

Synthesis and Characterization of New Binuclear Co(0) Complexes with Diphosphinoamine Ligands. A Potential Approach for Asymmetric Pauson–Khand Reactions

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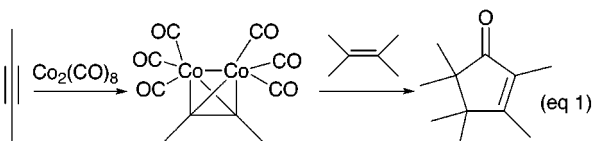
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The synthesis of P–N–P bidentate ligands and the evaluation, based on IR and X-ray data, of their π -acceptor properties in the complexes derived from phenylacetylene-dicobalt hexacarbonyl have been carried out. In addition, the reactivity of these complexes in the Pauson–Khand reaction has been examined.

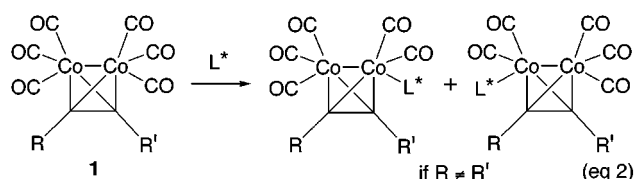
Introduction

Metal-mediated cyclization reactions have made significant contributions in organic synthesis.¹ One of the earliest and most useful of these is the Pauson–Khand reaction.² In this reaction, promoted by $\text{Co}_2(\text{CO})_8$, a cyclopentenone is formed through a formal [2 + 2 + 1] cycloaddition that involves an alkyne, an alkene, and carbon monoxide (eq 1).

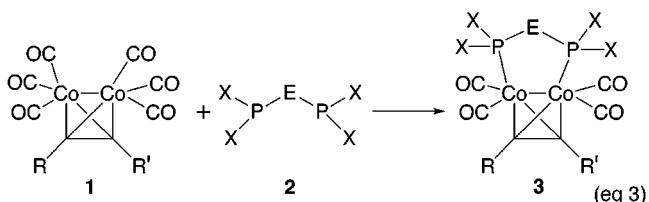


Considerable effort has been invested to develop asymmetric variants of this novel reaction.³ Among the different approaches examined, one of the most interesting appears to be that which involves complexes in which a carbon monoxide ligand in the dicobalt hexacarbonyl adducts is replaced by the chiral phosphine glyphos (eq 2, $\text{L}^* = \text{glyphos}$). The purified phosphine complexes react to afford the expected cyclopentenones with up to total enantioselectivity.⁴

Nonetheless, the approach is not of preparative value because of a major drawback, i.e., with this monodentate ligand, the formation of two diastereomeric complexes in roughly equimolar amounts results (except if $\text{R} = \text{R}'$). To circumvent this problem, C_2 bidentate ligands **2** (eq 3),



which if appropriately chosen would give rise to unique complexes, seemed to be of potential interest.



Diphosphorus compounds, having a single methylene group or an amino group between the two phosphorus atoms, have been used as chelating and bridging ligands to transition-metal centers.⁵ However, examples of the utilization of such ligands in the Pauson–Khand reaction are rare. A complex involving bis(diphenylphosphino)methane (dppm) **2a** (Chart 1) has been reported,⁶ but the authors found that the ligand had a deleterious effect on the yield of the Pauson–Khand reaction.

The Pauson–Khand reaction is a multistep process, but no definitive mechanistic pathway has been described to date. Nevertheless, from various observations⁷ it appears likely that before insertion the alkene coordinates to a cobalt atom, with the displacement of a carbon monoxide ligand. The ability of carbon monoxide, a ubiquitous ligand in organometallic chemistry,⁸ to stabilize transition-metal centers in low oxidation states is associated with its electron-withdrawing properties. The replacement of carbon monoxide in various complexes

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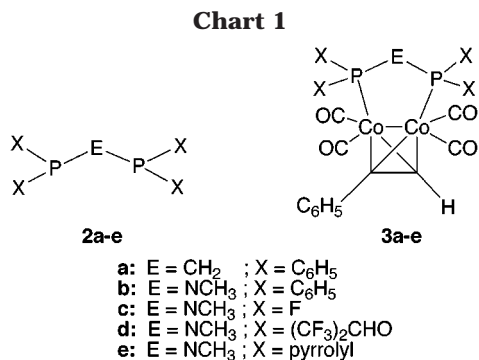
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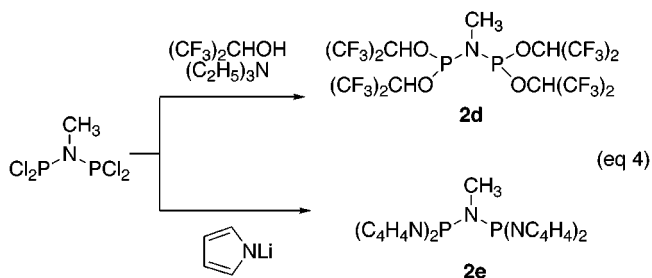


with a ligand, in particular a C₂ bidentate ligand⁹ having similar bonding characteristics, is potentially of considerable interest; unfortunately, however, the number of ligands with nearly the π -acceptor ability of carbon monoxide is rather small.¹⁰ Kündig and co-workers have recently reported one such C₂ ligand: two phosphorus centers bearing electron-withdrawing fluoro groups and linked by a *trans*-1,2-cyclopentane-1,2-diol-derived bridge.^{9b}

