

Diphenylphosphine derivatives of $\text{Co}(\text{NO})(\text{CO})_3$, $\text{Fe}(\text{NO})_2(\text{CO})_2$ and $\text{Mn}(\text{NO})(\text{CO})_4$

Jiann T. Lin ^{a,*}, Shiow Y. Wang ^b, Yung C. Chou ^a, Ming L. Gong ^{a,c}, Yui-May Shiow ^a,
 Han-Mou Gau ^c, Yuh S. Wen ^a

^a Institute of Chemistry, Academia Sinica, Taipei, Taiwan

^b Private Chung Chou Junior College of Technology and Commerce, Chung Hua, Taiwan

^c Department of Chemistry, National Chung-Hsin University, Taichung, Taiwan

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Abstract

The complexes $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PH})_2$ (**1**), $\text{Fe}(\text{NO})_2(\text{Ph}_2\text{PH})_2$ (**2**) and $\text{Mn}(\text{NO})(\text{CO})_2(\text{Ph}_2\text{PH})_2$ (**3**) are synthesized from $\text{Co}(\text{NO})(\text{CO})_3$, $\text{Fe}(\text{NO})_2(\text{CO})_2$ and $\text{Mn}(\text{NO})(\text{CO})_4$ respectively. Deprotonation of **1** with two equivalents of BuLi followed by subsequent addition of methyl iodide, allyl bromide and propargyl bromide provides $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PMe})_2$ (**4**), $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CHCH}_2)_2$ (**5**) and $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CCH})_2$ (**6**) respectively. X-ray crystal structure analyses for **1**, **3** and **4–6** were carried out to give data as followed. **1**: monoclinic; $C2/c$; $Z = 4$; $a = 17.130(5)$, $b = 9.894(2)$ and $c = 42.607(1)$ Å; $\beta = 93.29(2)^\circ$; $V = 7210(2)$ Å³; $R = 0.056$; $R_w = 0.058$. **3**: monoclinic; $C2/c$; $Z = 4$; $a = 15.231(5)$, $b = 10.247(2)$ and $c = 16.311(2)$ Å; $\beta = 102.29(2)^\circ$; $V = 2488(1)$ Å³; $R = 0.041$; $R_w = 0.042$. **4**: monoclinic; $C2/c$; $Z = 4$; $a = 15.556(3)$, $b = 12.072(1)$ and $c = 14.809(2)$ Å; $\beta = 114.43(1)^\circ$; $V = 2532.0(7)$ Å³; $R = 0.032$; $R_w = 0.031$. **5**: monoclinic; $P2_1/c$; $Z = 4$; $a = 15.427(2)$, $b = 10.118(2)$ and $c = 18.793(6)$ Å; $\beta = 102.56(1)^\circ$; $V = 2863(1)$ Å³; $R = 0.042$; $R_w = 0.046$. **6**: monoclinic; $P2_1/n$; $Z = 4$; $a = 9.3393(8)$, $b = 19.035(4)$ and $c = 16.007(1)$ Å; $\beta = 94.912(7)^\circ$; $V = 2845.8(6)$ Å³; $R = 0.052$; $R_w = 0.059$.

Keywords: Nitrosyl; Carbonyl; Manganese; Phosphine; Cobalt; Iron

1. Introduction

Coordinated NO ligands are usually much more resistant to ligand substitution than are CO groups [1]. Being a better π acceptor than CO, a NO ligand frequently labilizes the CO ligands coordinated to the same metal atoms and sometimes causes ligand substitution to occur in rather mild conditions [2]. We are interested in dinuclear complexes with a phosphide bridge [3] since such a bridge normally is robust enough to prevent fragmentation of the dimer during reaction [4]. We therefore set out to synthesize the bis(diphenylphosphine) derivatives of $\text{Co}(\text{NO})(\text{CO})_3$, $\text{Fe}(\text{NO})_2(\text{CO})_2$, and $\text{Mn}(\text{NO})(\text{CO})_4$ since these metal nitrosyl carbonyls have been reported to react with various tertiary phosphines to form monosubstituted and disubstituted derivatives via carbonyl substitution [5], and deprotonation of $[\text{M}](\text{R}_2\text{PH})$ has been one of the most

