100.6(7)	P(1)–Co–C(5)	82.1(4)
C(1)–Co–C(5)	107.1(7)	C(2)–Co–C(5)	151.7(5)
P(1)–Co–C(6)	107.2(3)	C(1)–Co–C(6)	134.0(7)
C(2)–Co–C(6)	111.4(6)	C(5)–Co–C(6)	43.2(5)
P(1)–Co–C(7)	146.3(3)	C(1)–Co–C(7)	100.1(7)
C(2)–Co–C(7)	104.3(6)	C(5)–Co–C(7)	65.9(5)
C(6)–Co–C(7)	41.3(4)	Co–P(1)–C(3)	104.7(5)
Co–P(1)–C(31)	123.1(4)	C(3)–P(1)–C(31)	105.0(6)
Co–P(1)–C(51)	112.2(4)	C(3)–P(1)–C(51)	104.4(6)
C(31)–P(1)–C(51)	105.8(7)	Co–C(1)–O(1)	177.8(15)
Co–C(2)–O(2)	177.7(13)	P(1)–C(3)–C(4)	113.4(8)
P(1)–C(3)–C(21)	122.2(11)	C(4)–C(3)–C(21)	124.3(12)
C(3)–C(4)–C(5)	116.3(12)	C(3)–C(4)–C(41)	125.5(10)
C(5)–C(4)–C(41)	118.1(12)	Co–C(5)–C(4)	122.9(11)
Co–C(5)–C(6)	67.4(8)	C(4)–C(5)–C(6)	128.0(9)
Co–C(5)–O(3)	107.4(7)	C(4)–C(5)–O(3)	113.6(10)
C(6)–C(5)–O(3)	108.9(10)	Co–C(6)–C(5)	69.3(8)
Co–C(6)–C(7)	76.5(7)	C(5)–C(6)–C(7)	101.3(8)
Co–C(6)–C(11)	135.3(10)	C(5)–C(6)–C(11)	124.9(10)
C(7)–C(6)–C(11)	129.2(10)	Co–C(7)–C(6)	62.2(7)
Co–C(7)–C(8)	99.1(8)	C(6)–C(7)–C(8)	107.3(10)
Co–C(7)–C(61)	120.2(10)	C(6)–C(7)–C(61)	127.4(9)
C(8)–C(7)–C(61)	122.3(10)	C(7)–C(8)–O(3)	107.0(10)
C(7)–C(8)–O(4)	133.8(12)	O(3)–C(8)–O(4)	119.1(12)
C(5)–O(3)–C(8)	106.3(9)		

The IR spectrum in the ν_{CO} region of **5** is particularly informative with four absorption bands, two corresponding to terminal carbonyl bands (2045 s, 2001 s cm^{-1}) and two corresponding to ketonic bands (1740 s, 1703 s cm^{-1}). The fast atom bombardment (FAB) mass spectrum shows a molecular ion peak at 740 amu corresponding to an increase of 28 amu compared to the molecular ion peak found in the spectrum for **4**. The single-crystal X-ray structure for **5** is shown in Figure 2. Selected bond distances and angles are given in Table 2.

The structure of complex **5** resembles that of **4** with a single cobalt atom surrounded by two terminal car-

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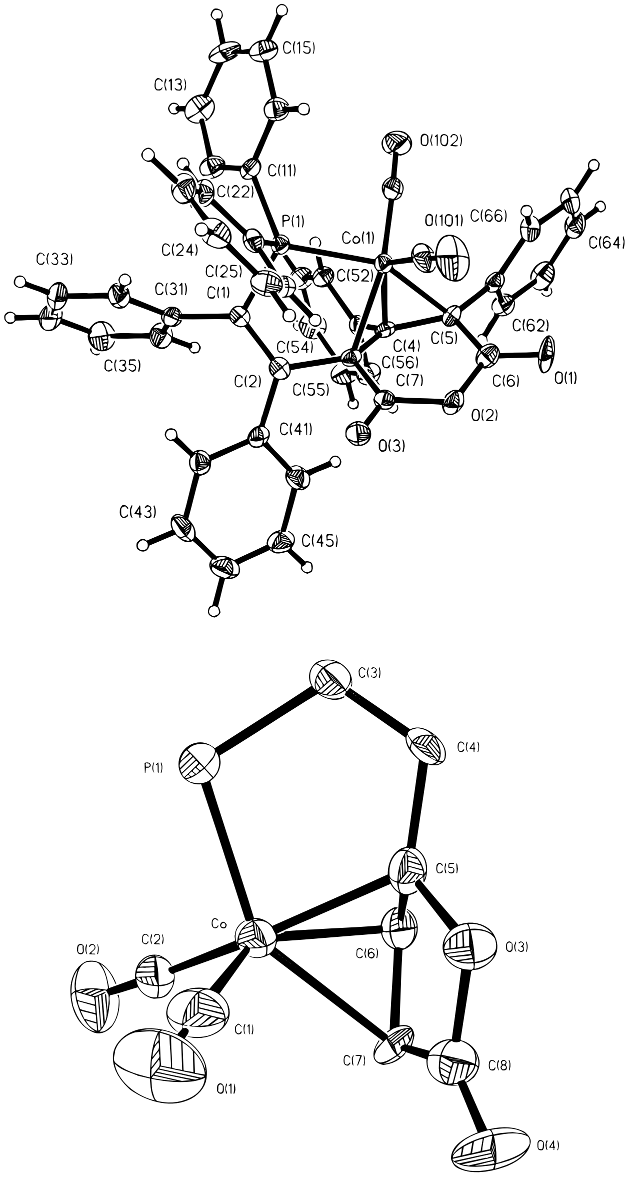


