

σ -Alkynyl complexes of manganese as ligands. Preparation, crystal structure and reactivity of $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCMn}(\text{CO})_4(\text{PCy}_3)]\}$ (Cy = cyclohexyl)

Gabino A. Carriedo, Daniel Miguel and Víctor Riera *

Departamento de Química Organometálica, Universidad de Oviedo, 33071 Oviedo (Spain)

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Abstract

The reaction of the alkynyl complex *cis*- $[\text{Mn}(\text{CCPh})(\text{CO})_4(\text{PCy}_3)]$ (I) with $[\text{Co}_2(\text{CO})_8]$ in hexane gives the compound $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCMn}(\text{CO})_4(\text{PCy}_3)]\}$ (II) in which, as revealed by an X-ray diffraction study, the PCy_3 ligand is *trans* to the CCPh group. Oxidation of II with $[\text{I}(\text{py})_2][\text{BF}_4]$ in CH_2Cl_2 gives the alkynyl complex *trans*- $[\text{Mn}(\text{CCPh})(\text{CO})_4(\text{PCy}_3)]$, (III), which on standing in solution isomerizes to the *cis* isomer I. Reactions of II with $\text{Na}[\text{Hg}]$ under a CO atmosphere or with $\text{Ce}(\text{SO}_4)_2$ give mixtures of I and II.

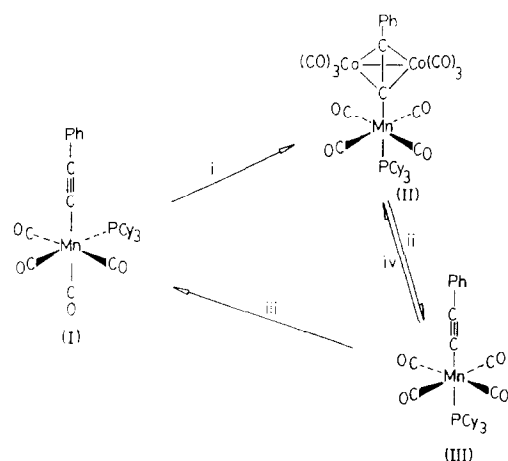
Introduction

The reaction of acetylenes with $[\text{Co}_2(\text{CO})_8]$ to give μ -alkyne complexes of formula $\{[\text{Co}_2(\text{CO})_6][\mu\text{-RCCR}]\}$ is a well established process and the stability of the products in some cases permits chemical modification of the acetylene substituents to give $\{[\text{Co}_2(\text{CO})_6][\mu\text{-RCCR}']\}$, from which the new acetylene can be recovered by, e.g., oxidation [1]. The alkynyl irons $[\text{Fe}(\text{CCR})(\text{CO})(\text{L})(\eta\text{-C}_5\text{H}_5)]$ (L = CO or PMe_2Ph , R = Me or Ph) are also known to react similarly with $[\text{Co}_2(\text{CO})_8]$ to give the complexes $\{[\text{Co}_2(\text{CO})_6][\mu\text{-RCCFe}(\text{CO})(\text{L})(\eta\text{-C}_5\text{H}_5)]\}$ [2]. We, therefore, examined the reaction of the alkynylmanganese *cis*- $[\text{Mn}(\text{CCPh})(\text{CO})_4(\text{PCy}_3)]$ (I) (Cy = cyclohexyl) with $[\text{Co}_2(\text{CO})_8]$, and found this to give an analogous compound of formula $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCMn}(\text{CO})_4(\text{PCy}_3)]\}$ (II). A crystal structure determination (see ref. 3 for a preliminary report) on this product revealed that the PCy_3 ligand is *trans* to the CCPh group, and this suggested the possibility of releasing the coordinated alkynyl from II to give the otherwise inaccessible *trans*- $[\text{Mn}(\text{CCPh})(\text{CO})_4(\text{PCy}_3)]$ (III). We report here the details of the results and discuss the structure and reactivity of II.