In this paper, we report the synthesis of new bidentate ligands with the backbone P–N–P, evaluate their π -acceptor properties in the complexes **3** (Chart 1), and describe the reactivity of these complexes in the Pauson–Khand reaction. We note in advance that the results obtained in these initial systems are expected to help in the design of effective chiral ligands for a new approach to asymmetric Pauson–Khand reactions.

Results and Discussion

Ligand Synthesis. Ligand **2a** is commercially available. Literature methods were used for the synthesis of ligands **2b**¹¹ and **2c**.¹² The diphosphorus compounds **2d** and **2e** were prepared (eq 4) through treatment of CH₃N–(PCl₂)₂ with (CF₃)₂CHOH in the presence of Et₃N and with N-lithiated pyrrole, respectively, and were purified by column chromatography on silica gel (**2d**, 50%, colorless oil; **2e**, 67%, colorless crystals).



The ³¹P NMR spectra of ligands **2b–e** each exhibited a singlet (apart from the P–F coupling in **2c**). We have assigned this resonance to the C_{2v} conformer (Figure 1)

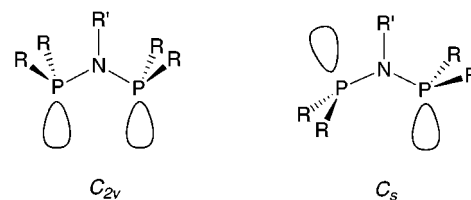


Figure 1. C_{2v} and C_s conformers of diphosphinoamines.

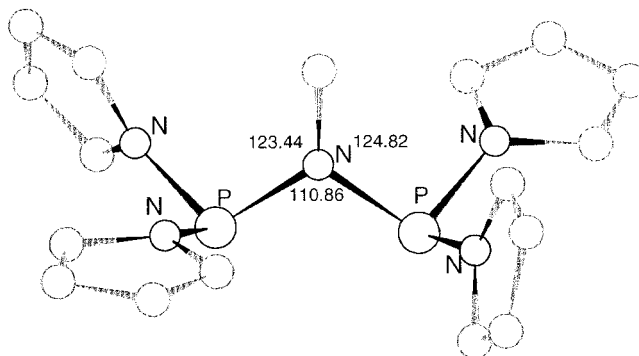


Figure 2. X-ray structure of ligand **2e** (selected angles in deg). Hydrogen atoms have been omitted for clarity.

on the basis of previously reported data.^{13a} Diphosphinoamines can also adopt a C_s conformation (Figure 1).¹³

In each, the lone pairs on N and P are orthogonal. NMR and electron and X-ray diffraction analyses¹⁴ show that in general the C_{2v} conformation is favored when the R and R' groups are relatively small, whereas the C_s conformation is preferred when the R and/or R' substituents are large. In **2b–e**, R and R' are rather small (R' = CH₃, R = C₆H₅, F, pyrrolyl, (CF₃)₂CHO), thus the C_{2v} conformation should in fact be preferred. X-ray diffraction studies of **2b** and **2e** (Figure 2) (**2d** has not yet been obtained in crystalline form) and an electron diffraction study of **2c**¹⁵ further support this conclusion. These studies also indicate partial double-bond character for the P–N bond in these ligands.^{13d}

In general, the P–N bond lengths reported in the literature¹⁶ for the diphosphinoamines lie in the 1.67–1.70 Å range (1.77 Å for a P–N single bond), and the P–N–P angles are in the 110–123° range. The important bond distances and angles in our ligands (Table 1) are in agreement with the literature values. Note the difference, however, between the P–C–P and P–N–P angles, which will be discussed below.

Crystallographic data for **2b** and **2e** are listed in Table 2. In **2b** and in **2e**, and by extrapolation in **2d**, the geometry around the phosphorus and nitrogen atoms is, respectively, pyramidal and almost planar.

