Reactivity of a (η^5-Phospholyl)cobalt Dicarbonyl Complex. Synthesis of [$Co_2(\eta^5\text{-}PC_4H_2{}^tBu_2)_2(CO)_2$] and [$Co_2(\eta^5\text{-}PC_4H_2{}^tBu_2)_2(\mu\text{-}CHCO_2Et)(CO)_2$]

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Thermolysis of 2,2′,5,5′-tetra-*tert*-butyl-1,1′-biphosphole with $Co_2(CO)_8$ gives good yields of (2,5-di-*tert*-butylphospholyl)dicarbonylcobalt (**1**), a compound which provided access to a range of cobalt phospholyl complexes. Thermolysis with trimethyl phosphite produced $C_{12}H_{20}PCo(CO)P(OMe)_3$ (**2**), while photolysis with 1,3-cyclohexadiene and 1,5-cyclooctadiene gave the corresponding complexes $C_{12}H_{20}PCo(diene)$ (**3**, **4**). In the absence of a donor ligand, a metal−metal doubly bridged dimer **6** was obtained; this reacted classically with ethyl diazoacetate to give the bridging complex $\{C_{12}H_{20}PCo(CO)\}_2(\mu\text{-}CHCO_2Et)$ (**7**). Prolonged heating of **1** with 3-hexyne in xylene gave the cyclotrimerization product C_6Et_6; an initial attempt to prepare pyridines by cocyclization of PrCN with PhC≡CH gave the cyclobutadiene complex $C_{12}H_{20}PCo(1,2\text{-}C_4H_2Ph_2)$ (**5**).

Introduction

Phospholyl anions are potentially ambidentate ligands which may bind to metals through (a) their lone pair of electrons in an η^1-coordination mode, (b) the delocalized 6π aromatic system as a pentahapto ligand, or (c) both functionalities simultaneously. These features suggest a useful coordination chemistry. However, the rational directed synthesis of phospholyl-containing compounds presents a considerable challenge: complicated mixtures of products or oligomeric materials are often produced.[1] As a consequence, systematic studies of the reactivity of η^5-phospholyl complexes have generally involved closed-shell, relatively substitution-inert complexes such as phosphaferrocenes and phosphacymantrenes.[1] To explore the possibility of modifying the properties of metal centers through substituting cyclopentadienyl ligands by phospholyls, we sought to develop routes which lead selectively to mononuclear η^5-complexes of phospholide anions. Compounds derived from the 2,5-di-*tert*-butylphospholyl ligand[2] were obvious targets because the sterical hindrance of their lone pairs impedes the oligomerization of their π-complexes.

Among classical cyclopentadienyl metal complexes, the η^5-CpCo moiety is particularly notable for its rich and diverse applications in catalysis and stoichiometric organic synthesis.[3−7] Catalysts based upon the η^5-CpCo fragment are employed in alkyne cyclotrimerizations and the cocyclization of alkynes and nitriles to produce pyridines.[3] Brookhart and co-workers have shown that [$Cp^*\{P(OMe)_3\}CoCH_2CH_2\text{-}\mu\text{-}H$][$BAr_4$] [Ar = 3,5-$(CF_3)_2C_6H_3$] and derivatives are effective ethylene polymerization and hydrosilylation catalysts.[7] Detailed studies of (η^5-cyclopentadienyl)cobalt dicarbonyl mediated [2 + 2 + 2]-cycloadditions have also demonstrated a high chemo-, regio-, and stereospecificity which has led to their use in natural product synthesis.[6] The ability of the 2,5-di-*tert*-butylphospholyl ligand to stabilize complexes having open coordination spheres[2b] suggested that its cobalt derivatives should have interesting stoichiometric and catalytic activity. Here, we describe the synthesis of (2,5-di-*tert*-butylphospholyl)cobalt derivatives, their chemistry, and preliminary tests of their catalytic capabilities.

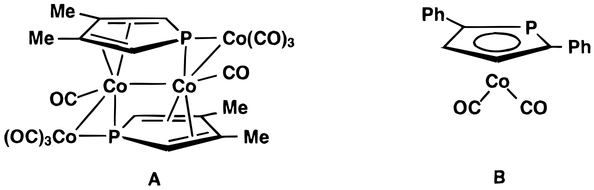
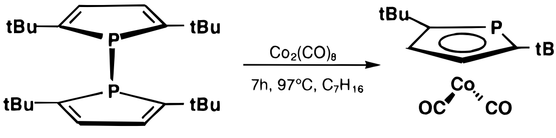


Figure 1.

Scheme 1



1, 80%

The thermolysis of $Co_2(CO)_8$ with 1,1′-biphospholes[8,9] was investigated shortly after their isolation. 3,3′,4,4′-tetramethyl-1,1′-biphosphole gave a tetracobalt complex

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[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