Results and discussion

The reaction of the alkynyl complex $[\text{Mn}(\text{CCPh})(\text{CO})_4(\text{PCy}_3)]$ (I) with $[\text{Co}_2(\text{CO})_8]$ in hexane at room temperature gave the dark green microcrystalline compound $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCMn}(\text{CO})_4(\text{PCy}_3)]\}$ (II) (reaction i in Scheme 1). The data for II (See Experimental and Table 1) were consistent with the formulation shown in Scheme 1. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed the signal of only one of the acetylene carbons at 120.3 ppm, the other (attached to the manganese) is probably too broad. The signal of C^1 of the phenyl substituent appeared at 147.1 ppm, close to the value observed [4] for the species $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCPh}]\}$ but higher than that for I (128.4 ppm). This is probably due to the shielding effect of the $\text{C}\equiv\text{C}$ triple bond in the region of the C^1 carbon of the Ph group in I. That shielding effect disappears upon coordination to the $\text{Co}_2(\text{CO})_6$ group to give II. From the spectroscopic data above it was not possible to establish the structure of II, and therefore it was determined by an X-ray diffraction study [3]. The results are summarized in Tables 2 and 3, and the structure is shown in Fig. 1.

In compound II there is a $\mu_3\text{-}\eta^2\text{-CCPh}$ ligand [5] σ -bonded to the manganese atom and π -bonded to the $\text{Co}_2(\text{CO})_6$ moiety, with non-bonding Mn–Co distances longer than 3.5 Å. The angle between the vectors Co(1)–Co(2) and C(11)–C(12) is 89.2° , therefore as suggested [2,6] for the analogous complexes $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCFe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]\}$, II can be compared with the perpendicular acetylene bridged compounds $\{[\text{Co}_2(\text{CO})_6][\text{RCCR}]\}$ [1]. In fact the dimensions of the Co_2C_2 core and the geometry of the $\text{Co}(\text{CO})_3$ groups in II are very similar to those in the μ -alkynyldicobalt complexes, although the C(11)–Co distances (2.045(9), 2.053(9) Å) are slightly longer than the C(12)–Co distances (2.002(10) and 1.971(11) Å), probably as a result of the presence of different substituents on the two carbons. The Mn–C(11)–C(12) and C(11)–C(12)–C(13) angles ($144.5(8)$ and $143.3(9)^\circ$) are normal for perpendicular acetylene complexes [7], and the dihedral angle Mn–C(11)–C(12)–C(13) is $-9.5(11)^\circ$. The C(11)–C(12) bond length (1.313(11) Å)



Scheme 1. (i) $[\text{Co}_2(\text{CO})_8]$, hexane, 10 h; (ii) $[\text{I}(\text{py})_2][\text{BF}_4]$, CH_2Cl_2 , 0°C , 5 min; (iii) hexane, reflux; (iv) $[\text{Co}_2(\text{CO})_8]$, hexane, 2 h.

Table 1
Spectroscopic data for the complexes described

Compound	IR ^a (cm ⁻¹)	NMR	
		³¹ P{ ¹ H} ^b	¹³ C{ ¹ H} ^c
<i>cis</i> -[Mn(CCPh)(CO) ₄ (PCy ₃)] (I)	2106w, 2074w, 2009w 1988s, 1952s	55.4	214.8–213.9 (m, CO), 130.9 (d, <i>J</i> (PC) 1.2 Hz, C ² of Ph), 128.4 (d, <i>J</i> (PC) 2 Hz, C ¹ of Ph), 127.8 (s, C ³ of Ph), 125.0 (s, C ⁴ of Ph), 116.8 (s, ≡C-Ph), 106.9 (d, <i>J</i> (PC) 26 Hz, ≡C-Mn), 36.4 (d, <i>J</i> (PC) 16.6 Hz, C ¹ of Cy), 29.4 (s, C ³ of Cy), 27.8 (d, <i>J</i> (PC) 9.8 Hz, C ² of Cy), 26.2 (s, C ⁴ of Cy)
{[Co ₂ (CO) ₈][PhCCMn(CO) ₄ (PCy ₃)]} (II)	2082w, 2057w, 2035s 2014m, 1998m, 1984m 1968m, 1958m	66.1 ^d	218(br) and 202.2(s)(CO), 141.7 (C ¹ of Ph), 129.3 and 128.4 (C ² and C ³ of Ph), 126.5 (C ⁴ of Ph), 120.2 (≡C-Ph), 37.9 (d, <i>J</i> (PC) 17.7 Hz, C ¹ of Cy), 29.6 (s, C ³ of Cy), 27.8 (d, <i>J</i> (PC) 10.3 Hz, C ² of Cy), 26.3 (s, C ⁴ of Cy) ^e
<i>trans</i> -[Mn(CCPh)(CO) ₄ (PCy ₃)] (III)	2103w, 1978s	68.0	215.9 (br, CO), 131.2 (s, C ² of Ph), 128.6 (s, C ¹ of Ph) 128.0 (s, C ³ of Ph), 125.0 (s, C ⁴ of Ph), 114.7 (s, ≡C-Ph) 103.0 (s, br, ≡C-Mn), 37.7 (d, <i>J</i> (PC) 18 Hz, C ¹ of Cy), 29.6 (s, C ³ of Cy), 27.8 (d, <i>J</i> (PC) 9.7 Hz, C ² of Cy), 26.3 (s, C ⁴ of Cy)

