Tris(pyrrolyl)phosphine-Substituted Acetylene−Dicobaltcarbonyl Complexes: Syntheses, Structural Characterization, and Reactivity Studies

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Received November 22, 1999

The first tris(pyrrolyl)phosphine-substituted alkyne−dicobaltcarbonyl complexes have been prepared by reaction of the corresponding dicobalthexacarbonyl complexes with tris(pyrrolyl)-phosphine, and their solid-state structures have been studied by X-ray diffraction. In accordance with the strong π-acceptor character of the tris(pyrrolyl)phosphine ligand, these complexes present a Pauson−Khand reactivity very similar to that of the parent, unsubstituted ones. On the other hand, the cobalt-stabilized propargyl cations derived from tris-(pyrrolyl)phosphine-substituted (2-propynol)dicobaltcarbonyl complexes undergo an unprecedented intramolecular Nicholas reaction in which one of the pyrrole rings acts as an internal nucleophile, and that gives rise to a new structural type of chelated alkyne−dicobaltcarbonyl complexes.

Introduction

Trivalent phosphorus derivatives (phosphines or phosphites) find wide application in coordination chemistry, organometallic chemistry, and homogeneous catalysis.[1] Smooth variation of the steric or electronic characteristics of the phosphorus substituents allows the modulation of the character (σ-donor, π-acceptor) of these ligands; this fact has stimulated research in this area toward the preparation of new ligands with designed properties.

Phosphine-substituted alkyne−dicobaltcarbonyl complexes[2] have been studied in connection with two important synthetic processes: the Pauson−Khand[3] and Nicholas[4] reactions. Both achiral[5] and chiral[6] phosphines have been investigated, the latter in the context of the development of enantioselective versions of these reactions. However, the substitution of a carbon monoxide by a phosphine ligand is usually accompanied by a loss of reactivity of the corresponding complexes.

Billington and Pauson[7] have employed a variety of substituted alkyne−dicobaltcarbonyl complexes in Pauson−Khand reactions using 2,5-dihydrofuran as a

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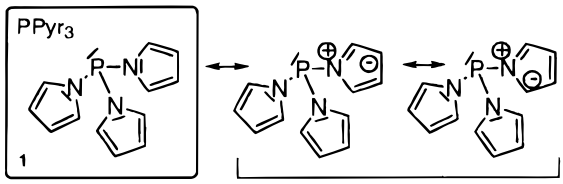
10.1021/om990914y CCC: $19.00
Publication on Web 04/06/2000

typically reactive alkene. In every case, replacement of carbonyl by phosphine (PPh_3, PBu_3) or phosphite ($P(OPh)_3$, $P(OMe)_3$) ligands resulted in reduced product yields and/or strongly diminished reaction rates. Complexes arising from the moderately diastereoselective substitution of a carbon monoxide of the phenylacetylene−dicobalthexacarbonyl complex by an optically active phosphine like (*R*)-glyphos have been used, after diastereomer separation, as starting materials for enantioselective intermolecular Pauson−Khand reactions.[6a−c] The scope of this approach remains however very limited, since the mixtures of phosphine-substituted complexes can be separated only with difficulty (HPLC) and exhibit again a low reactivity, so that epimerization processes take place concurrently with the desired Pauson−Khand reaction when using less strained olefins. Recently, Laschat and co-workers have found that alkyne-dicobaltcarbonyl complexes substituted with bridging bidentate phosphines (dppm, dppe, (*R*)-Binap) are completely unreactive in their attempted Pauson−Khand reactions with norbornene.[6e] The search for new phosphorus-based ligands that do not diminish the Pauson−Khand reactivity of alkyne−dicobaltcarbonyl complexes is therefore of great interest.

The reaction of dicobalthexacarbonyl-stabilized propargylium ions, the Nicholas cations,[4] with a variety of nucleophiles[8−12] is a versatile synthetic process that can lead to the formation of either carbon−carbon or carbon−heteroatom bonds. Among others, electron-rich benzenes[13] and indoles[14] have been used as carbon nucleophiles. Some examples of intramolecular Nicholas reactions have also been reported.[15] With the aim of developing asymmetric coupling reactions of Nicholas cations, the reaction of several phosphines with chiral propargyl alcohol−dicobalthexacarbonyl complexes has been described.[5b,16] However, except for the case of the strongly π-accepting tris(1,1,1,3,3,3-hexafluoroisopropyl)phosphite ligand,[16b] cobalt-substituted Nicholas cations show a highly reduced electrophilicity[17] and are unreactive toward mild nucleophiles. In conclusion, the number of phosphine or phosphite ligands approaching the π-accepting ability of carbon monoxide and that can therefore replace it in alkyne−dicobaltcarbonyl complexes without detrimental effects on the reactivity is still very limited.

In the search for a new π-acceptor ligand in acetylene−dicobaltcarbonyl complexes, we have taken a look at tris(pyrrolyl)phosphine ($PPyr_3$, **1**), a compound that has been known for more than 25 years.[18,19] However, only from 1995 has its coordination chemistry[20] been studied. The structure of a great number of complexes containing **1** as a ligand has been determined,[20,21] and in addition to the structural studies, a variety of spectroscopic, kinetic,[22] and thermochemical[23] measurements have shown that **1** is an exceptional π-acceptor (and a very poor σ-donor) phosphine ligand. This characteristic is best illustrated by the low-energy resonance forms II (which account for the aromaticity of the pyrrole rings), which place a positive charge in the nitrogen (Scheme 1). The ligand **1** is most conveniently prepared by direct reaction of pyrrole with PCl_3 in the presence of Et_3N.[20]

Scheme 1. General Structure and Resonance Forms of Tris(pyrrolyl)phosphine 1



There are only a few studies on the use of coordination complexes with **1** in catalytic processes, which include olefin coupling, hydroformylation, and hydrogenation reactions.[20,24] However, no examples of tris(pyrrolyl)-phosphine-substituted alkyne−dicobaltcarbonyl complexes can be found in the literature.[25] We report herein

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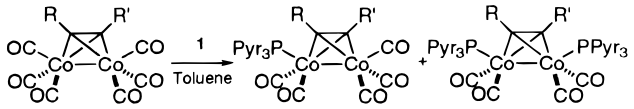
Table 1. Preparation of Complexes 5−9

	initial complex			reaction conditions			final products			
entry		R	R′	molar ratio[a]	*T* (°C)	time (h)	yield (%)		yield (%)	
1	**2**	Ph	H	1.1	70	1	**5**	51	**7**	22
2	**2**	Ph	H	1.5	70	0.75	**5**	67	**7**	21
3	**3**	CH_2OH	H	1.0	75	6	**6**	52	**8**	12
4	**3**	CH_2OH	H	0.56	75	6	**6**	22	**8**	59
5	**4**	CH(OH)Et	Ph	1.1	75	3	**9a/9b**	76[b]		

[a] Molar ratio: initial complex/$PPyr_3$ **1**. [b] Diastereomeric ratio **9a**/**9b**, 2.8/1. Conditions for the determination of the diastereomeric purity of **9a** and **9b** by HPLC analysis: CHIRALCEL OD (25 cm) column, 1% isopropyl alcohol−99% hexane, 0.5 mL/min, 30 °C, $\lambda = 254$ nm, $P = 14$ bar. t_R(**9a**): 10.45 min; t_R(**9b**): 10.05 min; t_R(**4**): 14.03 min.