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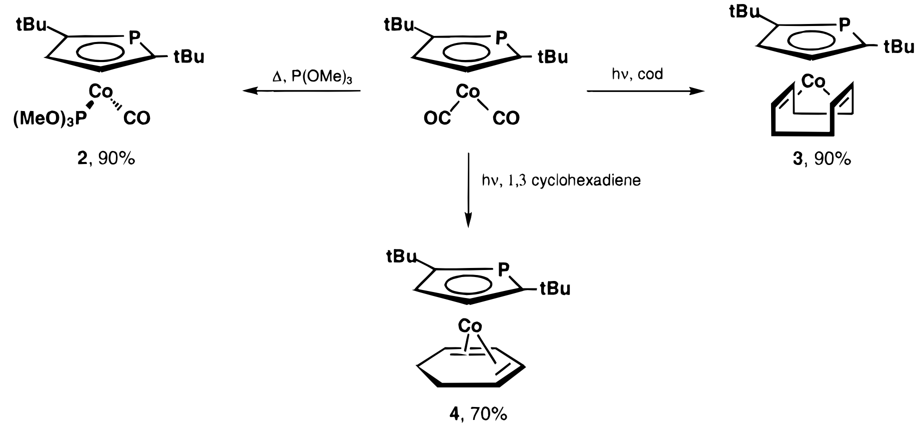
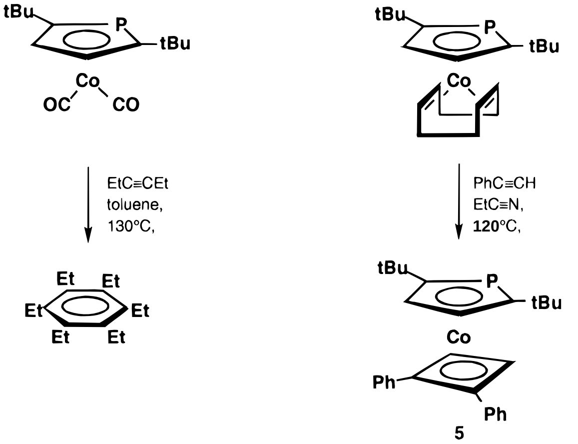
Scheme 2



Scheme 3



A (Figure 1) which incorporates bridging η^1,η^5-phospholyl ligands.[10] 2,2′,5,5′-Tetraphenyl-1,1′-biphosphole gave a (η^5-phospholyl)cobalt dicarbonyl complex **B**,[9] whose poor stability and inability to catalyze alkyne cyclooligomerization meant that studies of its reactivity were not pursued further. A number of non-carbonyl-containing cobalt phospholyl complexes have subsequently been reported by Nixon,[11] Grimes,[12] and their co-workers.

Results

Complex **1** was selected as the starting material for this study. It was conveniently prepared in 80% yield as a red liquid by thermolysis of 2,2′,5,5′-tetra-*tert*-butyl-1,1′-biphosphole with $Co_2(CO)_8$ (Scheme 1).

The carbonyl ligands appear as a single peak in the ^{13}C NMR spectrum of **1**, both at room temperature and at −80 °C (THF). The two coordination sites at cobalt are normally asymmetrically oriented with respect to the di-*tert*-butylphospholyl ligand (*vide infra*), and it seems probable that a low-energy rotational process is causing a rapid exchange of the CO sites. A preliminary catalytic study in toluene at 130 °C indicates that **1** is active in the cyclotrimerization of hex-3-yne to hexaethylbenzene (Scheme 3; products detected by ^{13}C NMR and GC measurements). Consequently, the inability of $(C_4H_2Ph_2P)Co(CO)_2$ (**B**) to catalyze alkyne cyclization[9] probably results from cluster formation through the phosphorus lone pair, as was found for the 3,4-dimethylphospholyl complex **A**.[10]

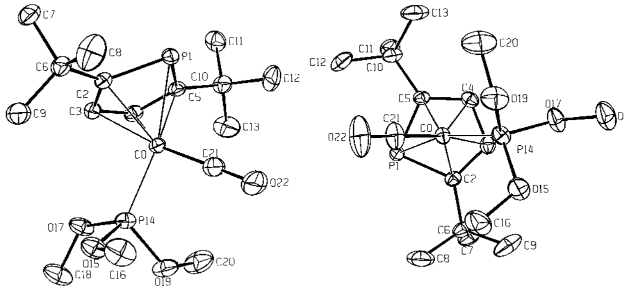


Figure 2. Two views of the molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Co−P(1), 2.3061(5); Co−P(14), 2.0921(5); Co−C(2), 2.147(2); Co−C(3), 2.072(2); Co−C(4), 2.102(2); Co−C(5), 2.148(2); Co−C(21), 1.704(2); C(21)−O(22), 1.159(2); P(1)−C(2), 1.775(2); P(1)−C(5), 1.805(2); P(14)−O(15), 1.604(1); P(14)−O(17), 1.594(1); P(14)−O(19), 1.604(1); C(2)−C(3), 1.413(3); C(3)−C(4), 1.434(2); C(4)−C(5), 1.391(2); C(2)−P(1)−C(5), 91.27(8); C(2)−C(3)−C(4), 114.2(2); C(3)−C(4)−C(5), 113.1(1); C(4)−C(5)−P(1), 111.0(1); P(1)−C(2)−C(3), 110.4(1); P(14)−Co−C(21), 90.72(7); P(14)−Co−P(1), 164.23(2); P(1)−Co−C(21), 98.09(7); Co−C(21)−O(22), 179.3(2).

Thermolysis of **1** with excess $P(OMe)_3$ produced **2** in 90% yield (Scheme 2). The ^{31}P NMR resonance of the $P(OMe)_3$ ligand shows greater ^{59}Co quadrupole broadening than the phosphorus of the phospholyl, probably because of a greater Fermi-contact contribution in the η^1 ligating mode than in the η^5 case. For further characterization, a high-resolution X-ray crystal structure of **2** was also performed (Figure 2).