^a Hexane solution. ^b Spectra in CH₂Cl₂, δ(ppm) downfield from external 85% H₃PO₄. ^c Spectra in CDCl₃, δ (ppm) from internal TMS. ^d At -60 °C. ^e CH₂Cl₂ solution.

Table 2

Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms ^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Co(1)	3265(1)	3501(1)	2196(1)	C(14)	2822(12)	1559(6)	2541(8)
Co(2)	3881(1)	3097(1)	1063(1)	C(15)	3027(14)	882(7)	2927(7)
Mn	928(1)	2826(1)	302(1)	C(16)	3891(15)	478(9)	2891(12)
P	-828(2)	2769(1)	-667(1)	C(17)	4535(15)	751(9)	2501(15)
O(1)	1760(8)	3546(6)	3041(7)	C(18)	4322(11)	1425(7)	2127(11)
O(2)	3115(7)	5005(5)	1700(6)	C(19)	-1323(7)	1860(5)	-1061(6)
O(3)	5254(7)	3422(6)	3658(6)	C(20)	-683(8)	1530(5)	-1588(6)
O(4)	3860(9)	2039(6)	-199(7)	C(21)	-1131(10)	780(5)	-1923(7)
O(5)	3412(9)	4359(6)	-9(7)	C(22)	-1059(10)	293(6)	-1166(7)
O(6)	6150(6)	3209(6)	2105(7)	C(23)	-1722(9)	605(5)	-679(8)
O(7)	1668(6)	3064(5)	-1136(5)	C(24)	-1281(8)	1359(5)	-321(6)
O(8)	922(6)	4390(4)	602(5)	C(25)	-1833(7)	3063(5)	-217(6)
O(9)	209(7)	2476(6)	1719(6)	C(26)	-2984(7)	2983(6)	-792(7)
O(10)	1621(6)	1319(4)	287(6)	C(27)	-3724(8)	3113(7)	-266(9)
C(1)	2336(9)	3509(6)	2703(8)	C(28)	-3540(9)	3840(7)	128(7)
C(2)	3144(8)	4421(7)	1887(7)	C(29)	-2388(8)	3911(7)	708(7)
C(3)	4489(9)	3441(7)	3104(9)	C(30)	-1637(8)	3800(6)	199(7)
C(4)	3876(9)	2451(8)	300(9)	C(31)	-1000(7)	3262(5)	-1663(6)
C(5)	3570(10)	3865(7)	405(8)	C(32)	-702(9)	4056(5)	-1536(7)
C(6)	5276(10)	3167(7)	1694(8)	C(33)	-608(11)	4369(6)	-2364(8)
C(7)	1390(7)	2983(5)	-592(7)	C(34)	-1632(12)	4295(7)	-3077(8)
C(8)	880(7)	3792(6)	479(6)	C(35)	-2033(10)	3502(7)	-3227(7)
C(9)	475(7)	2621(6)	1158(7)	C(36)	-2078(8)	3185(6)	-2388(7)
C(10)	1307(8)	1887(6)	280(7)	*C(37)	3990(21)	4901(15)	4669(18)
C(11)	2451(6)	2885(5)	1166(6)	*C(38)	4754(29)	4825(19)	5700(23)
C(12)	3220(7)	2519(5)	1713(6)	*O(11)	4406(15)	5344(10)	4268(12)
C(13)	3479(8)	1831(5)	2149(6)				

^a Crystal data (from ref. 3): $C_{36}H_{38}Co_2MnO_{10}P \cdot 1/2C_2H_5OH$, $M = 1715.01$, monoclinic, space group $P2_1/c$, a 13.545(5), b 18.691(7), c 16.944(9) Å, β 110.89(3)°, V 4008(3) Å³, $Z = 4$, D_c 1.421 g cm⁻³, $F(000) = 1764$, (Mo- K_α) 12.06 cm⁻¹. The starred atoms (of the solvent molecule) are statistically distributed between two positions of equal occupancy.