Scheme 2. Preparation of Tris(pyrrolyl)phosphine-Substituted Alkyne−Dicobaltcarbonyl Complexes



2 R= Ph; R'=H **5** **7**
3 R= CH_2OH; R'=H **6** **8**
4 R= Ph, R'= $CH(OH)CH_2CH_3$ **9a,b**

the first syntheses of this type of complexes and their characterization by X-ray diffraction analysis and by IR spectroscopy, and we describe their use in the Pauson−Khand reaction. We also disclose the first example of the trapping of a cobalt-stabilized propargyl cation by a ligand through an intramolecular Nicholas reaction.

Results and Discussion

Synthesis of Acetylene−Dicobaltcarbonyl Complexes Containing Tris(pyrrolyl)phosphine Ligands. The preparation of tris(pyrrolyl)phosphine-substituted alkyne−dicobaltcarbonyl complexes is summarized in Scheme 2 and Table 1. The reaction of a slight excess (1.1 molar equiv) of the phenylacetylene−dicobalthexacarbonyl complex **2** with tris(pyrrolyl)-phosphine **1** in hot toluene gave a 2.3/1 mixture of mono- (**5**) and disubstituted (**7**) complexes, which were easily separated by column chromatography (entry 1). When 1.5 equiv of **2** were used (entry 2), both the global reaction yield and the **5**/**7** ratio increased. In a similar way (entry 3), the reaction of the propargyl alcohol complex **3** with 1.0 molar equiv of **1** gave a 4.3/1 mixture of monosubstituted and disubstituted complexes (**6** and **8**, respectively). In this case, the complexes were not separable by chromatography. Purification was achieved by the complete and totally selective crystallization of **8** from a hexane solution of the reaction mixture. The treatment of **3** with 1.8 equiv of **1** led to a significant increase in the amount of **8** formed (entry 4). As a matter of fact, the formation of disubstituted complexes could only be suppressed by the use of a more hindered alkyne complex (entry 5). It is therefore clear that monosubstituted complexes **5** and **6** still exhibit an appreciable reactivity toward **1**. This behavior contrasts with that of acetylene−dicobaltcarbonyl complexes containing aryl or alkyl phosphines, which in general show less tendency to give further substitution; for instance, the reaction of **2** with triphenylphosphine under the conditions of entry 1 gave only traces of the disubstituted complex. Since a number of studies[20] have shown that **1** is isosteric with triphenylphosphine, the difference in reactivity between these two ligands is almost certainly due to electronic reasons.

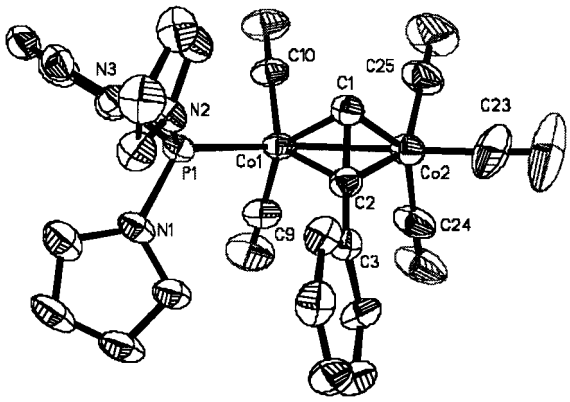


Figure 1. Crystal structure of **5**. Hydrogen atoms have been omitted for clarity.

Complexes **5**, **7**, and **8** are crystalline solids. The structures of **5** and **7** were unambiguously determined by X-ray diffraction. The structures of **6** and **8** were assigned by comparison of their spectral data with those of **5** and **7**. In the ^{1}H NMR spectrum, the acetylenic proton of the monosubstituted complexes **5** and **6** appears as a doublet by coupling with one phosphorus atom, while in the disubstituted complexes **7** and **8** it gives a triplet by coupling with two phosphorus atoms. Very few differences can be appreciated between the ^{31}P NMR spectra of the mono- and disubstituted complexes, a singlet at δ = ca. 127 ppm being observed in both cases.

In complex **4**, the cobalt atoms are diastereotopic, so that a preference in the ligand coordination to one or another cobalt can be observed. The reaction of **4** with **1** gives two diastereomers (**9a** and **9b**) in a 2.8:1 ratio, determined by HPLC. This diastereoselectivity is sensibly higher than that usually observed in the reaction of related propargyl complexes with triphenylphosphine.[16a]

Molecular Structure of 5 and 7. For the accurate determination of the structure and in order to explore the steric and electronic properties of the tris(pyrrolyl)-phosphine ligand, X-ray crystallographic analyses were carried out. Single crystals of **5** and **7** were obtained by crystallization from hexane. Perspective views of the complexes **5** and **7** are shown in Figures 1 and 2, respectively; hydrogen atoms have been omitted for clarity. Relevant crystallographic data, bond distances, and angles are given in Tables 2−5. In the case of **5** the unit cell contains two crystallographically independent molecules of the complex, which show slight differences in the relative orientations of the pyrrolyl groups.

In both **5** and **7**, the tris(pyrrolyl)phosphine moieties occupy axial coordination positions around the metal, trans to the cobalt−cobalt bond, and appear to undergo

Table 2. Crystal Data and Structure Refinement for Complexes 5, 7, and 15

	5	7	15
formula	$C_{25}H_{18}Co_2N_3O_5P$	$C_{36}H_{30}Co_2N_6O_4P_2$	$C_{20}H_{14}Co_2N_3O_5P$
cryst syst	orthorhombic	triclinic	monoclinic
space group	$P2_1ca$	$P\bar{1}$	$P2(1)/n$
a, Å	8.1554(3)	9.434(2)	10.92600(10)
b, Å	21.5857(6)	13.136(4)	18.3592(2)
c, Å	29.8363(9)	16.781(5)	11.139
α, deg	90	100.34(3)	90
β, deg	90	103.86(2)	103.4969(10)
γ, deg	90	108.44(2)	90
V, Å^3	5252.4(3)	1840.3(9)	2172.66(3)
Z	8	2	4
D_{calc}, mg m^{-3}	1.490	1.427	1.606
mol wt	589.25	790.46	525.17
F(000)	2384	808	1056
cryst dimens, mm	0.45 × 0.20 × 0.05	0.35 × 0.25 × 0.20	0.30 × 0.15 × 0.10
linear abs coeff, mm^{-1}	1.363	1.035	1.637
scan type	ω scans	ω scans	ω scans
radiation	Mo Kα (λ = 0.70173 Å)	Mo Kα (λ = 0.70173 Å)	Mo Kα (λ = 0.70173 Å)
θ range, deg	0.94−25.03	1.30−28.28	2.18−28.27
no. of reflns measd	21 719	22 277	11 943
no. of unique total data	8897 (R_{int} = 0.0556)	8998 (R_{int} = 0.0480)	5352 (R_{int} = 0.0336)
criterion for obsn	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no. of unique obsd data	5975	5439	3853
no. of variables	649	451	280
GOF	1.012	1.040	1.054
Rl ($I > 2\sigma(I)$)[a]	0.0543	0.0552	0.0394
wR2 (all data)[b]	0.1423	0.1327	0.0877
largest diff peak/hole (e Å^{-3})	0.68 and −0.48	0.53 and −0.32	0.33 and −0.31
Flack parameter	0.09(2)		