The phosphite lies beneath the CH carbons of the phospholyl ring and well away from the two *tert*-butyl substituents, probably for steric reasons. The phosphite and carbonyl ligands are displaced from the local symmetry plane which bisects the phospholyl, and the ring bond lengths suggest that the coordination of the two filled phospholyl π orbitals to the cobalt center provokes a distortion toward a η^3-(1-phosphaallyl) η^2-(olefin) type coordination mode (Figure 3). A related effect of very similar magnitude provokes the “ring slippage” which permits thermally driven ligand sub-

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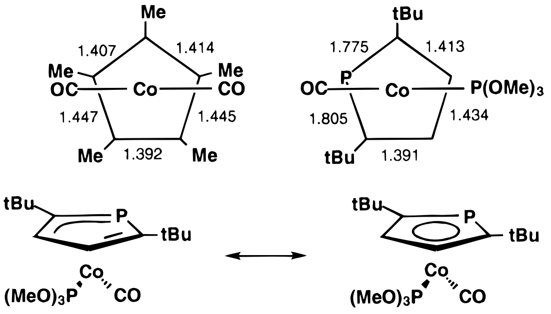

Figure 3.

stitutions in complexes such as $Cp^{*}Co(CO)_2$.[13] Phosphorus atoms that are sp^2 hybridized tend to conjugate more effectively with a delocalized system from terminal rather than internal positions,[14] so a bonding mode involving a 1-phosphaallyl functionality seems to be logical.

The reactivity of **1** toward both conjugated and nonconjugated cyclodienes is entirely classical. Thus, photolysis of **1** with an excess of 1,5-cyclooctadiene in hexane produced good yields of **3** (Scheme 2), whose room temperature ^1H NMR spectrum shows a singlet at δ 4.02 ppm assigned to the olefinic protons and two multiplets at 2.40 and 1.67 ppm for the protons of the COD ligand. These chemical shifts are comparable with the analogous resonances in $CpCo(C_8H_{12})$.[15] Similarly, photolysis of **1** with an excess of 1,3-cyclohexadiene in hexane gave **4**. The η^4-cyclohexadiene proton resonances are shifted downfield by 0.5−1 ppm from those observed for the parent Cp complex,[15] which probably indicates a weaker cobalt−diene interaction than is found in the cyclopentadienyl case, because of lower electron donation from the phospholyl ligand. The simplicity of the spectra in **3** and **4** again suggests that the diolefin ligands rotate with respect to the phospholyl: the ^{13}C NMR spectrum of **3** showed no changes between room temperature and −80 °C.[16]

In an initial attempt to investigate the feasibility of catalytic pyridine production,[3] complex **3** was heated for 3 days in a sealed tube at 120 °C with a large excess of phenylacetylene in propionitrile. The yellow solution which was obtained gave no evidence of pyridines, presumably because more forcing conditions are required. However, workup by column chromatography gave the yellow cyclobutadiene complex **5** (Scheme 3).

It is difficult to differentiate between 1,2- and 1,3-diphenylcyclobutadiene ligands by NMR spectroscopy,[17] so **5** was identified as the 1,2-isomer by a single-crystal X-ray diffraction study (Figure 4). The β carbons of the phospholyl ligand are not perfectly resolved, but the 3.2° dihedral angle between the best planes of the phospholyl and cyclobutadiene rings is sufficiently small to imply little strain in the molecule, presumably because the two phenyl substituents are oriented well away from the *tert*-butyl groups of the phospholyl ring. This arrangement strongly suggests that the "bar-like" sterical properties[18] of the phospholyl ligand dictate the regiochemistry of the cycloaddition reaction at the cobalt center.

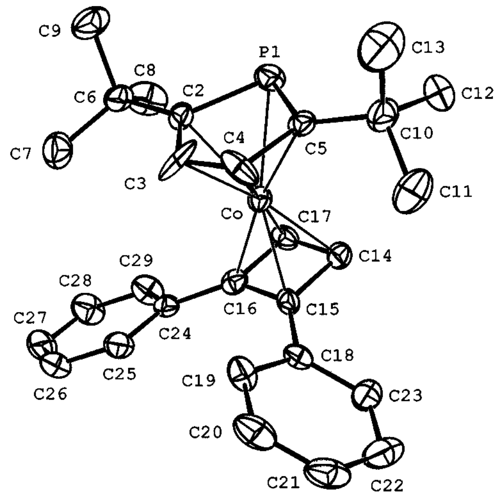

Figure 4. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): Co−P(1), 2.249(2); Co−C(2), 2.106(5); Co−C(3), 2.077(6); Co−C(4), 2.065(6); Co−C(5), 2.104(5); Co−C(14), 1.996(5); Co−C(15), 1.976(5); Co−C(16), 1.990(5); Co−C(17), 1.978(5); P(1)−C(2), 1.776(5); P(1)−C(5), 1.777(5); C(2)−C(3), 1.421(8); C(3)−C(4), 1.286(8); C(4)−C(5), 1.426(7); C(14)−C(15), 1.463(7); C(15)−C(16), 1.479(7); C(16)−C(17), 1.438(7); C(17)−C(14), 1.444(7); C(2)−P(1)−C(5), 90.8(2); P(1)−C(2)−C(3), 107.6(4); C(2)−C(3)−C(4), 118.0(5); C(3)−C(4)−C(5), 113.9(5); C(4)−C(5)−P(1), 109.6(4).

To further investigate the reactivity of **1**, photolysis under a nitrogen purge in the absence of a donor ligand was examined. This gave the dinuclear doubly bonded complex **6**, which was cleanly isolated in 80% yield as deep green microcrystals (Scheme 4). **6** has bridging CO ligands, according to spectroscopic studies which reveal a single broad ^{13}C NMR peak at δ 260.5 ppm and a ν(CO) stretching band at 1796 cm^{-1} in hexane (Table 1).