Coordination of Co(0) Complex **1** (R = C₆H₅, R' = H) with Ligands **2a–e** To Give **3**. Complexes **3a–e**

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Table 1. Selected Bond Distances and Angles for Ligands 2a–c,e^a

ligand	P–E(Å)	P–E–P (deg)	P···P(Å)	symmetry	ref
2a	1.858	106.2	2.970	C_{2v}	17
2b	1.701(1), 1.704(1)	114.86(4)	2.8699(5)	C_{2v}	this work
2c	1.680	116.1	2.850	C_{2v}	14 ^b
2e	1.6991(9), 1.685(1)	110.89(5)	2.7874(7)	C_{2v}	this work

^a The esd's are given in parentheses. ^b By electron diffraction.

Table 2. Crystal Data, Data Collection Parameters and Refinement Conditions, and Results for Compounds 2b and 2e

formula	compound 2b	compound 2e
fw, g/mol	399.41	355.32
color/habit	colorless	colorless
dimensions, mm	0.48 × 0.48 × 0.45	0.45 × 0.42 × 0.42
<i>a</i> , Å	10.091(6)	7.594(3)
<i>b</i> , Å	10.002(2)	17.346(4)
<i>c</i> , Å	11.524(3)	14.106(2)
α, deg	90.00	90.00
β, deg	105.06(4)	98.74(2)
γ, deg	90.00	90.00
<i>V</i> , Å ³ ; <i>Z</i>	1123.2(7); 2	1836.5(8); 4
space group	$P2_1$	$P2_1/a$
<i>d</i> _{calc} , g/cm ³	1.181	1.28
μ(Mo Kα), cm ⁻¹	2.032	2.45
scan type	ω	ω
2θ max, deg	59.9	59.9
reflections:		
measd/unique	3596/3461	5717/5533
decay, %	no	0.5
with $F_o^2 > n\sigma(F_o^2)$	3084 (<i>n</i> = 1)	4034 (<i>n</i> = 2)
no. of variables	253	293
<i>R</i> / <i>R</i> _w ^a	0.032/0.039	0.033/0.046
fudge factor	0.030	0.035
extinction coeff	0.261 × 10 ⁻⁵	none

^a See Experimental Section.

Table 3. IR CO Frequencies for Complexes 3a–e

complex	<i>v</i> _{CO} (cm ⁻¹) ^a
3a	2020
3b	2020
3c	2065
3d	2061
3e	2042

^a Only highest CO stretch frequency is given.

were prepared by stirring **1** with **2a–e** in dry toluene at 70–80 °C until the starting complex **1** was consumed (1–3 h, TLC), followed by evaporation of the toluene under reduced pressure and purification of the residue by flash chromatography. All of the complexes are dark red, crystalline compounds, which can be easily recrystallized from ethanol and stored at –30 °C for several weeks. Despite the decreased nucleophilicity of the phosphorus atoms in the ligands **2c–e** in comparison with **2a,b**, the complexation yields were uniformly good: for **3a**, **3b**, **3c**, **3d**, and **3e**, 70% (lit. 67%⁶), 75%, 72%, 72%, and 58%, respectively. Furthermore, with the diphosphinoamines, complexes in which the ligand chelated one metal center were found, if at all, in only trace amounts. It is known that replacing the methylene group in dpmm with a small amino group increases the ligand's propensity to bridge two metal centers. This has been interpreted in terms of the ring-strain energy associated with the difference between the P–C–P and P–N–P angles in the free ligand and in the ligand coordinated to one metal center versus two.¹⁸