[a] $Rl = \sum||F_o| - ||F_c|/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

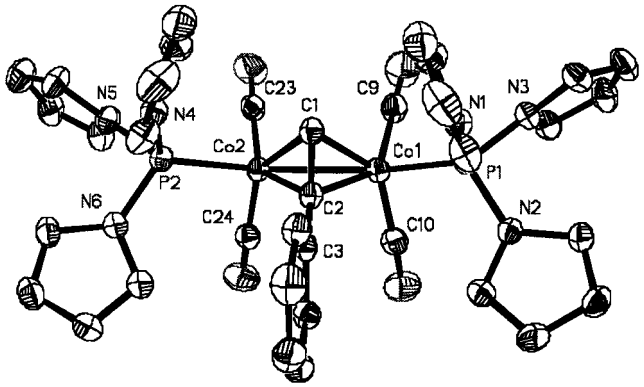


Figure 2. Crystal structure of **7**. Hydrogen atoms have been omitted for clarity.

very minimal structural changes upon coordination. In both complexes the nitrogen−phosphorus distances (1.70−1.71 Å) are indistinguishable from those found in the free ligand (1.70 Å).[19] As expected, the pyrrole rings are planar, with sp^2-hybridized nitrogen atoms. The bond distances within the pyrrole rings are also similar to those found in the free ligand. Thus, the average distances for N−C_α (1.39 Å), C_α−C_β (1.34 Å), and C_β−C_β (1.40 Å) in **1** are equivalent to those given in Table 3, within experimental error.

It is interesting to compare the molecular structure of the monosubstituted (**5**) and the disubstituted (**7**) complexes. Indeed, it appears that the substitution of one or two carbonyl ligand groups by **1** induces some changes at the metal−metal bond, since a progressive increase of the cobalt−cobalt bond length takes place: 2.483 Å for **5** and 2.509 Å for **7**. Cobalt−cobalt bond lengths in acetylene−dicobalthexacarbonyl complexes fall in the 2.463−2.473 Å range.[26] This could be indicative of a decrease of the electronic density in the metal−metal bond due to the π-accepting character of the PPy_3 ligand. On the other hand, it has been reported that the substitution of two axial carbonyl groups for trimethylphosphine ligands does not affect the cobalt−cobalt bond length.[5d]

Table 3. Selected Bond Distances (Å) for Complexes 5, 7, and 15

5		7		15	
Co1−Co2	2.4827(14)	Co1−Co2	2.5094(10)	Co1−Co2	2.4800(5)
Co1−C1	1.955(8)	Co2−C1	1.950(4)	Co1−C1	1.947(3)
Co1−C2	1.988(7)	Co2−C2	1.987(3)	Co1−C2	1.950(3)
Co2−C1	1.959(6)	Co1−C1	1.961(4)	Co2−C1	1.957(3)
Co2−C2	1.978(7)	Co1−C2	1.978(3)	Co2−C2	1.951(3)
Co1−P	2.145(2)	Co2−P2	2.1559(12)	Co1−P	2.1245(7)
C1−C2	1.342(9)	C1−C2	1.331(5)	C1−C2	1.326(4)
				C2−C8	1.498(4)
				C8−C9	1.488(4)
Co1−C9	1.806(9)	Co2−C24	1.797(4)	Co1−C6	1.785(3)
Co1−C10	1.776(7)	Co2−C23	1.793(4)	Co1−C7	1.816(3)
Co2−C23	1.774(14)	Co1−P1	2.1543(12)	Co2−C4	1.792(3)
Co2−C24	1.829(10)	Co1−C10	1.802(5)	Co2−C3	1.817(4)
Co2−C25	1.819(10)	Co1−C9	1.798(4)	Co2−C5	1.822(3)
P−N1	1.701(5)	P2−N6	1.708(3)	P−N1	1.708(2)
P−N2	1.701(5)	P2−N4	1.711(3)	P−N2	1.707(2)
P−N3	1.715(6)	P2−N5	1.700(3)	P−N3	1.704(2)
		P1−N2	1.708(3)		
		P1−N1	1.707(3)		
		P1−N3	1.705(3)		
				N1−C9	1.402(3)
				N1−C12	1.407(3)
				N2−C16	1.388(4)
				N2−C13	1.390(3)
				N3−C17	1.390(3)
				N3−C20	1.392(3)

Some regular trends are also apparent in the metal−ligand bond lengths. The cobalt−phosphorus distance in both **5** and **7** is ca. 0.07 Å shorter than the cobalt−phosphorus distance in trimethylphosphine-substituted acetylene−dicobaltcarbonyl complexes.[5d] This is in complete accordance with the observation that the rhodium−

(26) Castro, J.; Moyano, A.; Pericás, M. A.; Riera, A. *Tetrahedron* **1995**, *51*, 6541−6556, and references therein.

Table 4. Selected Bond Angles (deg) for Complexes 5, 7, and 15

5		7		15	
P−Co1−Co2	151.27(7)	P2−Co2−Co1	148.42(4)	P−Co1−Co2	141.56(3)
		P1−Co1−Co2	148.32(4)		
C1−Co1−Co2	50.7(2)	C2−Co2−Co1	50.57(10)	C1−Co1−Co2	50.73(8)
C2−Co2−Co1	51.4(2)	C1−Co1−Co2	49.89(11)	C2−Co2−Co1	50.51(8)
C1−Co1−P	104.1(2)	C1−Co2−P2	99.78(11)	C1−Co1−P	98.78(8)
C2−Co1−P	101.4(2)	C2−Co2−P2	101.08(11)	C2−Co1−P	91.28(8)
C23−Co2−C1	100.0(4)	C1−Co1−P1	100.19(11)	C4−Co2−C1	102.09(12)
C23−Co2−C2	98.7(4)	C2−Co1−P1	100.52(11)	C4−Co2−C2	99.13(12)
C10−Co1−P	100.3(2)	C23−Co2−P2	96.83(14)	C7−Co1−P	105.85(9)
C10−Co1−C9	106.3(4)	C23−Co2−C24	106.0(2)	C6−Co1−C7	106.95(14)
C9−Co1−P	96.3(3)	C24−Co2−P2	100.72(13)	C6−Co1−P	98.85(10)
C23−Co2−C25	98.6(6)	C9−Co1−P1	97.91(14)	C4−Co2−C5	100.09(13)
C25−Co2−C24	106.4(4)	C9−Co1−C10	109.0(2)	C3−Co2−C5	106.64(15)
C23−Co2−C24	101.0(5)	C10−Co1−P1	100.04(14)	C4−Co2−C3	98.63(14)
C1−C2−C3	142.1(7)	C1−C2−C3	141.3(4)	C1−C2−C8	139.3(3)
C3−C2−Co1	135.4(5)	C3−C2−Co2	135.1(3)	C8−C2−Co1	128.64(19)
C3−C2−Co2	134.7(5)	C3−C2−Co1	134.9(3)	C8−C2−Co2	141.1(2)
				Co1−P−N1	114.45(8)
				Co1−P−N2	118.90(9)
				Co1−P−N3	118.56(8)