The stability of the coordinatively unsaturated dimer **6** emphasizes that bonding through the phosphorus lone

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(16) Trimethylphosphine ligands are known to restrict rotation about the (di-*tert*-butylcyclopentadienyl)cobalt fragment: Hofmann, W.; Buchner, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 795.

(17) Both the 1,2- and 1,3-substituted diphenylcyclobutadiene complexes are formed in the related [CpCo] system, whose 1,2- and 1,3-isomers were tentatively assigned proton C*H* chemical shifts of δ 4.30 and 4.82 ppm, respectively, in CCl_4. The ^1H NMR spectrum of **5** in $CHCl_3$ shows a single product having a C*H* resonance at δ 4.59 ppm. See: Helling, J. F.; Rennison, S. C.; Merijan, A. *J. Am. Chem. Soc.* **1967**, *89*, 7140.

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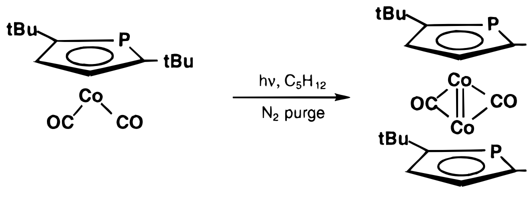
Table 1. IR Spectroscopic Data

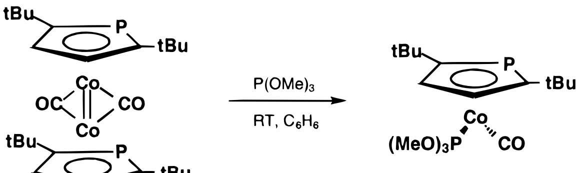
compound	ν(CO) (cm^{-1})	solvent	ref
$(C_4H_2{}^tBu_2P)Co(CO)_2$ (**1**)	2023 s, 1968 s	hexane	this work
$(C_5H_5)Co(CO)_2$	2033 s, 1972 s	*c*-hexane	15, 19
$(C_5Me_5)Co(CO)_2$	2011 s, 1949 s	*c*-hexane	19
$(C_5H_3{}^tBu_2)Co(CO)_2$	2013 s, 1953 s	hexane	20
$(C_4H_2Ph_2P)Co(CO)_2$	2030 s, 1980 s	$CDCl_3$	9
$[(C_5H_3{}^tBu_2)Co(CO)]_2$	1780		20
$[(C_4H_2{}^tBu_2P)Co(CO)]_2$ (**6**)	1796 s	hexane	this work
$[(C_5H_5)Co(CO)]_2$	1765 s	Nujol	21
$[(C_5Me_5)Co(CO)]_2$	1760 s	hexane	22
$(C_4H_2{}^tBu_2P)_2Co_2(\mu\text{-}CHCO_2Et)(CO)_2$ (**7**)	1995 m, 1964 s, 1734 s	hexane	this work
$(C_5H_5)_2Co_2(\mu\text{-}CHCO_2Et)(CO)_2$	1955 s, 1670 m	KBr	23
$(C_5Me_5)_2Co_2(\mu\text{-}CHCO_2Et)(CO)_2$	1847 m, 1796 s, 1659 w, 1638 s	THF	24

Scheme 4



6, 70%

Scheme 5



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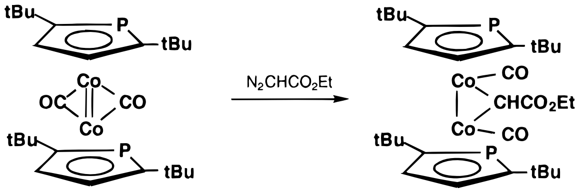
Scheme 6



7, 85%, mixture of isomers

pair of the 2,5-di-*tert*-butylphospholyl ligand is seriously impeded. This is confirmed by the observation that the cobalt−cobalt double bond is sufficiently exposed to react readily with trimethyl phosphite (Scheme 5).

The reaction of **6** with diazoalkanes provides a useful comparison of the relative reactivities of the metal−metal double bond and the phospholyl lone pairs. Ethyl diazoacetate reacted exclusively at the Co═Co linkage with formation of a dimeric phospholyl-supported carbene complex **7** (Scheme 6).

Purification of **7** by column chromatography and recrystallization gave a product which was shown to comprise two isomers by solution NMR spectroscopy. IR studies showing ν(CO) bands at 1995 and 1964 cm^{-1} establish the presence of terminal carbonyl ligands. Thus, the metal−metal bond is bridged only by the carbene ligand. A number of structures having *trans* carbonyls and two with *cis* carbonyls can be drawn (Figure 5).

The *cis* isomers have a plane of symmetry which bisects the cobalt−cobalt bond and passes through the μ-carbene carbon.[25] Each product showed one phospholyl signal in the ^{31}P NMR, two ^{13}C signals each for the α and β carbon resonances, and two β ring protons in the ^1H NMR spectra, so **7** is probably a 2:1 mixture of *cis* compounds, differing in the orientation of their carbene substituents with respect to the carbonyl ligands. *Trans* isomers, which have no symmetry, would require much more complicated patterns. An X-ray diffraction study of one of the components of **7** was performed. Besides confirming the *cis* configuration, it shows a C(33)−Co(1)−Co(2)−C(35) torsion angle of 8.4° linking the *cis*-configured carbonyl ligands (Figure 6). The related cyclopentadienyl complex $Cp_2Co_2(\mu\text{-}CHCO_2Et)(CO)_2$ has a pseudo-*trans* structure and a corresponding torsion angle of 159.8°.[25] These differences probably reflect the anisotropic sterical demands of the phospholyl ligands in **7**, whose "back-to-back" arrangement minimizes nonbonding interactions between their *tert*-butyl groups.