frequently used methods to obtain phosphide-bridged complexes [6]. In this report we shall describe the syntheses of $[\text{M}](\text{Ph}_2\text{PH})_2$ ($[\text{M}] = \text{Co}(\text{NO})(\text{CO})$ (**1**), $\text{Fe}(\text{NO})_2$ (**2**) or $\text{Mn}(\text{NO})(\text{CO})_2$ (**3**)) from the aforementioned metal nitrosyl carbonyls. Such complexes could potentially form dinuclear complexes bridged by two diphenylphosphide [7], or phosphide-bridged trinuclear complexes. Some derivatives of **1** are also described.

2. Experimental section

2.1. General procedures

All reactions and manipulations were carried out under N_2 with use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed under N_2 with use of silica gel (230–400 mesh ASTM; Merck) as the stationary phase in a column 35 cm in length and 2.5 cm in diameter. The compounds

* Corresponding author.

[PPN][Fe(CO)₃(NO)] (PPN⁺ = (Ph₃P)₂N⁺) [8], Co(NO)(CO)₃ [9], Fe(NO)₂(CO)₂ [9] or Mn(NO)(CO)₄ [10] were prepared by published procedures with modifications. IR measurements were measured on a Perkin–Elmer 880 spectrometer. The NMR spectra were measured using Bruker AMX500 (¹H and ³¹P), AC200 (¹H) and AC300 (¹H and ³¹P) spectrometers. Elementary analyses were performed on a Perkin–Elmer 2400 CHN analyzer.

2.2. Preparations

2.2.1. Co(NO)(CO)(Ph₂PH)₂ (1)

To a solution of 3.0 g of Co(NO)(CO)₃ (17.3 mmol) in 150 ml of CH₃CN pre-chilled to –20°C was added 2.01 equivalents of Ph₂PH (6.1 ml). The low temperature bath was then removed, and the solution was stirred at room temperature for 24 h and then at 40°C for 72 h. After removal of the solvent the residue was chromatographed. Elution with CH₂Cl₂:hexane (1:10 by volume) gave the orange first band which was identified to be Co(NO)(CO)₂(Ph₂PH). The dark-red second band eluted from CH₂Cl₂/hexane (1:10 by vol) provided **1**

(44%) after removal of the solvent. Anal. Found: C, 61.26; H, 4.39; N, 2.86. C₂₅H₂₂NO₂P₂Co calc.: C, 61.36; H, 4.53; N, 2.86.

2.2.2. Fe(NO)₂(Ph₂PH)₂ (2)

One equivalent of NO⁺BF₄[–] (0.857 g, 7.34 mmol) was added all at once via a Schlenk tube into a vigorously stirred CH₂Cl₂ solution (30 ml) of [PPN][Fe(CO)₃(NO)] (5.00 g, 7.34 mmol) pre-chilled to –78°C. After 12 h at –78°C the solution was slowly warmed to room temperature. An acetonitrile solution (60 ml) of Ph₂PH (14.8 mmol, 2.60 ml) was then added and the solution was heated at 55°C for 48 h. The solvent was removed under reduced pressure and the residue was chromatographed. Elution with CH₂Cl₂:hexane (1:5 by volume) gave the orange–red first band, from which trace amounts of Fe(NO)₂(CO)₂ was isolated. The dark-red second band eluted with CH₂Cl₂:hexane (1:3 by volume) provided **2** with a yield of 2.11 g (59%). Anal. Found: C, 58.56; H, 4.15; N, 5.36. C₂₄H₂₂N₂O₂P₂Fe calc.: C, 59.04; H, 4.13; N, 5.36%.