Table 5. Selected Torsion Angles (deg) for Complexes 5, 7, and 15

5		7		15	
H1A−C1−C2−C3	1.4	H1A−C1−C2−C3	0.9	H−C1−C2−C8	11.1
C1−C2−C3−C4	19.4(14)	C1−C2−C3−C4	1.0(7)		
C23−Co2−Co1−P	−5.9(8)	P1−Co1−Co2−P2	0.76(10)	P−Co1−Co2−C4	−10.53(19)
N2−P−Co1−Co2	29.8(3)	N4−P2−Co2−Co1	24.69(15)	Co2−Co1−P−N1	2.2(10)
		N1−P1−Co1−Co2	−18.22(15)		

phosphorus distance is ca. 0.08 Å shorter in $PPyr_3$-substituted complexes than in PPh_3-substituted ones.[20] This shortening could again be attributed to the greater π-acceptor character in the case of **1**. It has also been suggested that it might be due to a change in phosphorus hybridization resulting from the greater electronegativity of the pyrrolyl substituents relative to phenyl.[20]

Another interesting observation concerns the metal−carbonyl bond lengths. The data in Table 3 show that substitution by **1** brings about a small decrease of the cobalt−carbonyl distances with respect to the starting complex **2**, which is in any case much less significant than that caused by poorer π-accepting ligands such as trialkylphosphines.[5d]

IR Spectra of Tris(pyrrolyl)phosphine-Substituted Complexes. The analysis of carbonyl infrared frequencies in substituted metal−carbonyl complexes is a useful tool for the evaluation of the electronic properties of ligands, due to the direct relationship between these frequencies and electron density at the metal.[27] The carbonyl stretching zone of the infrared spectra of complexes **2**, **5**, and **7** is shown in Figure 3. The spectrum of the $(PhCCH)Co_2CO_5(PPh_3)$ complex **10**[28c] has also been included for comparison purposes. It can be readily seen that the carbonyl frequencies of **5** are ca. 14 cm^{-1} higher than those of **10**, but lower than those of **2**. These trends are similar to those observed in other metal−carbonyl complexes.[20] The carbonyl frequencies of the disubstituted complex **7** are in turn very similar to those reported for acetylene−dicobaltcarbonyl complexes with π-acceptor bidentate phosphine or phosphite

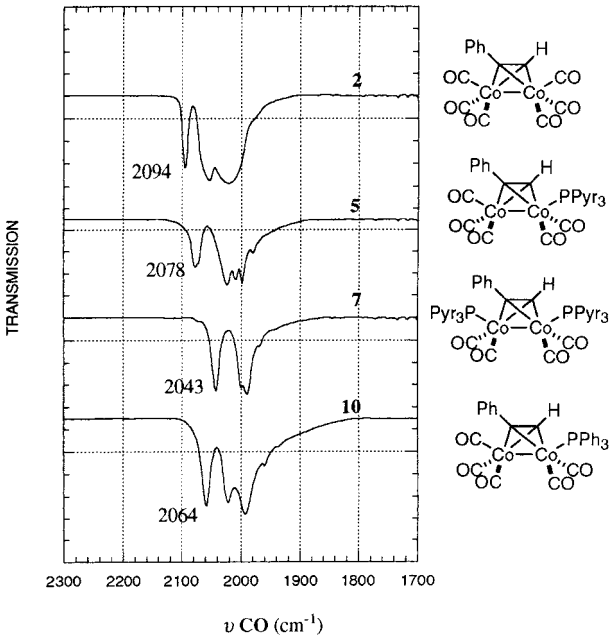


Figure 3. IR spectra (ν_{CO} cm^{-1}) of compounds **2**, **5**, **7**, and **10**.

ligands[25] and ca. 20 cm^{-1} higher than in the disubstituted $(PhCCH)Co_2CO_4(PPh_3)_2$ complex.[28c] It is also worth noting that the replacement of a triphenylphosphine ligand by trimethyl phosphite leads to significantly minor increases in the carbonyl frequencies of the complex.[28c] As expected, the carbonyl stretching zone of the propargyl complexes **6** and **8** is practically identical to that of **5** and **7**, respectively. All in all, these shifts in the carbonyl frequencies confirm the weak σ-donor and the strong π-acceptor character of **1**.

Pauson−Khand Reactivity of Tris(pyrrolyl)-phosphine-Substituted Complexes. The structural and spectroscopic studies of complexes **5**−**8** described

(27) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; pp 638, 642−43.

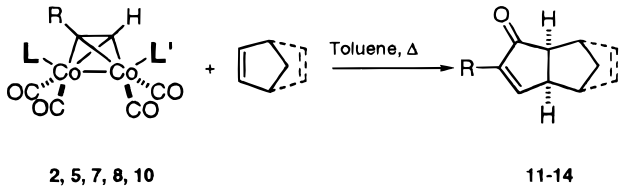
(28) (a) Greenfield, H.; Stenberg, R. H.; Friedel, J. H.; Wotiz, R.; Manhby, I.; Wender, J. *J. Am. Chem. Soc.* **1954**, *76*, 1457−1458. (b) Váradi, G.; Vizi-Orosz, A.; Vastag, S.; Pályi, G. *J. Organomet. Chem.* **1976**, *108*, 225−233. (c) Chia, L. S.; Cullen, W. R.; Franklin, M.; Manning, A. R. *Inorg. Chem.* **1975**, *14*, 2521−2525.

Table 6. Pauson−Khand Reactions of Complexes 2, 5, 7, 8, and 10

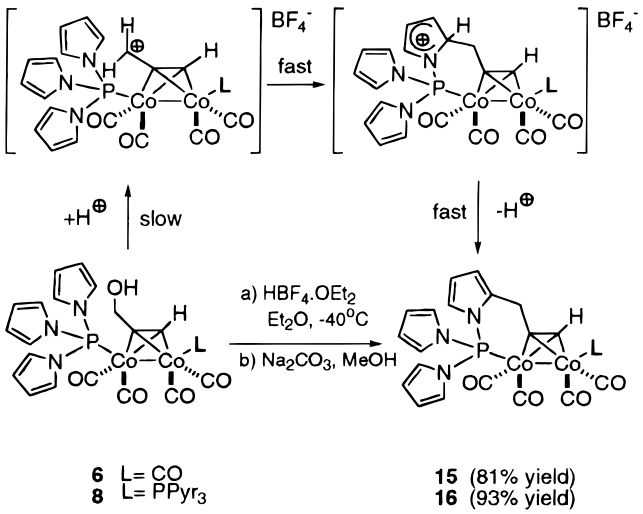
	initial complex					react. cond.		final product
entry		R	L	L′	olefin[a]	*T* (°C)	time (h)	(yield, conv., %)
1	**2**	Ph	CO	CO	Nbd	70	0.5	**11** (82,100)
2	**5**	Ph	$PPyr_3$	CO	Nbd	70	0.5	**11** (82, 100)
3	**10**	Ph	PPh_3	CO	Nbd	70	0.5	**11** (72, 91)
4	**2**	Ph	CO	CO	Nbe	60	4	**12** (81, 89)
5	**5**	Ph	$PPyr_3$	CO	Nbe	60	4	**12** (97, 100)
6	**10**	Ph	PPh_3	CO	Nbe	60	4	**12** (33, 78)
7	**2**	Ph	CO	CO	Cyc	50	4	**13** (66, 76)
8	**5**	Ph	$PPyr_3$	CO	Cyc	50	4	**13** (56, 63)
9	**10**	Ph	PPh_3	CO	Cyc	50	4	**13** (10, 33)
10	**7**	Ph	$PPyr_3$	$PPyr_3$	Nbd	70	2	**11** (85, 100)
11	**8**	CH_2OH	$PPyr_3$	$PPyr_3$	Nbd	70	2	**14** (47, 100)

[a] 5 equivalents of olefin are employed. Nbd: Norbornadiene. Nbe: Norbornene. Cyc: Cyclopentene.