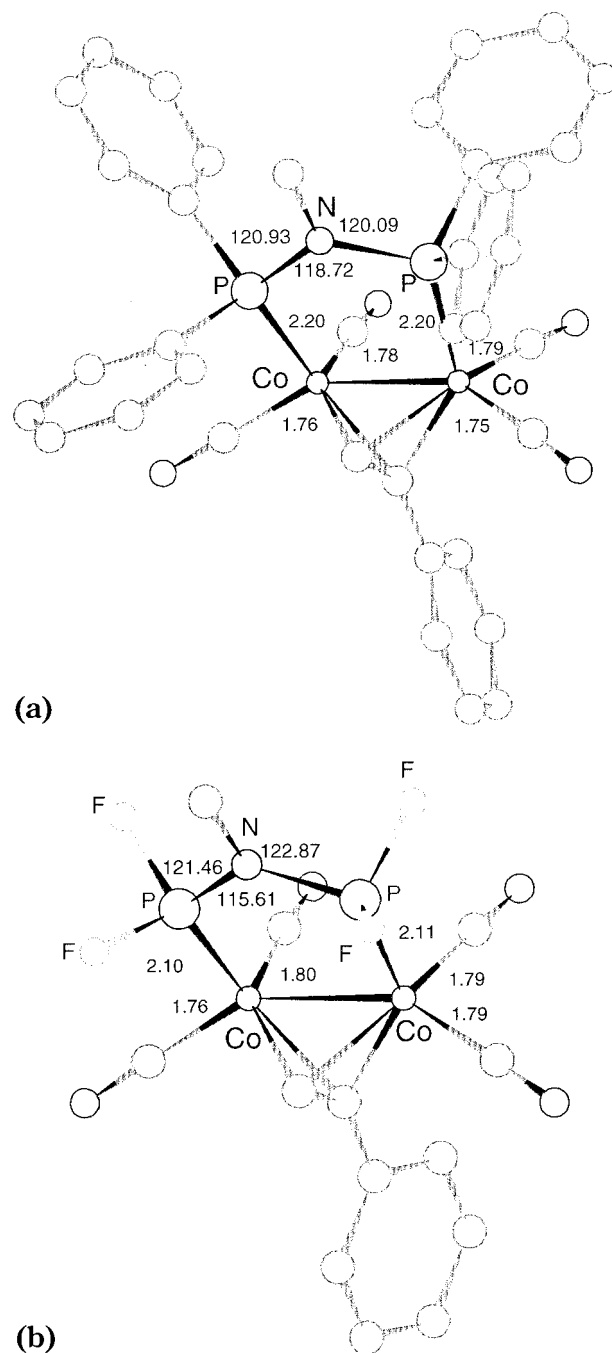


Figure 3. X-ray structure of complexes **3b** (a) and **3c** (b) (selected bond lengths in Å and angles in deg). Hydrogen atoms have been omitted for clarity.

The usefulness of the carbon monoxide infrared frequency to evaluate ligand electronic properties in complexes of this type has been recognized.⁸ The frequency is sensitive to changes in the electron density at the metal and reflects the extent of π -back-bonding into the carbon monoxide π^* orbital. The infrared spectra of complexes **3c–e** indicate, as expected, that the substituents on phosphorus act as electron-withdrawing groups. As shown in Table 3, the carbonyl frequencies are significantly higher than that with the phenyl substituent (**3b**) but

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Table 4. Crystal Data, Data Collection Parameters and Refinement Conditions, and Results for Compounds 3a–c

formula	compound 3a	compound 3b	compound 3c
fw, g/mol	716.44	731.45	499.03
color/habit	dark red	dark red	dark red
dimensions, mm	0.35 × 0.33 × 0.30	0.45 × 0.45 × 0.32	0.30 × 0.26 × 0.25
<i>a</i> , Å	40.127(6)	14.128(5)	7.166(2)
<i>b</i> , Å	12.434(3)	14.927(6)	9.205(3)
<i>c</i> , Å	14.716(2)	17.277(9)	28.231(9)
α, deg	90.0	90.00	90.0
β, deg	92.87(2)	110.70(4)	90.0
γ, deg	90.0	90.00	90.0
<i>V</i> , Å ³ ; <i>Z</i>	7333(2); 8	3408(3); 4	1862.2(9); 4
space group	<i>C2/c</i>	<i>P2₁/a</i>	<i>P2₁2₁2₁</i>
<i>d</i> _{calc} , g/cm ³	1.30	1.425	1.78
μ(Mo Kα), cm ⁻¹	10.27	11.07	20.09
scan type	ω	ω	ω
2θ max, deg	51.9	60.0	59.9
reflections:			
measd/unique	7112/6810	10 957/10 304	3114/3114
decay, %	0	7.085	0.0
with <i>F</i> _o ² > <i>nσ</i> (<i>F</i> _o ²)	2853 (<i>n</i> = 3)	6338 (<i>n</i> = 1)	2671 (<i>n</i> = 1)
no. of variables	406	532	236
<i>R</i> / <i>R</i> _w	0.034/0.043	0.046/0.037	0.040/0.048
fudge factor	0.030	0.020	0.035
extinction coeff	none	0.231 × 10 ⁻⁶	0.131 × 10 ⁻⁴

Table 5. Crystal Data, Data Collection Parameters and Refinement Conditions, and Results for Compounds 3d and 3e

formula	compound 3d	compound 3e
fw, g/mol	1091.16	691.39
color/habit	dark red	dark red
dimensions, mm	0.35 × 0.30 × 0.25	0.35 × 0.30 × 0.30
<i>a</i> , Å	10.611(2)	14.148(4)
<i>b</i> , Å	12.401(6)	13.928(4)
<i>c</i> , Å	15.960(4)	17.126(3)
α, deg	111.07(4)	90.0
β, deg	98.14(2)	111.54(2)
γ, deg	76.85(3)	90.0
<i>V</i> , Å ³ ; <i>Z</i>	1904.2(1.2); 2	3139(1); 4
space group	<i>P1</i>	<i>P2₁/a</i>
<i>d</i> _{calc} , g/cm ³	1.90	1.45
μ(Mo Kα), cm ⁻¹	11.19	12.00
scan type	ω	ω
2θ max, deg	59.9	49.9
reflections:		
measd/unique	9738/9210	5515/5515
decay, %	5.4	0.0
with <i>F</i> _o ² > <i>nσ</i> (<i>F</i> _o ²)	5632 (<i>n</i> = 2)	3051 (<i>n</i> = 2)
no. of variables	406	380
<i>R</i> / <i>R</i> _w	0.039/0.043	0.034/0.021
fudge factor	0.025	0.000
extinction coeff	none	0.996 × 10 ⁻⁷

lower than in the parent hexacarbonyl complex (2098 cm⁻¹). Most notable is the carbon monoxide stretch in **3c**, which is 45 cm⁻¹ higher than in **3b**. These shifts to higher frequency clearly indicate reduced electron density donation from cobalt to the carbonyl ligands.