Table 1
Crystal data for **1** and **3–6**

	1	3	4	5	6
Formula	C ₇₅ H ₆₀ Co ₃ N ₃ O ₆ P ₆	C ₂₆ H ₂₂ MnNO ₃ P ₂	C ₂₇ H ₂₆ CoNO ₂ P ₂	C ₃₁ H ₃₀ CoNO ₂ P ₂	C ₃₁ H ₂₆ CoNO ₂ P ₂
Formula weight	1461.96	513.35	517.39	569.46	565.43
<i>a</i> (Å)	17.130(5)	15.231(5)	15.556(3)	15.427(2)	9.3393(8)
<i>b</i> (Å)	9.894(2)	10.247(2)	12.072(1)	10.118(2)	19.035(4)
<i>c</i> (Å)	42.607(1)	16.311(2)	14.809(2)	18.793(6)	16.007(1)
<i>β</i> (°)	93.29(2)	102.29(2)	114.43(1)	102.56(1)	94.912(7)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4	4	4	4	4
<i>V</i> (Å ³)	7210(2)	2488(1)	2532.0(7)	2863(1)	2845.8(6)
<i>D</i> _{calc} (g cm ^{–3})	1.347	1.371	1.357	1.321	1.320
Crystal size (mm)	0.28 × 0.07 × 0.19	0.41 × 0.22 × 0.13	0.25 × 0.30 × 0.38	0.06 × 0.12 × 0.22	0.38 × 0.19 × 0.14
Radiation	Cu Kα (λ = 1.5406 Å)	Mo Kα (λ = 0.7107 Å)	Same	Same	Same
μ (mm ^{–1})	9.75	0.66	0.82	0.75	0.74
Transmission factors (maximum–minimum)	1.00–0.34	1.00–0.88	1.00–0.94	1.00–0.87	1.00–0.97
2θ range (°)	2.0–130	2.0–5.0	2.0–50	2.0–45	2.0–45
Octants	± <i>h</i> (–20–20), + <i>k</i> (0–11), + <i>l</i> (0–50)	± <i>h</i> (–18–18), + <i>k</i> (0–12), + <i>l</i> (0–19)	± <i>h</i> (–18–18), + <i>k</i> (0–14), + <i>l</i> (0–17)	± <i>h</i> (–16–16), + <i>k</i> (0–10), + <i>l</i> (0–20)	± <i>h</i> (–10–10), + <i>k</i> (0–20), + <i>l</i> (0–17)
Number of unique reflections	6135	2186	2234	3730	3700
Number of reflections with <i>I</i> > <i>nσ</i>	2752 (<i>n</i> = 2)	1105 (<i>n</i> = 2)	1567 (<i>n</i> = 2)	1632 (<i>n</i> = 2.5)	2341 (<i>n</i> = 2)
Number of variables	421	155	150	334	335
<i>R</i> , <i>R</i> _w	0.056, 0.058	0.041, 0.042	0.032, 0.031	0.042, 0.046	0.052, 0.059
Goodness of fit	2.06	1.68	2.04	1.45	2.46
Maximum Δ/ <i>σ</i>	0.221	0.007	0.028	0.002	0.001

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$. For **1**, *k* = 0.00015; for **3**, *k* = 0.0001; for **4**, *k* = 0.00002; for **5**, *k* = 0.0001; for **6**, *k* = 0.00005.

2.2.3. $Mn(NO)(CO)_2(Ph_2PH)_2$ (3)

The complex $Mn(NO)(CO)_4$ (0.745 g, 3.78 mmol) was vacuum transferred to a flask containing EtOH solution (50 ml) of Ph_2PH (1.25 ml, 7.18 mmol). The flask containing the mixture was immersed in a cold bath at $-20^\circ C$ and an EtOH solution (20 ml) of Me_3NO

(0.292 g, 3.39 mmol) was added dropwise. When the addition of Me_3NO was complete, the solution was slowly warmed to room temperature and stirred for 24 h, and then at $50^\circ C$ for 48 h. After removal of the solvent the residue was chromatographed rapidly. The orange–red first band eluted with CH_2Cl_2 : hexane (1 : 3