A study of several analogous cobalt and rhodium complexes,[26] including the $Cp_2Co_2(\mu\text{-}CHCO_2Et)(CO)_2$ and $Cp^*{}_2Co_2(\mu\text{-}CHCO_2Et)(\mu\text{-}CO)_2$ couple given in Figure 7, has suggested that electronic effects outweigh steric factors in explaining why the Cp* complex is triply bridged.[24] This theory explains the configuration of the phospholyl complex. Although more hindered than the Cp ligand, it adopts a similar structure, apparently for electronic reasons.

Overview

The present study comprises one of the most complete investigations of the influence of a phospholyl ligand upon a well-known series of metal−ligand fragments. Startling similarities between the reactivity of the cyclopentadienyl- and phospholyl-substituted complexes are clear, because each reaction which has been presented here has a well-established parallel in cyclopentadienyl cobalt chemistry. To pursue this analogy a little further, we prepared a sample of $^tBu_2C_5H_3Co(CO)_2$[20] to permit a direct comparison with **1**. The slightly greater electron richness of the cyclopentadienyl compound is revealed in lower CO stretching frequencies, a slightly higher carbonyl resonance frequency (^{13}C NMR in THF, −50 °C: **1**, 205.2 ppm; $^tBu_2C_5H_3Co(CO)_2$, 207.2 ppm), and much greater sensitivity to air, which renders its manipulation far more difficult. Nonetheless, the overall differences appear to be relatively small. We therefore feel that the substitution of cyclopentadienyl ligands by a suitable phospholyl analog may offer a useful method for fine-tuning the electronics of a metal center.

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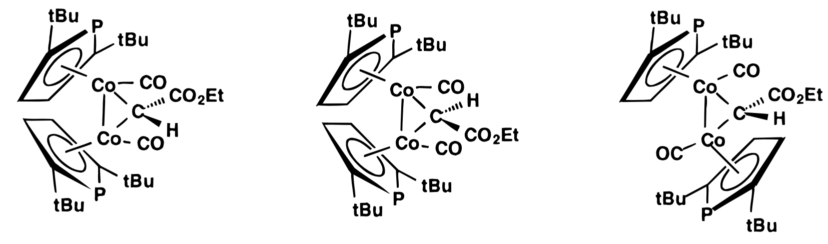


cis   cis   trans

Figure 5.

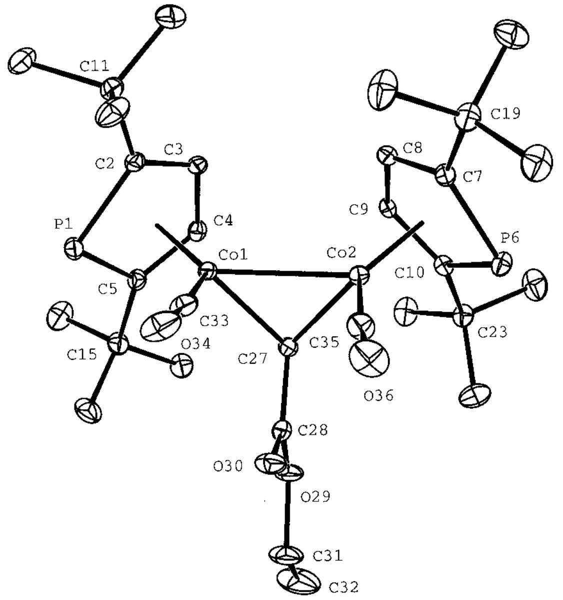
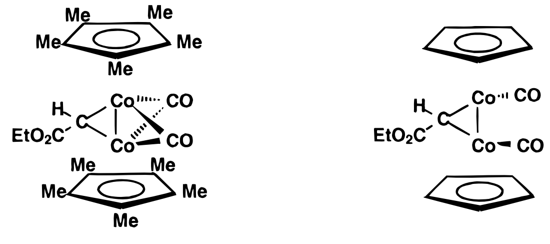


Figure 6. Molecular structure of **7**. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): Co(1)−Co(2), 2.5668(4); Co(1)−P(1), 2.3189(7); Co(2)−P(6), 2.3267(7); Co(1)−C(27), 1.933(2); Co(2)−C(27), 1.922(2); Co(1)−C(33), 1.735(3); Co(2)−C(35), 1.749(3); P(1)−C(2), 1.801(2); P(1)−C(5), 1.776(2); P(6)−C(7), 1.795(2); P(6)−C(10), 1.771(2); C(2)−C(3), 1.392(3); C(3)−C(4), 1.421(3); C(4)−C(5), 1.403(3); C(7)−C(8), 1.389(3); C(8)−C(9), 1.427(3); C(9)−C(10), 1.409(3); C(33)−O(34), 1.144(3); C(35)−O(36), 1.143(3); C(27)−C(28), 1.476(3); P(1)−C(2)−C(3), 110.7(2); C(2)−C(3)−C(4), 113.7(2); C(3)−C(4)−C(5), 113.8(2); C(4)−C(5)−P(1), 111.0(2); P(6)−C(7)−C(8), 111.5(2); C(7)−C(8)−C(9), 113.3(2); C(8)−C(9)−C(10), 113.1(2); C(9)−C(10)−P(6), 111.5(2); Co(2)−Co(1)−C(27), 48.08(7); Co(1)−Co(2)−C(27), 48.43(7); Co(1)−Co(2)−C(35), 98.81(9); Co(2)−Co(1)−C(33), 89.01(9); Co(1)−C(27)−O(28), 119.7(2); Co(2)−C(27)−C(28), 119.7(2); C(33)−Co(1)−Co(2)−C(35), 8.38(1); P(1)−Co(1)−Co(2)−P(6), −83.0(2).