is longer by ca. 0.1 Å than those in the alkynylmanganese complex [Mn(CCBu¹)(CO)₃(dppe)] (1.214(8) Å) [8] and the compounds [CuCl(η^2 -PhCCMn(CO)₃(dppe)] (1.226(5) Å) [9] and {Cu[η^2 -Bu¹CCMn(CO)₃(dppe)]₂}PF₆ (1.237(18) Å) [10] that have alkynylmanganese groups η^2 -bonded to copper. The C(11)–C(12) distance in compound II is close to the ethylenic bond length (1.337 Å), and may indicate a double bond, as suggested for the dicobalt-hexacarbonyl-acetylene species [11]. The Mn–C(11) bond length (2.063(7) Å) is similar to those in the above mentioned copper adducts of the alkynyl [Mn(CCBu¹)(CO)₃(dppe)] (2.023(4) and 2.032(11) Å, respectively), but longer than the Mn–C distance in the free alkynyl corresponding to the latter (1.996(6) Å).

The bond angles around the manganese atom (Table 3) are close to those corresponding to octahedral coordination, and only the C(8)–Mn–C(10) angle (166.4(5)°) deviates significantly from the ideal value. The Mn–CO and Mn–P distances are not unusual.

Rather unexpectedly, however, the four carbonyl ligands bonded to the manganese atom are mutually *trans*, whereas the starting alkynyl (I) had a *cis* stereochemistry.

Table 3
Selected bond lengths (Å) and angles (°)

Co(1)–Co(2)	2.469(3)	Mn–C(9)	1.806(13)
Co(1)–C(11)	2.053(9)	Mn–C(10)	1.833(11)
Co(1)–C(12)	2.002(10)	Mn–P	2.362(3)
Co(2)–C(11)	2.045(9)	Co(1)–C(1)	1.759(15)
Co(2)–C(12)	1.971(11)	Co(1)–C(2)	1.788(13)
C(11)–C(12)	1.313(11)	Co(1)–C(3)	1.819(11)
C(12)–C(13)	1.462(13)	Co(2)–C(4)	1.767(16)
C(11)–Mn	2.063(7)	Co(2)–C(5)	1.774(13)
Mn–C(7)	1.857(13)	Co(2)–C(6)	1.814(12)
Mn–C(8)	1.835(11)		
C(11)–C(12)–C(13)	143.3(10)	C(11)–Co(1)–C(12)	37.8(4)
Mn–C(11)–C(12)	144.5(8)	C(1)–Co(1)–C(2)	97.4(5)
C(11)–Mn–P	178.8(3)	C(1)–Co(1)–C(3)	100.5(6)
C(11)–Mn–C(7)	91.6(4)	C(2)–Co(1)–C(3)	105.5(6)
C(11)–Mn–C(8)	85.2(4)	C(11)–Co(2)–C(12)	38.1(4)
C(11)–Mn–C(9)	88.9(4)	C(4)–Co(2)–C(5)	98.9(6)
C(11)–Mn–C(10)	81.3(5)	C(4)–Co(2)–C(6)	102.2(6)
C(7)–Mn–C(8)	91.1(4)	C(5)–Co(2)–C(6)	106.0(6)
C(7)–Mn–C(9)	176.8(5)	Co(1)–C(11)–Co(2)	74.1(3)
C(7)–Mn–C(10)	87.5(5)	Co(1)–C(12)–Co(2)	76.8(4)
C(8)–Mn–C(9)	92.0(5)		
C(8)–Mn–C(10)	166.4(5)		
C(9)–Mn–C(10)	89.5(5)		
P–Mn–C(7)	89.4(4)		
P–Mn–C(8)	94.1(3)		
P–Mn–C(9)	90.1(4)		
P–Mn–C(10)	99.4(4)		

Compound II is therefore a $\text{Co}_2(\text{CO})_6$ complex of the *trans* isomer of I, and this means that during the formation of II (i in the Scheme) there is a change in the stereochemistry of I. This may take place after the coordination of I to the $\text{Co}_2(\text{CO})_6$ group, but it is possible that in solution I is in equilibrium with a small amount (not detectable in the spectra of I) of the *trans* isomer which is the one that reacts with $[\text{Co}_2(\text{CO})_8]$ to give II.