Scheme 3. Pauson−Khand Reactions of Complexes 5−10



Scheme 4. Generation and Trapping of Nicholas Cations Derived fromComplexes 6 and 8



above clearly indicate that tris(pyrrolyl)phosphine, acting as ligand in acetylene−dicobaltcarbonyl complexes, exerts a relatively high electron-withdrawing effect, nearly comparable to that of carbon monoxide. The Pauson−Khand reaction is initiated by a reversible loss of a carbonyl ligand, followed by coordination of the olefin to the corresponding cobalt atom.[3c,26] The loss of reactivity of acetylene complexes upon substitution of carbon monoxide by an electron-donating aryl- or alkylphosphine could therefore be due to the decrease in electrophilicity of the intermediate coordinatively unsaturated complex. One should expect that, on the contrary, tris(pyrrolyl)phosphine-substituted acetylene−dicobaltcarbonyl complexes would present a Pauson−Khand reactivity much more similar to that of the parent hexacarbonyl complexes. To verify this hypothesis, we undertook a study of the intermolecular Pauson−Khand reactions of complexes **5**, **7**, and **8** with a set of representative olefins (norbornadiene, norbornene, and cyclopentene) of decreasing reactivity (Scheme 3 and Table 6). Both the parent phenylacetylene complex **2** and the triphenylphosphine-substituted complex **10** were included for comparison purposes.

For a given olefin, the reactions were run in parallel, and in the case of norbornadiene and norbornene they were stopped when one of the starting complexes had reacted completely. In this way we could show that, as anticipated, the reactivity of **5** (entries 2 and 5 of Table 6) nearly approached that of **2** (entries 1 and 4) and was notably superior to that of **10** (entries 3 and 6). The reactions with cyclopentene were stopped after 4 h at 50 °C (entries 7−9). Both the yields and the conversions show similar trends. Finally, it is interesting to note that even the disubstituted complexes **7** and **8** (entries 10 and 11) exhibit a high Pauson−Khand reactivity toward norbornadiene.

Attempted Nicholas Reactions of Cobalt-Stabilized Propargyl Cations Containing Tris(pyrrolyl)phosphine Ligands: Internal Trapping by a Pyrrolyl Substituent. The electrophilicity of dicobalt carbonyl-stabilized propargylium ions is reduced by a factor of ca. 10^5 upon replacement of one carbonyl group by triphenylphosphine.[17] We anticipated that substitution by tris(pyrrolyl)phosphine should have a much less dramatic effect on the reactivity of these cations. Therefore, we decided to generate the propargylium ion derived from complex **6** in order to study its quenching with oxygenated nucleophiles.[5b] When an ethereal solution of **6** was treated at −40 °C with tetrafluoroboric acid, no propargylium salt formation could be detected. Instead, the reaction led to the high yield formation of a new complex, **15**, resulting from the formation of a single bond between the α-carbon of one of the pyrrole rings and the propargylic carbon of the starting complex (Scheme 4).

This structural assignment, first done on the basis of spectral data, was fully confirmed by the X-ray diffraction analysis of a single crystal of the complex. Some comments on the structure of **15** are warranted. A perspective view of the molecule is shown in Figure 4, and important crystallographic data can be found in Tables 2−5. The most conspicuous feature of **15** is the presence of a C_3CoNP six-membered ring, whose formation is accompanied by some geometrical changes with respect to **5**: a shortening of the cobalt−phosphorus bond length (from 2.145 Å in **5** to 2.125 Å in **15**) and a decrease of the P−Co−Co (141.6° in front of 150° in **5** and **7**) and C−Co−P (91.3° in front of 101° in **5** and **7**) angles are perhaps the most significant features. The

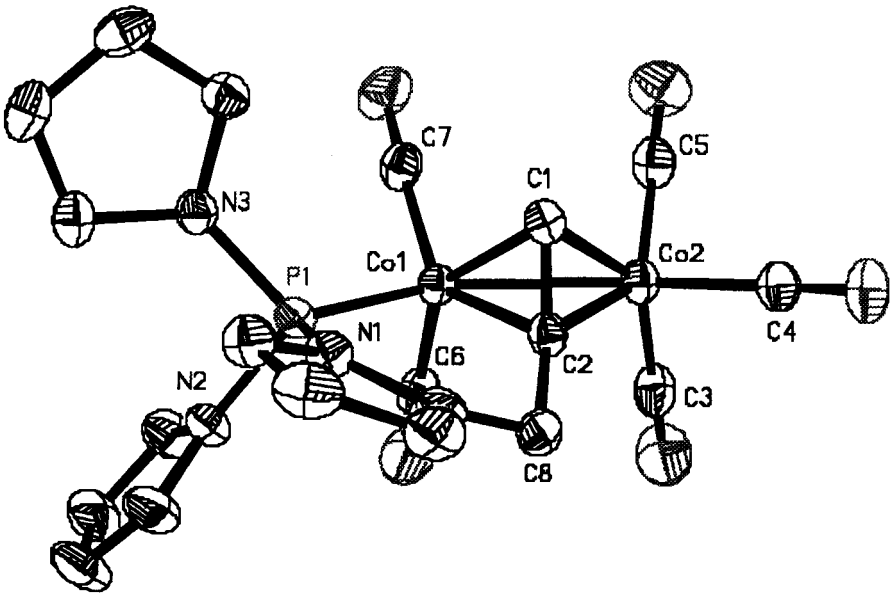


Figure 4. Crystal structure of **15**. Hydrogen atoms have been omitted for clarity.

six-membered ring adopts a twisted boat conformation, in which the phosphorus and the methylene carbon occupy the "bow" and "stern" positions.

In a totally parallel way, treatment of the disubstituted complex **7** with tetrafluoroboric acid led to the isolation of the chelated complex **16** in 93% yield. As shown in Scheme 4, the highly efficient formation of **15** and **16** can be readily explained by a mechanism in which the initially formed propargylium ion undergoes a fast nucleophilic attack by a pyrrole ring followed by an equally rapid, irreversible proton loss. The nucleophilic attack on the pyrrole ring is in accordance both with the known substitution chemistry of pyrroles and with the charge distribution shown by the resonance structures drawn in Scheme 1. These reactions represent the first examples both of the use of pyrroles as nucleophiles and of intramolecular ligand participation in the Nicholas reaction and are in accordance with the anticipated relatively high electrophilicity of the tris(pyrrolyl)phosphine-substituted, cobalt-stabilized propargylium ions.