Experimental Section

Materials and Methods. NMR spectra were recorded on Bruker AC 200 SY spectrometers operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external tetramethylsilane (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Elemental analyses were performed by the "Service de microanalyse du CNRS" at Gif-sur-Yvette, France. All reactions were performed under an atmosphere of dry nitrogen in solvents which were dried and degassed by standard methods. Silica gel (230−400 mesh) was used as received; reactions on a scale of 0.5 g employed columns 20 cm × 2 cm in diameter; those for smaller quantities were 6 cm × 1 cm unless otherwise stated. 2,2′,5,5′-Tetra-*tert*-butyl-1,1′-biphosphole was prepared from di-*tert*-butylbutadiyne and phenylphosphine according to the method described previously.[2a]



triply bridged   singly bridged

Figure 7.

(2,5-Di-*tert*-butylphospholyl)dicarbonylcobalt (1). A solution of 2,2′,5,5′-tetra-*tert*-butyl-1,1′-biphosphole (1.21 g, 3.10 mmol) and $Co_2(CO)_8$ (1.32 g, 3.86 mmol) was refluxed in hexane (60 mL). After 4 h an additional portion of $Co_2(CO)_8$ (0.5 g, 1.46 mmol) was added to the reaction mixture. After 7 h, when ^{31}P NMR indicated that no more biphosphole remained, the solution was reduced *in vacuo* to about 10 mL and the residue was purified by column chromatography (silica, pentane as eluent). **1** (1.6 g, 80%) was isolated as a red-orange oil. **1**: IR (hexane, cm^{-1}) ν(CO) 2023 (s), 1968 (s); ^{1}H NMR (C_6D_6) δ 5.12 [d, ^3J(H−P) = 4.2 Hz, 2H, C*H*], 1.07 (s, 18H, C*H*$_3$); ^{31}P{^{1}H} NMR (C_6D_6) δ −9.6; ^{13}C{^{1}H} NMR (C_6D_6) δ 204 (s, br, *C*O), 136.2 [d, ^1J(C−P) = 64 Hz, *C*P], 91.9 [d, ^2J(C−P) = 4 Hz, *C*H], 33.0 [d, ^3J(C−P) = 6 Hz, *C*H$_3$], 30.2 (s, *C*Me$_3$).

Complex **1** (0.030 g, 0.08 mmol) was dissolved in toluene (10 mL, degassed by freeze−pump−thaw cycles), and hex-3-yne (0.25 mL) was added. The solution was heated at 140 °C in a sealed tube for 3 days. The mixture was sampled and shown by ^{13}C{^{1}H} NMR and gas chromatography to have undergone *ca.* 40% conversion to hexaethylbenzene. Control experiments indicated no formation of hexaethylbenzene in the absence of catalyst under these conditions.

(2,5-Di-*tert*-butylphospholyl)(trimethyl phosphite)carbonylcobalt (2). Complex **1** (0.09 g, 0.28 mmol) was dissolved in octane (5 mL), and trimethyl phosphite (0.05 mL, 0.57 mmol) was added. The solution was heated at reflux for 4.5 h. The solvent and excess trimethyl phosphite were removed *in vacuo*, and the product was purified by chromatography (silica, pentane as eluent). Complex **2** (0.11 g, 90%) was isolated as an orange solid. **2**: ^{1}H NMR (C_6D_6) δ 5.14 (s, br, 2H, C*H*), 3.43 [d, ^3J(H−P) = 12.0 Hz, 9H, OC*H*$_3$], 1.29 (s, 18H, C*H*$_3$]; ^{31}P{^{1}H} NMR (C_6H_6) 176 [br, P(OMe)$_3$], −24.9 [d, ^2J(P−P) = 26 Hz, *P*C]; ^{13}C{^{1}H} NMR (C_6D_6) δ 208 (s, br, *C*O), 134.7 [d, ^1J(C−P) = 63 Hz, C*P*], 90.5 [d, ^2J(C−P) = 3 Hz, *C*H], 52.0 [d, ^2J(C−P) = 2 Hz, O*C*H$_3$], 34.3 [d, ^3J(C−P) = 6 Hz, *C*H$_3$], 33.8 [d, ^2J(C−P) = 13 Hz, *C*Me$_3$]; EIMS *m/z* (relative intensity) 406 (M$^+$, 58), 378 (M$^+$ − CO, 100). Anal. Calcd for $C_{16}H_{29}CoO_4P_2$: C, 47.29; H, 7.14. Found: C, 47.49; H, 7.11.