Structural Studies of Complexes 3. To explore further the steric and electronic properties of these ligands, X-ray crystallographic determinations have been carried out. Views of the complexes **3b** and **3c** are shown in Figure 3. Crystallographic data for **3a–c** and **3d,e** are listed in Tables 4 and 5, respectively. Relevant bond lengths and angles are listed in Table 6. The electronic effects of the ligands can be evaluated through examination of the structural parameters of the complexes in the solid state. Furthermore, by comparison of the structures of free ligands **2** with the structures of the same ligands in the complexes **3**, it is possible to gain insight into the

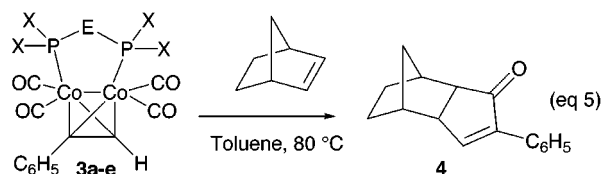
parameters that may influence the efficiency of the complexation process (apart from nucleophilicity).

1. Effect of the Electronic Properties of the Ligand. Bond lengths involving cobalt are of particular interest. Indeed, complexes **3c–e** have Co–P bonds lengths that are shorter than in **3b**. The shift toward shorter Co–P bonds is fully consistent with the IR data for these electron-deficient phosphorus-containing complexes. Although phosphorus in these complexes is a poor σ-donor, the shortened Co–P distance indicates that there is enhanced π-back-bonding from cobalt to phosphorus. As might be expected, **3c–e** possess Co–C(CO) bonds that are longer than those in **3b**, carbon monoxide now being more seriously challenged by the diphosphinoamine ligands as the π-acceptor.

2. Effect of Structural Parameters on the Efficiency of the Complexation. From the crystallographic data, it is possible to evaluate the distortion from their normal geometries the ligands experience on bridging the two cobalt atoms. The amount of distortion determines, at least in part, the difficulty of complexation¹⁸ and thus should roughly correlate with the efficiency of the latter process (for invariable nucleophilicity). It can be assumed that the smaller the difference between the P–E–P angle in the free ligand and in the bridged complex, as with the P···P distance, the more favorable the complexation. The differences in the measured values are reported in Table 7.

From these values, it is possible to understand why **2c** despite its low nucleophilicity in comparison with **2a,b** is, in fact, a good bridging ligand and **2e**, which exhibits the largest Δ(P–E–P), is a relatively poor one.

Reactivity of Complexes 3 in the Intermolecular Pauson–Khand Reaction. Norbornene was used to evaluate the reactivity of the complexes **3c–e** (eq 5). A stirred solution of the complex and norbornene (5 equiv) in dry toluene was heated at 80 °C for 3–5 days (disappearance of **3** monitored by TLC). After evaporation of the solvent under reduced pressure, the crude product was purified by flash chromatography to give the expected adduct, 3a,4,5,6,7,7a-hexahydro-4,7-methano-2-phenyl-1*H*-inden-1-one (**4**), in 24% from **3a**, 65% from **3b**, 92% from **3c**, >98% from **3d**, and 90% from **3e**.



Our results show that complexes **3c–e** are highly effective in the Pauson–Khand reaction, giving excellent yields of the cyclopentenone product **4** in comparison with the reaction of the dicobalt hexacarbonyl complex under purely thermal conditions (toluene, 110 °C, 58%).^{4c} The complex **3c** has also been treated with the less reactive alkene indene (toluene, 110 °C, 5 days) to give the expected product in 72% yield, which compares favorably with the best literature¹⁹ yield for this reaction (52%, toluene, 110 °C, 5 h).