Table 2
Atomic coordinates for 1

Atom	x	y	z	B_{iso} ($\text{\AA}^2$)
Co(1)	0.16949(7)	0.21127(12)	0.57245(3)	4.83(7)
Co(2)	0.50000	0.97853(18)	0.25000	5.79(11)
P(1)	0.23524(11)	0.03390(19)	0.55837(5)	4.11(10)
P(2)	0.26141(11)	0.33427(20)	0.59679(5)	4.36(10)
P(3)	0.59358(12)	0.83202(22)	0.25997(5)	4.99(11)
N	0.1266(4)	0.2825(7)	0.5409(2)	6.8(4)
O(1)	0.0879(4)	0.1258(9)	0.6254(2)	10.9(5)
O(2)	0.0958(5)	0.3280(6)	0.5184(2)	10.2(5)
O(3)	0.5224(4)	1.1357(8)	0.1955(2)	10.0(5)
C(1)	0.1209(5)	0.1590(9)	0.6046(2)	6.0(5)
C(N)(3)	0.5152(5)	1.0665(8)	0.2167(2)	6.5(5)
C(11)	0.1800(4)	−0.1210(7)	0.5506(2)	4.0(4)
C(12)	0.2144(4)	−0.2341(8)	0.5382(2)	4.5(4)
C(13)	0.1693(5)	−0.3455(8)	0.5295(2)	5.0(4)
C(14)	0.0896(5)	−0.3453(8)	0.5332(2)	5.4(4)
C(15)	0.0560(4)	−0.2353(8)	0.5456(2)	5.5(5)
C(16)	0.0998(4)	−0.1225(7)	0.5546(2)	4.7(4)
C(21)	0.3212(4)	−0.0180(7)	0.5826(2)	4.3(4)
C(22)	0.3143(5)	−0.0757(10)	0.6112(2)	6.6(5)
O(23)	0.3805(7)	−0.1055(11)	0.6305(2)	8.0(6)
C(24)	0.4531(6)	−0.0743(11)	0.6213(2)	7.1(6)
C(25)	0.4596(5)	−0.0197(10)	0.5930(3)	7.6(6)
C(26)	0.3950(5)	0.0122(9)	0.5737(2)	6.3(4)
C(31)	0.3257(4)	0.4334(7)	0.5731(2)	3.7(3)
C(32)	0.3335(4)	0.3991(7)	0.5419(2)	4.3(4)
C(33)	0.3824(5)	0.4717(9)	0.5240(2)	5.0(4)
C(34)	0.4232(4)	0.5823(9)	0.5365(2)	5.2(4)
C(35)	0.4150(5)	0.6165(8)	0.5674(2)	5.3(4)
C(36)	0.3670(4)	0.5448(8)	0.5854(2)	4.7(4)
C(41)	0.2255(4)	0.4507(8)	0.6252(2)	4.2(4)
C(42)	0.1784(5)	0.5604(9)	0.6147(2)	5.5(5)
C(43)	0.1436(5)	0.6446(9)	0.6356(2)	6.1(5)
C(14)	0.1537(6)	0.6213(12)	0.6667(2)	8.0(6)
C(45)	0.1989(7)	0.5162(13)	0.6775(2)	9.9(7)
C(46)	0.2347(5)	0.4322(10)	0.6570(2)	7.1(5)
C(51)	0.6890(5)	0.8945(11)	0.2753(2)	6.1(5)
C(52)	0.6931(6)	1.0192(16)	0.2884(3)	12.1(9)
C(53)	0.7640(9)	1.0719(19)	0.3029(3)	15.7(12)
C(54)	0.8220(12)	0.9762(28)	0.3024(5)	17.0(20)
C(55)	0.8325(15)	0.8666(24)	0.2877(7)	21.1(21)
C(56)	0.7538(8)	0.8224(12)	0.2757(4)	14.0(10)
C(61)	0.5753(4)	0.6968(10)	0.2878(2)	5.5(5)
C(62)	0.5528(5)	0.7270(10)	0.3171(2)	6.7(5)
C(63)	0.5383(6)	0.6197(16)	0.3373(3)	9.5(8)
C(64)	0.5461(8)	0.4883(19)	0.3284(4)	10.5(10)
C(65)	0.5691(8)	0.4615(13)	0.2995(4)	11.3(9)
C(66)	0.5832(6)	0.5629(11)	0.2784(2)	8.2(6)