Structural variations and further use of acetylene−dicobaltcarbonyl complexes with tris(pyrrolyl)phosphine ligands are currently being studied in our laboratories.

Experimental Section

Melting points were determined either by differential scanning calorimetry (DSC) or (uncorrected) in an open capillary tube. Infrared spectra were recorded in a Fourier transform mode, using film (NaCl) or KBr pellet techniques. ^{1}H NMR spectra were recorded at 500 MHz, and ^{13}C NMR spectra were recorded at 75.4 MHz. Chemical shifts are given in ppm and referenced to TMS or $CHCl_3$. ^{31}P NMR spectra were recorded at 121.4 MHz; chemical shifts are given in ppm and using phosphoric acid as an external reference. *J* values are given in Hz. Signal multiplicities were established by DEPT experiments. Exact mass measurements (HRMS) were performed by the "Servicio de Espectroscopía de Masas de la Universidad de Córdoba" and by the "Unidade de Espectrometría de Masas, Universidade de Santiago de Compostela". All reactions were performed in flame- or oven-dried glassware under a N_2 atmosphere. Reaction progress was followed by TLC (Merck DC-Alufolien KIESELGEL 60 F254). Silica gel (70−230 mesh) was used for column chromatography. Alkyne−dicobaltcarbonyl complexes **2**, **3**, **4**, and **10** were prepared by standard procedures.[13a,28]

Preparation of Alkyne−Dicobaltcarbonyl Complexes Substituted by Ligand 1. Reaction of Complex 2 with 1. To a solution of phenylacetylene−dicobalthexacarbonyl complex **2** (250 mg, 0.644 mmol) in toluene (8 mL) was added solid ligand **1** (98 mg, 0.43 mmol) in one portion. The dark-red solution was heated to 70 °C for 45 min. The reaction progress was monitored by TLC, and two new spots were detected. The reaction mixture was cooled to room temperature and filtered through Celite, which was thoroughly washed with dichloromethane. The solvents were eliminated under reduced pressure, and the dark-brown residue was purified by column chromatography on SiO_2 (previously washed with ether and hexane), eluting with hexane−ethyl acetate mixtures of increasing polarity. This afforded 171 mg (67%) of **5** and 36 mg (21%) of **7** as air-stable, dark-colored, crystalline solids. The global yield is 88%. Both complexes were recrystallized from hexane/CH_2Cl_2. Single crystals of each **5** and **7** were X-ray diffracted.

Complex 5: red crystalline solid; mp 109−110 °C; IR (KBr) ν 2078, 2024, 2010, 1998, 1977, 1182, 1057 cm^{-1}; ^{1}H NMR δ 5.56 (d, J = 3.0 Hz, 1H), 6.04 (m, 6H), 6.34 (m, 6H), 6.70−7.40 (m, 5H); ^{13}C NMR δ 72.3 (CH), 88.0 (C_q), 113.5 (6CH), 123.3 (6CH), 129.1 (2CH), 130.9 (2CH), 137.9 (C_q), 200−202 (broad, 5CO); ^{31}P NMR δ +127.8; MS (FAB(+)) *m/e* 589 (M^+, 3), 533 ($M^+ - 2CO$, 20), 505 ($M^+ - 3CO$, 75), 477 ($M^+ - 4CO$, 8), 449 ($M^+ - 5CO$, 100); HRMS (FAB+) calcd for $C_{22}H_{18}Co_2N_3O_2P$ ($M^+ - 3CO$) 504.980, found 504.979 (90%) and calcd for $C_{20}H_{18}Co_2N_3P$ ($M^+ - 5CO$) 448.990, found 448.991 (100%).

Complex 7: red crystalline solid; mp 155.0 °C (DSC); IR (KBr) ν 2043, 2000, 1989, 1970, 1182, 1055 cm^{-1}; ^{1}H NMR δ 5.51 (t, J = 3.4, 1H), 6.03 (m, 12H), 6.43 (m, 12H), 6.75−6.95 (m, 3H), 7.05−7.20 (m, 2H); ^{13}C NMR δ 71.5 (CH), 86.0 (C_q), 113.4 (12CH), 123.3 (12CH), 129.0 (2CH), 131.4 (2CH), 137.9 (C_q), 203.6 (broad, 2CO), 204.0 (broad, 2CO); ^{31}P NMR δ +127.45; MS (FAB(+)) *m/e* 790 (M^+, 2), 762 ($M^+ - 2CO$, 2), 734 ($M^+ - 3CO$, 10), 505 ($M^+ - 2CO - PPy_3$, 65), 449 ($M^+ - 5CO$, 100); HRMS (FAB+) calcd for $C_{22}H_{18}Co_2N_3O_2P$ ($M^+ - 3CO$) 504.980, found 504.981 (75%) and calcd for $C_{20}H_{18}Co_2N_3P$ ($M^+ - 5CO$) 448.990, found 448.992 (100%).

Reaction of Complex 3 with Ligand 1. Following the general procedure described above, and starting from propargyl alcohol−dicobalthexacarbonyl complex **3** (200 mg, 0.585 mmol) in toluene (10 mL) and the solid phosphine **1** (134 mg,

0.585 mmol), the reaction was run at 75 °C for 6 h, after which some starting complex still remained. Column chromatography afforded 25 mg (12% recovery) of **3** and a mixture of complexes **6** and **8.** This mixture was recrystallized by dissolving it in hot hexane and cooling in the freezer. Only complex **8** crystallized, and spectroscopically pure **6** was obtained by evaporation of the solution. In this way, 164 mg (52%) of **6** and 51 mg (12%) of **8** were isolated.

Complex 6: red oil; IR (KBr) ν 2076, 2014 (broad), 1182, 1057 cm^{-1}; ^{1}H NMR δ 1.13 (t, J = 5.2, OH), 3.65−4.05 (m, 2H), 5.13 (d, J = 3.8, 1H), 6.12 (m, 6H), 6.60 (m, 6H); ^{13}C NMR δ 62.6 (CH_2), 71.2 (CH), 94.0 (C_q), 113.8 (d, J = 26.7, 6CH), 123.5 (d, J = 30.3, 6CH), 200−202 (broad, 3CO), 202−204 (broad, 2CO); ^{31}P NMR δ +128.8; HRMS (FAB+) calcd for $C_{18}H_{16}Co_2N_3O_4P$ (M^+ − 2CO) 486.954, found 486.955 (25%); calcd for $C_{17}H_{16}Co_2N_3O_3P$ (M^+ − 3CO) 458.959, found 458.959 (100%); calcd for $C_{16}H_{16}Co_2N_3O_2P$ (M^+ − 4CO) 430.964, found 430.964 (20%); calcd for $C_{15}H_{16}Co_2N_3OP$ (M^+ − 5CO) 402.969, found 402.969 (75%).

Complex 8: red crystalline solid; mp 148.6 °C (DSC); IR (KBr) ν 2045, 2008, 1989, 1971, 1178, 1061 cm^{-1}; ^{1}H NMR δ 1.14 (t, J = 4.5, OH), 3.68 (m, 2H), 5.19 (m, 1H), 6.12 (m, 12H), 6.68 (m, 12H); ^{13}C NMR δ 61.9 (CH_2), 70.6 (CH), 92.1 (C_q), 113.7 (12CH), 123.5 (12CH), 204.0 (broad, 4CO); ^{31}P NMR δ +129.17; MS (FAB(+)) *m/e* 744.1 (M^+, 3), 688.1 (M^+ − 2CO, 15), 459.0 (M^+ − 2CO − **1**, 100), 431.0 (M^+ − 3CO − **1**, 65), 403.0 (M^+ − 4CO − **1**, 35), 374.9 (50), 249.8 (80).