The relatively long reaction times with complexes **3c–e** may reflect the strengthening of the Co–CO bonds in the

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Table 6. Selected Bond Distances and Angles for Complexes **3a–e**^a

complex	P–Co	Co–C _(CO)	C–O _(CO)	Co–Co	P···P	E–P–Co	P–E–P
3a	2.225(1)	1.759(6)	1.138(6)	2.4776(9)	3.012(2)	108.4(1)	110.9(2)
	2.227(1)	1.781(6)	1.125(6)				
		1.788(6)	1.131(6)				
		1.762(5)	1.134(6)				
3b	2.2018(7)	1.759(2)	1.137(2)	2.4451(4)	2.9280(8)	112.00(6)	118.7(1)
	2.1958(9)	1.777(2)	1.144(3)				
		1.754(2)	1.141(3)				
		1.792(3)	1.136(3)				
3c	2.104(1)	1.802(4)	1.134(5)	2.4397(6)	2.799(1)	116.9(1)	115.6(2)
	2.109(1)	1.763(4)	1.129(5)				
		1.794(4)	1.129(5)				
		1.789(4)	1.129(5)				
3d	2.1301(7)	1.783(3)	1.135(4)	2.4434(5)	2.8545(9)	114.02(8)	118.0(1)
	2.1498(7)	1.787(3)	1.125(4)				
		1.804(3)	1.127(4)				
		1.779(3)	1.131(3)				
3e	2.154(1)	1.776(3)	1.139(4)	2.4287(6)	2.856(1)	113.68(9)	116.7(1)
	2.152(1)	1.755(3)	1.138(3)				
		1.792(3)	1.126(4)				
		1.743(3)	1.145(3)				

^a Bond lengths X–Y are given in Å and angles X–Y–Z in degrees. The esd's are in parentheses.

Table 7. Differences of Angles (P–E–P) and P···P Distances in Free and Complexed Ligands **2a–c,e**

ligand ^a	Δ(P–E–P) (deg)	Δ(P···P) (Å)
a (67%)	4.9	0.04
b (75%)	3.8	0.05
c (72%)	0.3	0.05
e (58%)	5.4	0.07

^a Yields of complexation given in parentheses.

complexes as the result of decreased back-bonding to the phosphorus ligands compared with carbon monoxide in the parent complex.²⁰ Steric and electronic factors though appear to combine to extend the effective lifetimes of the complexes by reducing their tendency toward clusterization²¹ and thereby allow the significantly improved yields to be attained.

In conclusion, in this study new bidentate P–N–P ligands have been designed so as to provide efficiently bridged complexes with dicobalt hexacarbonyl-acetylene. The derived complexes, as expected, manifest useful levels of reactivity, between that of the uncomplexed but reactive dicobalt hexacarbonyl intermediate and the complexed but unreactive bis(diphenylphosphino)methane derivative. This provides an excellent opportunity for asymmetric synthesis, and our preliminary results appear to bear this out: (+)- α -methylbenzylamine in place of methylamine in the ligand **2b**²² affords the norbornene adduct in 54% yield and with a small, but encouraging, 16% enantiomeric excess. Efforts to attain a practical induction level and yield through the use of other chiral amines and electron-withdrawing groups on phosphorus, as well as the study of other potential approaches to this important reaction (e.g., placing chiral groups on phosphorus), are being actively pursued in our laboratory.

(20) ¹³CO exchange experiments and theoretical studies are planned to examine this and other possible interpretations. We thank a referee for having suggested exchange experiments.

(21) Reduced tendency toward clusterization could eventually permit a catalytic version of the above chemistry; see: Lee, B. Y.; Chung, Y. K.; Jeong, N.; Lee, Y.; Hwang, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 8793; Lee, N. Y.; Chung, Y. K. *Tetrahedron Lett.* **1996**, *37*, 3145.

(22) A known, easily available chiral PNP ligand; see: Kamalesh Babu, R. P.; Krishnamurthy S. S.; Nethaji, M. *Tetrahedron: Asymmetry* **1995**, *6*, 427.

Experimental Section

Toluene and diethyl ether were distilled from sodium–benzophenone, and triethylamine and pyrrole were distilled from CaH₂ prior to use. Elemental analyses were performed by the Service Central d'Analyse du CNRS. Melting points are uncorrected. CH₃N(PF₂)₂, CH₃N(P(C₆H₅)₂)₂, and CH₃N(PCl₂)₂ were prepared according to literature procedures.^{11,12} Bis-(diphenylphosphino)methane (dppm, Aldrich) and dicobalt octacarbonyl (Fluka) were used as received.

***N,N*-Bis[di(1,1,1,3,3,3-hexafluoroisopropoxy)phosphino]-*N*-methylamine (2d).** To a solution of 1,1,1,3,3,3-hexafluoroisopropanol (2.1 mL, 20 mmol) and triethylamine (2.8 mL, 20 mmol) in 30 mL of ether at 0 °C was added a solution of CH₃N(PCl₂)₂ (932 mg, 4.0 mmol) in 5 mL of ether. After being allowed to warm to 20 °C, the mixture was refluxed for 4 h. The precipitate was filtered and washed with ether. After removal of the solvent under reduced pressure, the product was isolated by dry column chromatography with silica gel pretreated with 2.5% (v/v) of triethylamine (ethyl acetate/hexane, 5/95) to yield 1.48 g (49%) of colorless liquid: ¹H NMR (200 MHz, CDCl₃) δ 2.80 (t, $J_{\text{H-P}} = 3.8$ Hz, 3 H), 4.55 (hept, $J_{\text{H-F}} = 5.5$ Hz, 4 H); ³¹P NMR (81 MHz, CDCl₃) δ 153; IR 1373, 1297, 1202, 1109, 690 cm⁻¹. Anal. Calcd for C₁₃H₇F₂₄N₂O₄P₂: C, 20.56; H, 0.92; N, 1.84. Found: C, 20.66; H, 1.21; N, 2.00.