(2,5-Di-*tert*-butylphospholyl)(1,5-cyclooctadiene)cobalt (3). A photolysis glass outer jacket was charged with **1** (0.800 g, 2.58 mmol), 1,5-cyclooctadiene (0.4 mL, 3.26 mmol), and hexane (200 mL) under a nitrogen atmosphere. The solution was photolyzed and monitored by ^{31}P NMR. After 45 min the reaction was judged complete, and the solvent was removed on a rotary evaporator. The residue was purified by chromatography (silica, pentane as eluent). Complex **3** (0.84

g, 90%) was isolated as an orange solid. **3**: ^{1}H NMR (C_6D_6) δ 4.52 [d, J(H−P) = 4.4 Hz, 2H, C*H*], 4.02 (s, 4H, C*H*), 2.40 (m, 4H, C*H₂*), 1.67 (m, 4H, C*H₂*), 1.52 (s, 18H, C*H*$_3$); ^{31}P{^{1}H} NMR (C_6D_6) δ −19.6; ^{13}C{^{1}H} NMR (C_6D_6) δ 132.3 [d, ^1J(C−P) = 61 Hz,*C*P], 94.2 [d, J(C−P) = 5Hz, *C*H], 65.4 (s, *C*H), 34.5 [d, ^2J(C−P) = 14 Hz, *C*Me$_3$], 33.8 (s, *C*H$_3$), 32.2 (s, *C*H$_2$). EIMS *m/z* 362 (M$^+$). Anal. Calcd for $C_{20}H_{32}CoP$: C, 66.30; H, 8.84. Found: C, 66.08; H, 9.03.@@@

(2,5-Di-*tert*-butylphospholyl)(1,3-cyclohexadiene)-cobalt (4). A photolysis glass outer jacket was charged with **1** (0.330 g, 1.06 mmol), an excess of 1,3-cyclohexadiene (0.3 mL) and hexane (250 mL) under a nitrogen atmosphere. The solution was photolyzed and monitored by ^{31}P NMR. After 1 h, when the reaction was judged complete, the solvent was removed on a rotary evaporator. The residue was purified by chromatography on silica, using hexane as eluent. Complex **4** (0.260 g, 70%) was isolated as an orange solid. **4**: ^{1}H NMR (C_6D_6) δ 5.13 [d, ^3J(H−P) = 4.3 Hz, 2 H, C^{t}BuC*H*], 4.94 (m, 2H, C*H*), 3.40 (s, 2H, C*H*), 1.53 (m, 2H, C*H*$_a$H$_b$), 1.23 (s, 18H, C*H*$_3$), 0.86 (m, 2H, CH$_a$*H*$_b$); ^{31}P{^{1}H} NMR (C_6D_6) δ −33.0; ^{13}C{^{1}H} NMR (C_6D_6) δ 130.0 [d, ^1J(C−P) = 64 Hz, *C*P], 87.8 [d, ^2J(C−P) = 5 Hz, C^{t}Bu*C*H], 80.0 (s, *C*H), 56.5 (s, *C*H), 34.6 [d, ^2J(C−P) = 14 Hz, *C*Me$_3$], 33.9 [d, ^3J(C−P) = 6 Hz, *C*H$_3$], 26.4 (s, *C*H$_2$); EIMS *m/z* 334 (M$^+$). Anal. Calcd for $C_{18}H_{28}CoP$: C, 64.67; H, 8.38. Found: C, 64.66; H, 8.55.

(2,5-Di-*tert*-butylphospholyl)(1,2-diphenylcyclobuta-1,3-diene)cobalt (5). Complex **3** (0.030 g, 0.08 mmol) was dissolved in EtCN (10 mL), and phenylacetylene (0.25 mL) was added. The solution was heated at 120 °C in a sealed tube for 3 days to give a yellow solution. The volatiles were removed, and the yellow residue was chromatographed on silica. Elution with toluene/hexane (1:3) gave **5** (0.020 g, 50%) as a yellow solid. **5**: ^{1}H NMR ($CDCl_3$) δ 7.7−7.2 (m, 10H, Ph), 5.31 [d, ^3J(H−P) = 4.5 Hz, 2H, C^{t}BuC*H*], 4.59 (s, 2H, CPhC*H*), 0.96 (s, 18H, C*H*$_3$); ^{31}P{^{1}H} NMR ($CHCl_3$) δ −41.9; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 130.0 [d, ^1J(C−P) = 53 Hz, *C*P], 138−127 (m, Ph), 90.8 [d, ^2J(C−P) = 5 Hz, *C*H], 79.2 (s, *C*Ph), 58.3 (s, *C*HCPh), 34.2 [d, ^2J(C−P) = 13 Hz, *C*Me$_3$], 33.7 [d, ^3J(C−P) = 7 Hz, *C*H$_3$]. Anal. Calcd for $C_{28}H_{32}CoP$: C, 73.36; H, 6.99. Found: C, 73.20; H, 7.23.

Bis{2,5-di-*tert*-butylphospholyl}bis(μ-carbonyl)di-cobalt (6). A photolysis glass outer jacket was charged with **1** (1.66 g, 5.35 mmol) and pentane (150 mL) and photolyzed for 2.5 h under a nitrogen purge. The solvent was reduced to 20 mL *in vacuo*, and the solution was transfered *via* cannula onto a short degassed column comprising a silica plug (4 cm × 2 cm diameter). Rinsing with pentane afforded a trace of an orange compound, which was shown to be **1**, and further elution with toluene gave bright green **6** (1.18 g, 80%). **6**: IR (hexane, cm^{-1}) ν(CO) 1796 (s); ^{1}H NMR (C_6D_6) δ 5.34 [d, ^3J(H−P) = 3 Hz, 4H, C*H*], 0.86 (s, 36H, C*H*$_3$); ^{31}P{^{1}H} NMR 10.6; ^{13}C{^{1}H} NMR (C_6D_6) δ 260.5 (s, br, μ-*C*O), 129.5 [d, ^1J(C−P) = 53 Hz, *C*P], 98.6 [d,^2J(C−P) = 4 Hz, *C*H], 33.7 [d, ^2J(C−P) = 6.2 Hz, *C*Me$_3$], 33.0 [d, ^3J(C−P) = 6 Hz, *C*H$_3$]; EIMS *m/z* (relative intensity) 564 (M$^+$, 20), 536 (M$^+$ − CO, 30), 508 (M$^+$ − 2CO, 100). Anal. Calcd for $C_{26}H_{40}Co_2OP_2$: C, 55.33; H, 7.14. Found: C, 55.42; H, 7.15.