Reaction of Complex 4 with Ligand 1. Following the general procedure described above, and starting from racemic (1-phenyl-1-pentyn-3-ol)dicobalthexacarbonyl complex **4** (329 mg, 0.736 mmol) in toluene (15 mL) and the solid phosphine **1** (185 mg, 0.809 mmol), the reaction was run at 75 °C for 3 h. Column chromatography gave two fractions: (a) a mixture of 45 mg of starting complex **4** and 271 mg of the new complex **9a**; (b) 94 mg of the complex **9b**. The global yield is 76% and the **9a**/**9b** diastereomer ratio (2.8/1) was determined by HPLC. Conditions for HPLC analysis: CHIRALCEL OD (25 cm) column, 1% 2-propanol−99% hexane, 0.5 mL/min, 30 °C, λ = 254 nm, P = 14 bar. t_R(**9b**): 10.05 min. t_R(**9a**): 10.45 min. t_R-(**4**): 14.03 min.

Complex 9a: red oil; IR (KBr) ν 2072, 2054, 2016, 1180, 1057 cm^{-1}; ^{1}H NMR δ 0.83 (t, J = 7.5, 3H), 1.20−2.0 (m, 3H), 4.20−4.35 (m, 1H), 6.03 (m, 6H), 6.48 (m, 6H), 6.80−7.80 (m, 5H); ^{13}C NMR δ 11.6 (CH_3), 34.0 (CH_2), 73.2 (CH), 86.4 (C_q), 100.0 (C_q), 113.5 (6CH), 123.5 (6CH), 129.2 (2CH), 130.4 (2CH), 138.5 (C_q), 200−201 (broad, 5CO); ^{31}P NMR δ +126.1; MS (FAB(+)) *m/e* 591.0 (M^+ − 2CO, 8), 563.0 (M^+ − 3CO, 100), 535.0 (M^+ − 4CO, 18), 507.0 (M^+ − 5CO, 12); HRMS (FAB+) calcd for $C_{25}H_{24}Co_2N_3O_3P$ (M^+ − 3CO) 563.022, found 563.022 (100%); calcd for $C_{24}H_{24}Co_2N_3O_2P$ (M^+ − 4CO) 535.027, found 535.030 (15%); and calcd for $C_{23}H_{24}Co_2N_3OP$ (M − 5CO) 507.032, found 507.032 (45%).

Complex 9b: red oil; IR (KBr) ν 2072, 2012 (broad), 1180, 1057 cm^{-1}; ^{1}H NMR δ 0.93 (t, J = 7.2, 3H), 1.20−2.0 (m, 3H), 4.20−4.35 (m, 1H), 6.03 (m, 6H), 6.48 (m, 6H), 6.80−7.80 (m, 5H); ^{13}C NMR δ 11.0 (CH_3), 33.1 (CH_2), 73.9 (CH), 86.4 (C_q), 100.0 (C_q), 113.5 (6CH), 123.5 (6CH), 129.7 (2CH), 130.6 (2CH), 138.5 (C_q), 200−201 (broad, 5CO); ^{31}P NMR δ +126.1; MS (FAB(+)) *m/e* 619.0 (M^+ − CO, 12), 591.0 (M^+ − 2CO, 18), 563.0 (M^+ − 3CO, 100), 535.0 (M^+ − 4CO, 20), 507.0 (M^+ − 5CO, 15).

Pauson−Khand Reaction of Complexes 2, 5, 7, 8, and 10 with Norbornadiene. General Procedure for the Pauson−Khand Reaction. Reaction of Complex 2. To a stirred solution of complex **2** (100 mg, 0.258 mmol) in toluene (2 mL) was added dropwise norbornadiene (118 mg, 1.30 mmol). The resulting solution was heated for 0.5 h at 70 °C until complete disappearance of the starting material (TLC). The reaction mixture was cooled to room temperature and filtered through Celite, which was thoroughly washed with dichloromethane. The solvents were eliminated under reduced pressure, and the crude product was purified by column chromatography on silica gel, eluting with hexane−ethyl acetate mixtures of increasing polarity, to give 47 mg (83%) of (1*RS*,2*RS*,6*RS*,7*SR*)-4-phenyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one, **11**.[29]

Reaction of Complex 5. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 100 mg (0.169 mmol) of **5** and 78 mg (0.845 mmol) of norbornadiene in 1 mL of toluene. The reaction was conducted at 70 °C for 1 h and gave 58 mg (82% yield) of **11**.

Reaction of Complex 10. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 100 mg (0.160 mmol) of **10** and 74 mg (0.802 mmol) of norbornadiene in 1 mL of toluene. The reaction was conducted at 70 °C for 1 h and gave 5 mg of the starting complex and 27 mg (72% yield) of **11**.

Reaction of Complex 7. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 25 mg (0.031 mmol) of **7** and 15 mg (0.155 mmol) of norbornadiene in 1 mL of toluene. The reaction was conducted at 70 °C for 2 h and gave 9 mg (85% yield) of **11**.

Reaction of Complex 8. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 45 mg (0.060 mmol) of **8** and 28 mg (0.302 mmol) of norbornadiene in 1.5 mL of toluene. The reaction was conducted at 70 °C for 2 h and gave 5 mg (47% yield) of (1*RS*,2*RS*,6*RS*,7*SR*)-4-(hydroxymethyl)tricyclo-[5.2.1.0^{2,6}]deca-4,8-dien-3-one, **14**.[30]

Pauson−Khand Reaction of Complexes 2, 5, and 10 with Norbornene. Reaction of Complex 2. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 100 mg (0.257 mmol) of **2** and 121 mg (1.289 mmol) of norbornene in 1.5 mL of toluene. The reaction was conducted at 60 °C for 30 min and gave 10 mg of starting complex and 25 mg (43% yield) of (1*RS*,2*SR*,6*SR*,7*SR*)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one, **12**.[6d]

Reaction of Complex 5. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 100 mg (0.169 mmol) of **5** and 79 mg (0.845 mmol) of norbornene in 1 mL of toluene. The reaction was conducted at 60 °C for 30 min and gave 37 mg (97% yield) of **12**.

Reaction of Complex 10. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 100 mg (0.160 mmol) of **10** and 75 mg (0.802 mmol) of norbornene in 1 mL of toluene. The reaction was conducted at 60 °C for 30 min and gave 21 mg of starting complex and 12 mg (33% yield) of **12**.

Pauson−Khand Reaction of Complexes 2, 5, and 10 with Cyclopentene. Reaction of Complex 2. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 130 mg (0.335 mmol) of **2** and 114 mg (1.675 mmol) of cyclopentene in 2 mL of toluene. The reaction was conducted at 50 °C for 4 h and gave 32 mg of starting complex and 44 mg (66% yield) of (3a*RS*,6a*RS*)-2-phenyl-4,5,6,3a,6a-pentahydropentalen-1-one, **13**.[7]

Reaction of Complex 5. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 24 mg (0.040 mmol) of **5** and 14 mg (0.203 mmol) of cyclopentene in 0.25 mL of toluene. The reaction was conducted at 50 °C for 4 h and gave 9 mg of starting complex and 4.5 mg (56% yield) of **13**.