Table 3

Atomic coordinates for **3**

Atom	x	y	z	B_{iso} ($\text{\AA}^2$)
Mn	0.0	0.20155(12)	0.25	4.45(6)
P	0.13247(9)	0.19233(14)	0.21054(8)	4.15(7)
N	0.0	0.3708(7)	0.25	5.5(4)
O(1)	−0.0751(3)	0.0425(4)	0.1018(2)	7.3(2)
O(2)	0.0	0.4852(6)	0.25	7.7(4)
C(1)	−0.0458(3)	0.1035(5)	0.1598(3)	4.3(3)
C(11)	0.2325(4)	0.2476(5)	0.2840(3)	4.3(2)
C(12)	0.3171(4)	0.2318(6)	0.2673(3)	5.9(3)
C(13)	0.3927(4)	0.2701(7)	0.3238(4)	6.7(4)
C(14)	0.3850(4)	0.3250(6)	0.3988(4)	5.7(3)
C(15)	0.3028(4)	0.3428(5)	0.4168(3)	4.9(3)
C(16)	0.2259(3)	0.3050(5)	0.3600(3)	4.4(2)
C(21)	0.1354(3)	0.2747(5)	0.1127(3)	4.2(3)
C(22)	0.1384(5)	0.4077(7)	0.1084(4)	8.3(5)
C(23)	0.1335(6)	0.4712(7)	0.0335(5)	10.1(6)
C(24)	0.1273(5)	0.3998(7)	−0.0384(4)	6.7(4)
C(25)	0.1262(4)	0.2688(6)	−0.0353(3)	6.2(4)
C(26)	0.1307(4)	0.2058(5)	0.0403(3)	5.1(3)
H	0.162(2)	0.069(3)	0.196(2)	2.4(8)

Table 4

Atomic coordinates for **4**

Atom	x	y	z	B_{iso} ($\text{\AA}^2$)
Co	0.00000	0.19413(5)	0.25000	4.60(3)
P	−0.00952(5)	0.31213(7)	0.13234(5)	3.79(4)
C(N)	−0.1047(2)	0.1277(2)	0.2159(2)	5.2(1)
C(1)	0.1002(2)	0.3815(3)	0.1486(2)	5.0(2)
C(2)	−0.0939(2)	0.4242(2)	0.1090(2)	3.6(1)
C(3)	−0.0700(2)	0.5351(2)	0.1154(2)	4.6(2)
C(4)	−0.1377(2)	0.6167(3)	0.0982(2)	6.0(2)
C(5)	−0.2291(2)	0.5891(3)	0.0745(2)	6.1(2)
C(6)	−0.2548(2)	0.4792(3)	0.0686(2)	5.6(2)
C(7)	−0.1877(2)	0.3983(2)	0.0864(2)	4.6(2)
C(8)	−0.0422(2)	0.2519(2)	0.0086(2)	3.7(1)
C(9)	−0.1127(2)	0.2958(2)	−0.0773(2)	4.2(1)
C(10)	−0.1304(2)	0.2491(3)	−0.1690(2)	5.1(2)
C(11)	−0.0787(2)	0.1595(3)	−0.1759(2)	5.8(2)
C(12)	−0.0099(2)	0.1153(3)	−0.0925(2)	5.7(2)
C(13)	0.0079(2)	0.1609(2)	−0.0004(2)	4.8(2)
O	−0.1751(2)	0.0813(2)	0.1955(2)	9.4(2)