***N,N*-Bis(dipyrrolylphosphino)-*N*-methylamine (2e).** To a solution of pyrrole (1.4 mL, 20 mmol) in 20 mL of ether cooled to –78 °C under argon was added 8.7 mL of *n*-butyllithium (2.3 M/hexane, 20 mmol) dropwise. After the addition was complete, the solution was stirred at –78 °C for 1 h, whereupon CH₃N(PCl₂)₂ (932 mg, 4.0 mmol) in 4 mL of ether was added dropwise. The reaction mixture was then allowed to warm to 20 °C and stirred for an additional 12 h. The greenish precipitate was filtered, and the filtrate was concentrated under reduced pressure to leave the crude product, which was recrystallized from hexane to yield 950 mg (67%) of white solid: mp 116–119 °C; ¹H NMR (200 MHz, CDCl₃) δ 2.74 (t, $J_{\text{H-P}} = 3.4$ Hz, 3 H), 6.38 (t, $J_{\text{H-H}} = 2$ Hz, 8 H), 6.75 (t, $J_{\text{H-H}} = 2$ Hz, 8 H); ³¹P NMR (81 MHz, CDCl₃) δ 92.5; IR 1457, 1240, 1184, 1067, 815, 736 cm⁻¹. Anal. Calcd for C₁₇H₁₉N₅P₂: C, 57.47; H, 5.39; N, 19.71. Found: C, 57.46; H, 5.33; N, 19.98.

General Procedures for the Preparation of the Cobalt Complexes 3. To a solution of 188 mg (0.55 mmol) of dicobalt octacarbonyl in 4 mL of hexane at 20 °C was added 55 μ L (51 mg, 0.5 mmol) of phenylacetylene. The resulting mixture was stirred for 1 h, whereupon the solvent was removed under reduced pressure and the resulting crude product was purified by silica gel chromatography with pentane to yield 179 mg (92%) of the brown phenylacetylene-dicobalt hexacarbonyl complex.

Complexes **3** were prepared by warming (70–80 °C) a toluene solution (4 mL) of the phenylacetylene-dicobalt hexacarbonyl complex (0.5 mmol) with the appropriate ligand (0.45 mmol) until TLC indicated disappearance of the initial complex (1–3 h). After removal of the solvent, the crude product was purified by dry column silica gel chromatography (ethyl acetate/hexane, 5/95).

μ -[N,N-Bis(diphenylphosphino)-N-methylamine]tetracarbonyl- μ -[η^2 : η^2 -phenylacetylene]dicobalt (3b**):** ¹H NMR (200 MHz, CDCl₃) δ 2.25 (t, $J_{\text{H-P}} = 4.8$ Hz, 3 H), 5.37 (t, $J_{\text{H-P}} = 8.6$ Hz, 1 H), 7.1–8.0 (m, 25 H); ³¹P NMR (81 MHz, CDCl₃) δ 114.6; IR 2020, 1991, 1969 cm⁻¹; MS (FAB⁺) m/z 704 (3.7%, M⁺ – CO), 663 (13%), 648 (24%, M⁺ – 3CO), 620 (18.7%, M⁺ – 4CO), 432 (100%). Anal. Calcd for C₃₇H₂₉Co₂NO₄P₂: C, 60.75; H, 3.99; N, 1.91. Found: C, 60.89; H, 4.12; N, 2.04.

μ -[N,N-Bis(difluorophosphino)-N-methylamine]tetracarbonyl- μ -[η^2 : η^2 -phenylacetylene]dicobalt (3c**):** ¹H NMR (200 MHz, CDCl₃) δ 2.88 (t, $J_{\text{H-P}} = 6.1$ Hz, 3 H), 6.07 (t, $J_{\text{H-P}} = 10.6$ Hz, 1 H), 7.25–7.40 (m, 3 H), 7.50–7.65 (m, 2 H); ³¹P NMR (81 MHz, CDCl₃) δ 170 (t broad, $J_{\text{P-F}} = 1100$ Hz); IR 2065, 2031, 2011 cm⁻¹; MS (FAB⁺) m/z 499 (8.7%, M⁺), 471 (100%, M⁺ – CO). Anal. Calcd for C₁₃H₉Co₂F₄NO₄P₂: C, 31.29; H, 1.81; N, 2.80. Found: C, 31.31; H, 1.71; N, 2.71.