Figure 2. Molecular structure of [Co{PPh$_2$CPh=CPhCC(O)OC(O)CPhCPh}(CO)$_2$] (**5**) including the atom-numbering scheme.

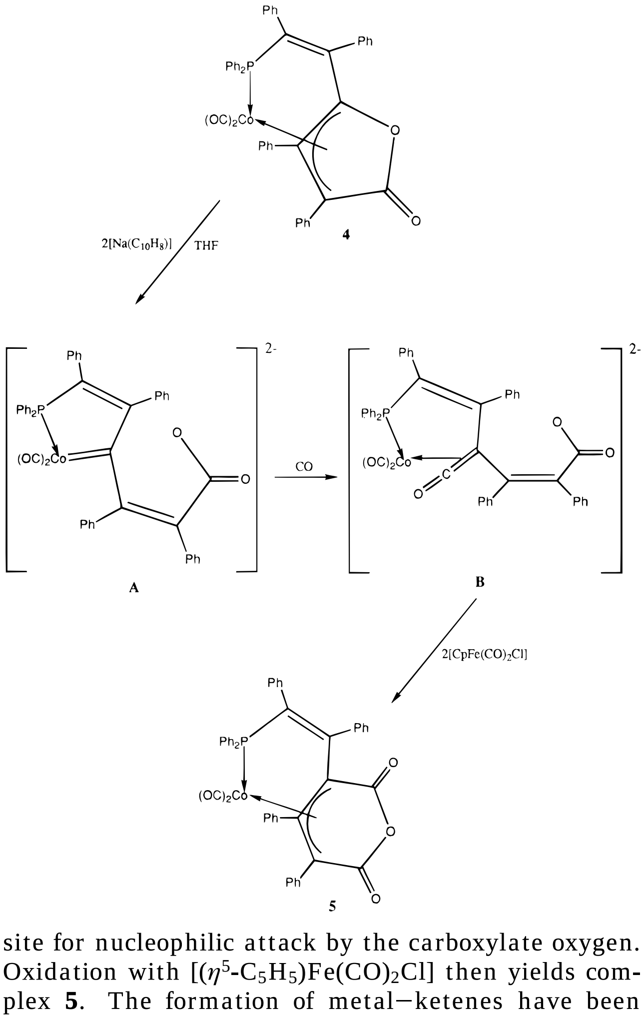
bonyl ligands and by a chelating 5-electron donor ligand. The nature of the 5-electron donating ligand in **5** differs from that in **4** with a cyclic anhydride group η^3-coordinating to cobalt through C(3)C(4)C(5), while the vinylphosphine arm, CPh=CPhPPh$_2$, as in **4**, wraps around to complete the distorted octahedral coordination at cobalt. The conversion of the lactone moiety in **4** to a cyclic anhydride in **5** has only a minor effect on the structural parameters, with the phosphorus–cobalt and carbon–cobalt distances being similar [Co–P(1) 2.190(4) (**4**) *vs* Co(1)–P(1) 2.204(1) Å (**5**) and Co–C(5) 2.002(14), Co–C(6) 1.976(14), Co–C(7) 2.172(13) (**4**) *vs* Co(1)–C(3) 2.074(4), Co(1)–C(4) 1.980(4), Co(1)–C(5) 2.117(4) Å (**5**)].