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Reaction of Complex 10. The procedure described above for the Pauson−Khand reaction was used, with the following reagents, conditions, and quantities: 55 mg (0.088 mmol) of **10** and 30 mg (0.441 mmol) of cyclopentene in 0.5 mL of toluene. The reaction was conducted at 50 °C for 4 h and gave 38 mg of starting complex and 1.8 mg (10% yield) of **13**.

Intramolecular Nicholas Reactions of Complexes 6 and 8. Preparation of Complex 15. A solution of complex **6** (45 mg, 0.083 mmol) in diethyl ether (3 mL) was cooled at −78 °C. $HBF_4{\cdot}OEt_2$ (67 mg, 0.414 mmol, 5 equiv) was added in one portion via syringe, followed by anhydrous diethyl ether (15 mL). The temperature was raised slowly to −40 °C, and stirring was maintained for 2 h. The appearance of a less polar new complex was revealed by TLC. After cooling again to −78 °C, the reaction was quenched by adding solid Na_2CO_3 (88 mg, 0.83 mmol, 10 equiv) and methanol (4 mL). The reaction mixture was warmed to room temperature and filtered through Celite, which was thoroughly washed with diethyl ether. The solvents were eliminated under reduced pressure, and the crude product was purified by column chromatography on silica gel, eluting with hexane−methylene chloride mixtures of increasing polarity, to give 35 mg (81% yield) of the new complex **15**: red crystalline solid; mp 104−105 °C; IR (KBr) ν 2076, 2031, 2014, 1984, 1184, 1057 cm^{-1}; ^1H NMR δ [AB: 3.65 (dd, J = 17.2 and 4.0, 1H), 3.75 (d, J = 17.2, 1H)], 5.04 (s, 1H), 5.88−5.82 (m, 1H), 5.97 (t, J = 3.6, 1H), 6.22−6.13 (m, 5H), 6.47−6.41 (m, 2H), 6.58−6.53 (m, 2H); ^{13}C NMR δ 30.3 (d, J = 5.8, $1CH_2$), 71.4 (1CH), 90.9 (C_q), 111.1 (d, J = 5.2, 1CH), 112.5 (d, J = 5.8, 1CH), 113.8 (d, J = 7.3, 2CH), 114.2 (d, J = 7.9, 2CH), 121.4 (d, J = 2.4, 1CH), 123.1 (4CH), 136.8 (d, J = 13, $1CH_q$), 200.6 (3CO), 202.8 (2CO); ^{31}P NMR δ (ppm) +128.8; MS (FAB(+)) *m/e* 524.9 (M^+, 10), 469.0 (M^+ − 2CO, 40), 441.0 (M^+ − 3CO, 85), 413.0 (M^+ − 4CO, 60), 384.9 (M^+ − 5CO, 100), 317.9 (50); HRMS (FAB+) calcd for $C_{20}H_{14}Co_2N_3O_5P$ (M^+) 524.933, found 524.932 (20%); calcd for $C_{18}H_{14}Co_2N_3O_3P$ (M^+ − 2CO) 468.943, found 468.945 (45%); calcd for $C_{17}H_{14}Co_2N_3O_2P$ (M^+ − 3CO) 440.948, found 440.949 (100%); calcd for $C_{16}H_{14}Co_2N_3OP$ (M^+ − 4CO) 412.953, found 412.954 (45%); and calcd for $C_{15}H_{14}Co_2N_3P$ (M^+ − 5CO) 384.959, found 384.959 (90%).

Preparation of Complex 16. The procedure described above for the Nicholas reaction was used, with the following reagents, conditions, and quantities: 100 mg (0.134 mmol) of **8** in 5 mL of diethyl ether, 109 mg (0.672 mmol) of $HBF_4{\cdot}OEt_2$, and 25 mL of diethyl ether. The quenching was done with Na_2CO_3 (142 mg, 1.34 mmol) and 5 mL of methanol. After chromatographic purification, 91 mg (93% yield) of complex **16** was obtained: red crystalline solid, mp 230−232 °C; IR (KBr) ν 2051, 2004, 1993, 1975, 1180, 1063 cm^{-1}; ^1H NMR δ [AB: 3.35 (dd, J = 17.4, 1H), 3.66 (d, J = 17.4, 1H)], 5.04 (s, 1H), 5.84 (s, 1H), 5.96 (s, 1H), 6.14 (s, 7H), 6.20 (s, 4H), 6.51 (m, 2H) 6.63 (s, 2H), 6.70 (s, 6H); ^{13}C NMR δ 29.8 (CH_2), 70.7 (CH), 90.8 (C_q), 110.8 (CH), 112.1 (CH), 113.8 (10CH), 121.4 (CH), 123.2 (4CH), 123.6 (6CH), 137.4 (d, J = 13, C_q), 203.8 (4CO); ^{31}P NMR δ +124.5 (broad), 121.5 (broad); MS (FAB(+)) *m/e* 726.0 (M^+, 5), 670.1 (M^+ − 2CO, 100), 642.1 (M^+ − 3CO, 30), 614.1 (M^+ − 4CO, 15), 548.0 (50), 423.1 (50), 385.0 (M^+ − 4CO − **1**), 317.9 (60); HRMS (FAB+) calcd for $C_{17}H_{14}Co_2N_3O_2P$ (M^+ − 2CO − **1**) 440.949, found 440.952 (30%); and calcd for $C_{15}H_{14}Co_2N_3P$ (M^+ − 4CO − **1**) 384.958, found 384.956 (80%).

Crystallography. Data were collected using a Bruker SMART CCD based diffractometer operating at room temperature. A total of 1271 frames of data were collected using ω scans with a scan width of 0.3° per frame for 20 s (**5** and **7**) and 10 s (**15**). Additional parameters are available in the CIF file. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software (V. 4.210, Bruker Analytical X-ray Systems, Madison, WI, 1995) and refined using SAINT (V. 4.050, Bruker Analytical X-ray Systems, Madison, WI, 1995) on all observed reflections. Data reduction was performed using the SAINT software. Absorption corrections were applied using SADABS (program for absorption corrections using Bruker CCD based on the method of Robert Blessing[31]). The structures were solved by the direct method using the SHELXS-97 program (Sheldrick, G. M., University of Göttingen, Germany, 1997) and refined by the least-squares method on F^2 using SHELXL-97, which is incorporated in SHELXTL-PC V 5.1 (PC version, Bruker Analytical X-ray Systems, Madison, WI, 1995). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined as a riding model. In each case, the crystals used for the diffraction studies showed no decomposition during data collection.

Acknowledgment. We gratefully acknowledge financial support from DGES (Grants PB95-0265 and PB96-0376). The establishment of the SMART CCD single-crystal diffractometer at the University of Coruña was supported by the Xunta de Galicia (XUGA INFRA-97).

Supporting Information Available: Tables of complete X-ray crystal data, refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and torsion angles for **5**, **7**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990914Y

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