μ -[N,N-Bis(di(1,1,1,3,3,3-hexafluoroisopropoxy)phosphino)-N-methylamine]tetracarbonyl- μ -[η^2 : η^2 -phenylacetylene]dicobalt (3d**):** ¹H NMR (200 MHz, CDCl₃) δ 2.81 (t, $J_{\text{H-P}} = 6.1$ Hz, 3 H), 4.70 (hept, $J_{\text{H-F}} = 5.5$ Hz, 2 H), 4.89 (hept, $J_{\text{H-F}} = 5.5$ Hz, 2 H), 5.70 (t, $J_{\text{H-P}} = 12$ Hz, 1 H), 7.38 (m, 3 H), 7.64 (m, 2 H); ³¹P NMR (81 MHz, CDCl₃) δ 181.5; IR 2061, 2037, 2015 cm⁻¹; MS (FAB⁺) m/z 1063 (6.5%, M⁺ – CO), 1035 (11.6%, M⁺ – 2CO), 1007 (2%, M⁺ – 3CO), 979 (14%, M⁺ – 4CO), 586 (100%). Anal. Calcd for C₂₅H₁₃Co₂F₂₄NO₈P₂: C, 27.51; H, 1.20; N, 1.28. Found: C, 27.61; H, 1.18; N, 1.48.

μ -[N,N-Bis(dipyrrolylphosphino)-N-methylamine]tetracarbonyl- μ -[η^2 : η^2 -phenylacetylene]dicobalt (3e**):** ¹H NMR (200 MHz, CDCl₃) δ 2.50 (t, $J_{\text{H-P}} = 5.8$ Hz, 3 H), 5.51 (t, $J_{\text{H-P}} = 11$ Hz, 1 H), 6.42 (t, $J_{\text{H-H}} = 2$ Hz, 4 H), 6.45 (t, $J_{\text{H-H}} = 2$ Hz, 4 H), 6.87 (q, $J_{\text{H-H}} = 2$ Hz, 4 H), 6.98 (q, $J_{\text{H-H}} = 2$ Hz, 4 H), 7.22–7.34 (m, 3 H), 7.50–7.60 (m, 2 H); ³¹P NMR (81 MHz, CDCl₃) δ 132.1; IR 2042, 2016, 1998 cm⁻¹; MS (FAB⁺) m/z 687 (1%, M⁺), 659 (13%, M⁺ – CO), 631 (2%, M⁺ – 2CO), 603 (32%, M⁺ – 3CO), 575 (100%, M⁺ – 4CO). Anal. Calcd for C₂₉H₂₅Co₂N₅O₄P₂: C, 50.67; H, 3.66; N, 10.18. Found: C, 50.74; H, 3.91; N, 9.96.

General Procedure for the Pauson–Khand Reaction.

A solution of the complex **3** (0.2 mmol) and norbornene (1 mmol) in 4 mL of toluene was heated at 80 °C for 3–5 days (until no starting complex remained). After removal of the solvent, the crude mixture was purified by dry column silica

gel chromatography (ethyl acetate/hexane, 5/95) to yield **3a,4,5,6,7,7a-hexahydro-4,7-methano-2-phenyl-1H-inden-1-one** (**4**).²³

Crystallographic Studies. Single-Crystal X-ray Diffraction. The main crystallographic features for the seven compounds examined are gathered in Tables 2, 4, and 5. All of the X-ray single-crystal data reported in the present study were collected on an Enraf-Nonius CAD4 four-circle diffractometer operating with Mo K α radiation, monochromated with a graphite plate. All measurements were run at room temperature. In all cases, the accurate unit-cell dimensions were obtained by least-squares refinements of angular data of 25 reflections centered in a range of 20–24° (2 θ). The stability of the experimental setup and crystal integrity were monitored by measuring two standard orientation reflections every 400 measurements and two standard intensity reflections every 2 h. Eventual intensity decays are reported. No absorption correction was made. All structures were solved by using the direct methods of the teXsan software package.²⁴ When possible, the secondary extinction was taken into account and the various values of the coefficients are given. All non-hydrogen atoms were refined anisotropically. The complete data-collection parameters and details of the structure solution and refinement for all compounds are given in Tables 2, 4, and 5. In all cases, the following formulae were used for refinements:

$$R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$$

$$\text{with } w = [\sigma^2(F_o) + p^2/4|F_o|^2]^{-1}$$

The final atomic coordinates, temperature factors, and their estimated standard deviations are deposited as Supporting Information.

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Supporting Information Available: Listings of atomic positional and thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(23) Reg. No. [122986-92-9]; see: Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977.

(24) *teXsan: Single-Crystal Structure Analysis Software*, Version 1.7; Molecular Structure Corporation: The Woodlands, TX, 1995.