The mechanism by which a CO group inserts into a C–O bond in **4** to give **5** is uncertain, but Scheme 2 shows a possible pathway involving the formation of a dianionic intermediate **A**, in which cleavage of a carbon–oxygen bond and generation of a metal–carbene unit has occurred. A second dianionic intermediate **B**, in which a divinylketene coordinates to cobalt, provides a site for nucleophilic attack by the carboxylate oxygen. Oxidation with [(η^5-C$_5$H$_5$)Fe(CO)$_2$Cl] then yields complex **5**. The formation of metal–ketenes have been proposed as intermediates in the reactions of chromium–carbene complexes (i) with alkynes to give hydroquinone derivatives (the Dötz reaction)[9] and (ii) with imines to give β-lactams.[10]

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 5

Co(1)–C(102)	1.821(5)	Co(1)–C(101)	1.824(5)
Co(1)–C(4)	1.980(4)	Co(1)–C(3)	2.074(4)
Co(1)–C(5)	2.117(4)	Co(1)–P(1)	2.204(1)
P(1)–C(1)	1.845(4)	O(1)–C(6)	1.214(6)
O(2)–C(7)	1.400(5)	O(2)–C(6)	1.421(5)
O(3)–C(7)	1.212(5)	C(1)–C(2)	1.363(6)
C(2)–C(3)	1.512(6)	C(3)–C(4)	1.468(6)
C(3)–C(7)	1.485(7)	C(4)–C(5)	1.467(6)
C(5)–C(6)	1.472(7)	C(101)–O(101)	1.139(6)
C(102)–O(102)	1.154(6)	C–C(phenyl)	1.382(8)–1.421(7)
C(4)–Co(1)–C(3)	42.4(2)	C(4)–Co(1)–C(5)	41.8(2)
C(3)–Co(1)–C(5)	71.1(2)	C(4)–Co(1)–P(1)	106.4(1)
C(3)–Co(1)–P(1)	82.6(1)	C(5)–Co(1)–P(1)	148.1(1)
C(1)–P(1)–Co(1)	104.2(2)	C(7)–O(2)–C(6)	121.3(4)
C(2)–C(1)–P(1)	111.9(3)	C(1)–C(2)–C(3)	118.4(4)
C(4)–C(3)–C(7)	121.4(4)	C(4)–C(3)–C(2)	119.7(4)
C(7)–C(3)–C(2)	114.7(4)	C(4)–C(3)–Co(1)	65.4(2)
C(7)–C(3)–Co(1)	106.1(3)	C(2)–C(3)–Co(1)	118.1(3)
C(3)–C(4)–C(5)	112.3(4)	C(3)–C(4)–Co(1)	72.2(2)
C(5)–C(4)–Co(1)	74.1(2)	C(4)–C(5)–C(6)	119.4(4)
C(4)–C(5)–Co(1)	64.1(2)	C(6)–C(5)–Co(1)	104.8(3)
O(1)–C(6)–O(2)	115.6(4)	O(1)–C(6)–C(5)	125.1(4)
O(2)–C(6)–C(5)	119.3(4)	O(3)–C(7)–O(2)	116.6(4)
O(3)–C(7)–C(3)	126.2(4)	O(2)–C(7)–C(3)	117.2(4)
O(101)–C(101)–Co(1)	176.2(5)	O(102)–C(102)–Co(1)	177.7(4)

Scheme 2. Possible Reaction Pathway Accounting for the Insertion of CO into the Lactonyl Ring of 4 To Give 5



Experimental Section

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge, U.K. Column chromatography was performed on Kieselgel 60 (70-230 mesh) or (230-400 mesh). Products are given in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[11] Phosphorus-31 NMR chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. All NMR spectra were recorded at 293 K. Unless otherwise stated all reagents were obtained from commercial suppliers, and the compound $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ was prepared by the literature method.[6]

Reaction of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ with Diphenylacetylene. A solution of the freshly prepared complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (0.500 g, 0.762 mmol) in toluene (50 mL) was charged with 4 equiv of diphenylacetylene (0.543 g, 3.05 mmol), loaded into a 100 mL Roth autoclave, pressurized to 80 atm with carbon monoxide, and stirred overnight at 385 K. After removal of the solvent under reduced pressure, the residue was dissolved in the minimum quantity of dichloromethane and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column. Elution initially with hexane gave the green trinuclear species $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$ (0.014 g, 2%), and then elution with hexane−CH_2Cl_2 (1:1) gave the green complex $[Co_2(\mu\text{-}PPh_2CPhCPh)(\mu\text{-}PPh_2)(CO)_4]$ (0.018 g, 3%), a trace of $[Co_2\{\mu\text{-}PPh_2CPhCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$, and, on further elution with CH_2Cl_2, orange crystalline $[Co\{\mu\text{-}PPh_2CPhCPhCOC(O)CPhCPh\}(CO)_2]$ (**4**) (0.270 g, 50%): IR (CH_2Cl_2) ν_{CO} = 2032 s, 1984 s, 1741 m cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.1−6.8 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −63.8 [s, $Ph_2PCPhCPh$]; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 200.1 [d, ^2J(PC) 10, $Ph_2PCPhCPh$], 199.5 (s, 2CO), 172.6 [d, ^4J(PC) 4, COC(O)CPhCPh], 153.8 [d, ^1J(PC) 28, $Ph_2PCPhCPh$], 136−127 (m, Ph), 110.1 [s, COC(O)CPhCPh], 97.9 [s, COC(O)CPhCPh], 64.1 [s, COC(O)CPhCPh]. Anal. Calcd for $C_{44}H_{30}CoO_4P$: C, 71.06; H 4.21; P, 4.35. Found: C, 71.36; H, 4.11; P, 4.66. FABMS (*m*/*e*): 712 (M^+) and $M^+ - n$CO (n = 1−3).