It is known [1] that the acetylene ligands RCCR' can be recovered from the dicobalt hexacarbonyl complexes by chemical treatment (e.g. oxidation). This suggested the possibility of obtaining the *trans* isomer of I from II and this was achieved by treating II with $[\text{I}(\text{py})_2][\text{BF}_4]$ (1 : 2) in CH_2Cl_2 at 0°C (ii in Scheme 1), which immediately gave a deep green solution with evolution of CO. From the resulting mixture, the yellow *trans*- $[\text{Mn}(\text{CCPh})(\text{CO})_4(\text{PCy}_3)]$ (III) (Table 1) was obtained in ca. 60% yield. although, depending on the reaction conditions, variable (small) amounts of other product, probably *cis*- $[\text{Mn}(\text{I})(\text{CO})_4(\text{PCy}_3)]^*$ were detected by IR spectroscopy. The same compound is formed slowly when I, II, or III is treated with I_2 in hexane. In reaction ii, the blue crystalline complex $[\text{Co}(\text{I})_2(\text{py})_2]$ is

* $\nu(\text{CO})$ (hexane, cm^{-1}) 2074m, 2009m, 1992s, 1947s, the spectrum is very similar to that of I [12] but without the $\nu(\text{C}\equiv\text{C})$ band. The presence of the *trans*- $[\text{Mn}(\text{I})(\text{CO})_4(\text{PCy}_3)]$ isomer cannot be ruled out ($\nu(\text{CO})$ for this is close to that for I).

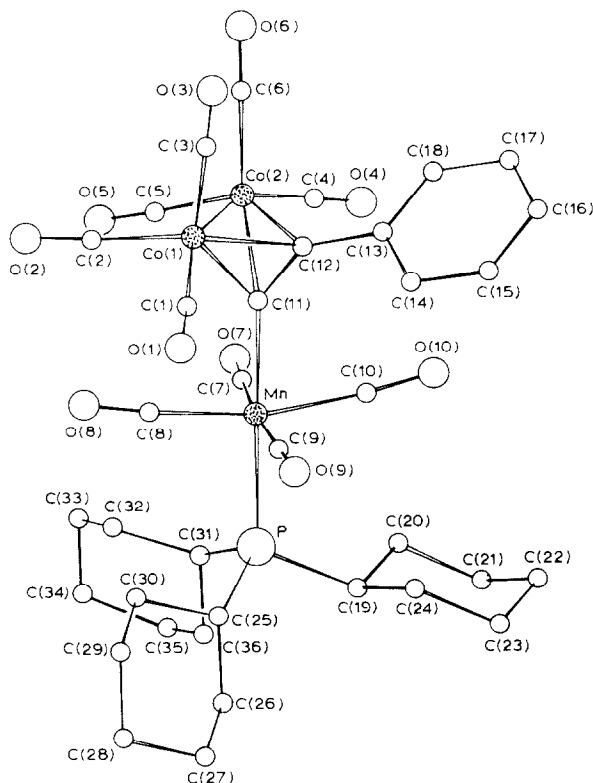


Fig. 1. Perspective view of the molecule $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCMn}(\text{CO})_4(\text{PCy}_3)]\}$ showing the atom numbering.

formed (as in the oxidation of $[\text{Co}_2(\text{CO})_6(\text{C}_6\text{F}_5\text{CCC}_6\text{F}_5)]$ [14], along with an off-white solid that probably contained $\text{Co}(\text{BF}_4)_2$ because it was very soluble in water to give pink Co^{2+} solutions, and shows a broad IR absorption in the range $1000\text{--}1100\text{ cm}^{-1}$.

The release of III from II by oxidation with $[\text{I}(\text{py})_2]^+$ is a kinetically controlled process because III slowly reverts in solution to the *cis* isomer I (iii, in Scheme 1). If the isomerization is accelerated by heating in hexane, the formation of the known [12] *mer*- $[\text{Mn}(\text{CCPh})(\text{CO})_3(\text{PCy}_3)_2]$ is observed. Compound I is therefore thermodynamically more stable than III, in keeping with observations for $[\text{Mn}(\text{X})(\text{CO})_4(\text{L})]$ complexes [13]. As expected, III reacted easily with $[\text{Co}_2(\text{CO})_8]$ to give II (iv in Scheme 1).