Bis{2,5-di-*tert*-butylphospholyl}-{μ-(ethoxycarbonyl)-methylene}dicarbonyldicobalt (7). Complex **6** (0.16 g, 0.28 mmol) was dissolved in pentane (20 mL), and excess ethyl diazoacetate (0.1 mL) was added. The solution was stirred for 30 min at room temperature, turning purple in color. The solvent was removed *in vacuo*, and the residue was chromatographed on silica. Elution with hexane gave a trace of orange **1**. Further elution with toluene/hexane (1:1) afforded **7** (0.16 g, 85%) as a purple solid, which was further purified by recrystallization from pentane. **7**: IR (hexane, cm^{-1}) ν(CO) 1995 (m), 1964 (s), 1734 (s); ^{1}H NMR (C_6D_6) (isomers, major: minor = 2:1) δ 4.1 (m, 2H, C*H₂*), 1.4−1.05 [m, 39H, C(C*H*$_3$)$_3$ and C*H*$_3$], (major isomer) 7.97 (s, 1H, C*H*CO$_2$Et), 5.58 (m, 2H, C*H*), 5.34 (m, 2H, C*H*), (minor isomer) 6.69 (s, C*H*CO$_2$Et), 5.86 (m, 2H, C*H*), 4.88 (m, 2H, C*H*); ^{31}P{^{1}H} NMR (C_6D_6) δ (major isomer) −18.3, (minor isomer) −16.8; ^{13}C{^{1}H} NMR (C_6D_6) δ 34.6−33.2 (m, *C*Me$_3$), 33.6−33.2 (m, *C*H$_3$), (major isomer) 183.5 (s, *C*O$_2$Et), 138.8 [d, ^1J(C−P) = 62 Hz, *C*P], 133.3 [d, ^1J(C−P) = 59 Hz, *C*P], 103.1 (s, *C*H), 102.0 (s, μ-*C*HCO$_2$Et), 98.7 [d, ^2J(C−P) = 15 Hz, *C*H], 59.7 (s, *C*H$_2$), 14.7(s, *C*H$_3$), (minor isomer) 181.5 (s, *C*O$_2$Et), 139.6 [d, ^1J(C−P) = 62 Hz, *C*P], 134.3 [d, ^1J(C−P) = 59 Hz, *C*P], 109.9 (s, μ-*C*HCO$_2$Et), 95.0 (s, *C*H), 93.4 [d, ^2J(C−P) = 15 Hz, *C*H], 59.8 (s, *C*H$_2$), 14.4 (s, *C* H$_3$); EIMS *m/z* (relative intensity) 653 (M$^+$ + 3, 1), 622 (M$^+$ − CO, 15), 594 (M$^+$ − 2CO, 100). Anal. Calcd for $C_{30}H_{46}Co_2O_4P_2$: C, 55.38; H, 7.12; N, 0. Found: C, 55.06; H, 6.81; N, 0.46.

Table 2. Crystal Data[a]

compound	**2**	**5**	**7**
formula	$C_{16}H_{29}CoO_4P_2$	$C_{28}H_{32}CoP$	$C_{30}H_{46}Co_2O_4P_2$
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	10.384(1)	9.297(1)	10.990(1)
b (Å)	16.252(2)	17.733(2)	19.808(2)
c (Å)	12.505(1)	14.180(2)	15.086(2)
β (deg)	108.80(1)	93.11(1)	97.05(1)
V (Å^3)	1997.67(71)	2334.40(89)	3259.2(1.1)
Z	4	4	4
d_{calc} (g/cm^3)	1.351	1.306	1.326
μ (cm^{-1})	10.3	8.1	11.4
F(000)	856	968	1368
no. of rflns included	4249	4628	5179
no. of params refined	324	271	343
unweighted R	0.028	0.056	0.029
weighted R	0.040	0.061	0.041
GOF	1.01	1.02	1.02
instrument instability factor, p	0.06	0.08	0.06

[a] Minimization function: $w(|F_o| - |F_c|)^2$, where $w = 4F^2/\sigma^2(F^2)$. Least-squares weights: $4F_o{}^2/\sigma^2(F_o{}^2)$, with $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$.

X-ray Structure Determinations. Crystal data were collected at −150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer in the range 2 ≤ 2q ≤ 60.0° using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structures were solved by direct methods and refined using the Enraf-Nonius MOLEN package. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while anisotropic temperature factors were used for all other atoms, using reflections with $F_o{}^2 > 3.0\sigma(F_o{}^2)$. Relevant crystallographic data are assembled in Table 2.

Supporting Information Available: Full tables of bond lengths, bond angles, and anisotropic thermal factors for **2**, **4**, and **7** and H atom coordinates for **2** (32 pages). Ordering information is given on any current masthead page.

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