Preparation of $[Co\{\mu\text{-}PPh_2CPhCPhC(O)COC(O)CPhCPh\}(CO)_2]$ (5). A THF solution of sodium naphthalenide was prepared by adding naphthalene (0.110 g, 0.86 mmol) to sodium metal (0.019 g, 0.84 mmol) in THF (30 mL) and was stirred until all the sodium had disappeared. The solution of sodium naphthalenide was then canulated into a Schlenk flask containing complex **4** (0.300 g, 0.42 mmol), dissolved in THF (20 mL), and was stirred overnight at room temperature. To this solution was added $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl]$ (0.176 g, 0.84 mmol), and the resultant brown solution was stirred for 3 h. The solvent was removed under reduced pressure, and the residue dissolved in the minimum quantity of CH_2Cl_2 was loaded onto the base of TLC plates. Elution with CH_2Cl_2 gave $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ [0.201 g, 68% based on η^5-$C_5H_5)Fe(CO)_2Cl$], unreacted **4** (0.03 g, 10%), and $[Co\{\mu\text{-}PPh_2CPhCPhC(O)COC(O)CPhCPh\}(CO)_2]$ (**5**) (0.059 g, 19%): IR (CH_2Cl_2) ν_{CO} = 2045 s, 2001 s, 1740 s, 1703 s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.1−6.8 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −72.7 [s, $Ph_2PCPhCPh$]. Anal. Calcd for $C_{45}H_{30}CoO_5P$: C, 71.06; H 4.21; P, 4.35. Found: C, 71.36; H, 4.11; P, 4.66. FABMS (*m*/*e*): 740 (M^+) and $M^+ - n$CO (n = 1−3).

Table 3. Crystallographic Data for the Complexes 4 and 5

	4	**5**·CH_2Cl_2
formula	$C_{44}H_{30}CoO_4P$	$C_{46}H_{32}Cl_2CoO_5P$
fw	712	825.5
cryst system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.737(4)	10.165(2)
b, Å	14.494(4)	11.936(2)
c, Å	16.801(6)	17.692(4)
α, deg	67.43(2)	73.13(3)
β, deg	76.98(3)	86.63(3)
γ, deg	83.85(3)	75.99(3)
V, Å^3	1985(2)	1993(1)
Z	2	2
D_{calcd}, g/cm^3	1.132	1.376
F(000)	700	848
cryst color and habit	red block	red block
cryst dimens, mm	0.25 × 0.31 × 0.34	0.41 × 0.32 × 0.31
μ, mm^{-1}	0.508	0.651
scan type	$2\theta-\theta$	
radiation	Mo Kα	Mo Kα
temp, K	290	153
θ range, deg	5−45	5−45
scan mode	$\omega/2\theta$	$\omega/2\theta$
reflcns, measd	5744	4625
no. of unique reflns	5195	4587
no. of reflns obsd[a]	2782 [$I > 5.0\sigma(I)$]	4581 [$I > 2\sigma(I)$]
refinement method	full-matrix least squares	full-matrix least squares
no. of params	291	496
R	0.0860	0.0486
R_w	0.1204	0.1336

Crystallographic Analysis. Suitable single crystals of complexes **4** and **5** for X-ray analysis were obtained by slow diffusion of pentane into dichloromethane solutions at 293 K (**4**) and 273 K (**5**). Crystal data are reported in Table 3. Data were collected on a Siemens R3m/V (**4**) and on a Stoe 4-circle diffractometer equipped with an Oxford Cryostream crystal cooling device (**5**).

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Supporting Information Available: Tables of crystal structure determination data, atomic coordinates and *U* values, anisotropic thermal parameters, and bond lengths and angles for complexes **4** and **5** (16 pages). Ordering information is given on any current masthead page.

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