Other attempts to obtain III from II were less successful. Thus, oxidation with $\text{Ce}(\text{SO}_4)_2$ in acetone was very slow and gave a mixture of I and II, and reduction with $\text{Na}[\text{Hg}]$ under a CO atmosphere gave $[\text{Co}(\text{CO})_4]^-$ and a mixture of I and II. The latter result is rather surprising, because the reaction is fast and the *trans*-alkynyl III does not react with $\text{Na}[\text{Hg}]$ in THF to give I.

Compound II was also found to react with bis(diphenylphosphino)methane (dppm) in THF at room temperature to give mainly III and $[\text{Co}_2(\text{CO})_6(\text{dppm})]$ [15], but did not react with $\text{O}_2(\text{g})$, in contrast to the behaviour of the analogous $\{[\text{Co}_2(\text{CO})_6][\mu\text{-PhCCFe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]\}$ [6].

Experimental

All reactions were carried out under N₂. IR spectra were recorded on a Perkin–Elmer 298 Spectrophotometer and calibrated by use of the 1602 cm⁻¹ band of polystyrene. NMR spectra were recorded on a Bruker AM 300 instrument. The compound *cis*-[Mn(CCPPh)(CO)₄(PCy₃)] was prepared by the published method [13].

Synthesis of $\{[Co_2(CO)_6][\mu\text{-PhCCMn}(CO)_4(PCy_3)]\}$ (II)

A mixture of [Co₂(CO)₈] (0.75 g, 2.19 mmol) and I (1.20 g, 2.19 mmol) in hexane (60 cm³) was stirred at room temperature for 10 h, then concentrated to half volume. The liquid was decanted off and the green crystalline residue was washed with hexane then dissolved in CH₂Cl₂ (30 cm³). The solution was filtered, hexane (20 cm³) was added, and the mixture was concentrated in vacuo to give III (1.10 g, 60%). From the mother liquors a further 0.2–0.3 g of product was recovered. M.p. 126 °C dec. Analysis. Found: C, 49.9; H, 4.64. MnCo₂C₃₆H₃₈O₁₀P · 1/2CH₂Cl₂ calcd.: C, 50.0; H, 4.45%.

Synthesis of trans-[Mn(CCPPh)(CO)₄(PCy₃)] (III)

Solid [I(py)₂][BF₄] (0.36 g, 0.97 mmol) was added to a solution of II (0.4 g, 0.48 mmol) in CH₂Cl₂ (25 cm³) at 0 °C and the mixture was stirred for 5 min (CO was evolved). The solvent was evaporated in vacuo and the residue extracted (5 × 20 cm³) with 50% mixture of hexane/diethyl ether. The extracts were filtered and concentrated to half volume, and the small amount of green solid which separated was discarded. The solution was filtered and then concentrated to ca. 1 cm³ to give yellow microcrystalline III (0.15 g, 58%). The product was recrystallized from diethyl ether/hexane. M.p. 126 °C. Analysis. Found: C, 65.6; H, 6.95. MnC₃₀H₃₈O₄P calcd.: C, 65.7; H, 6.93.

The green residue left after extraction of III was dissolved in CH₂Cl₂ (20 cm³) to leave an off-white water-soluble solid. The CH₂Cl₂ solution was filtered, hexane (20 cm³) was added, and concentration in vacuo gave blue microcrystalline [Co(I)₂(py)₂] (0.13 g, 56%). Analysis. Found: C, 26.4; H, 2.19; N, 5.90. CoI₂C₁₀H₁₀N₂ calcd.: C, 25.5; H, 2.12; N, 5.95%. IR spectrum (Nujol mull): 1600s, 1482m, 1442s, 1217m, 1154m, 1082(sh,br), 1062s, 1042s, 1012m, 752s, 689s, 677m, and 642m.

Reduction of II

A solution of II (0.1 g, 0.12 mmol) in THF (20 cm³) was treated with CO (1 atm) for 1 h without change. An excess of Na[Hg] (1%) was added and the green solution turned yellow. The solvent was evaporated and the residue was extracted with hexane to give a mixture of I and III. After addition of [Co₂(CO)₈] (0.05 g, 0.15 mmol) to the hexane solution the mixture was stirred for 2 h to give II (0.04 g).

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