Table 5

Atomic coordinates **5**

Atom	x	y	z	B_{iso} ($\text{\AA}^2$)
Co	0.76419(11)	0.31464(18)	0.10288(9)	3.61(8)
P(1)	0.65424(19)	0.1712(3)	0.08176(16)	3.15(16)
P(2)	0.87773(19)	0.1898(4)	0.15541(16)	3.06(16)
N	0.7419(7)	0.4270(11)	0.1640(6)	5.2(6)
C(1)	0.7802(7)	0.4132(11)	−0.0341(5)	7.9(7)
C(2)	0.7234(8)	0.5070(11)	0.2034(6)	8.1(7)
C(1)	0.7767(7)	0.3701(11)	0.0216(6)	3.1(6)
C(2)	0.6580(8)	0.0352(12)	0.0164(6)	4.0(7)
C(3)	0.6905(11)	0.0770(15)	−0.0511(8)	6.6(10)
C(4)	0.6509(11)	0.0603(16)	−0.1166(9)	8.1(11)
C(5)	0.8926(7)	0.1603(12)	0.2546(6)	3.9(7)
C(6)	0.9104(8)	0.2851(13)	0.2985(7)	4.4(7)
C(7)	0.8660(9)	0.3212(16)	0.3462(7)	6.3(8)
C(11)	0.5463(8)	0.2478(11)	0.0405(6)	3.4(6)
C(12)	0.5393(8)	0.3186(14)	−0.0246(7)	4.6(7)
C(13)	0.4590(10)	0.3708(14)	−0.0591(7)	5.6(8)
C(14)	0.3849(9)	0.3568(14)	−0.0297(8)	5.5(8)
C(15)	0.3898(9)	0.2890(14)	0.0337(8)	5.2(8)
C(16)	0.4713(9)	0.2347(14)	0.0688(7)	4.7(8)
C(21)	0.6320(7)	0.0855(12)	0.1603(7)	3.3(6)
C(22)	0.6336(10)	0.1551(14)	0.2231(8)	6.2(9)
C(23)	0.6139(11)	0.0926(20)	0.2833(9)	7.9(11)
C(24)	0.5984(11)	−0.0373(21)	0.2836(9)	7.0(11)
C(25)	0.5998(11)	−0.1088(16)	0.2240(11)	7.5(11)
C(26)	0.6163(9)	−0.0461(15)	0.1612(7)	5.1(8)
C(31)	0.8793(7)	0.0217(12)	0.1214(6)	3.0(6)
C(32)	0.8515(8)	−0.0870(12)	0.1568(7)	3.7(7)
C(33)	0.8460(8)	−0.2109(12)	0.1244(8)	4.3(7)
C(34)	0.8700(9)	−0.2314(14)	0.0586(8)	5.2(8)
C(35)	0.8986(9)	−0.1266(16)	0.0233(7)	5.3(8)
C(36)	0.9042(8)	−0.0011(13)	0.0551(7)	4.2(7)
C(41)	0.9869(7)	0.2514(13)	0.1483(6)	3.0(6)
C(42)	1.0649(8)	0.1794(14)	0.1784(6)	4.1(7)
C(43)	1.1458(8)	0.2294(14)	0.1717(7)	4.7(8)
C(44)	1.1505(8)	0.3493(15)	0.1365(7)	4.9(8)
C(45)	1.0754(9)	0.4190(12)	0.1081(7)	4.3(7)
C(46)	0.9943(8)	0.3708(12)	0.1145(6)	3.7(6)

by volume) provided 0.497 g (16.0%) of powdery **3**. Anal. Found: C, 60.44; H, 4.10; N, 2.51. $C_{26}H_{22}NO_3P_2Mn$ calc.: C, 60.83; H, 4.32; N, 2.73%.

2.2.4. $Co(NO)(CO)(Ph_2PMe)_2$ (**4**)

Two equivalents of BuLi (1.6 M in tetrahydrofuran (THF), 2.5 ml) was added dropwise to a THF solution (100 ml) of **1** (0.978 g, 2.00 mmol) pre-chilled to -78°C . After being stirred at -78°C for 1 h, to the solution was added 0.25 ml (4.00 mmol) of MeI. The solution was stirred at the same temperature for 30 min and then was slowly warmed to room temperature. After removal of the solvent the residue was chromatographed. Complex **4** was obtained (82%) from the reddish first band eluted with Et_2O :hexane (1:5 by volume). Anal. Found: C, 62.41; H, 4.95; N, 2.50. $C_{27}H_{26}NO_2P_2Co$ calc.: C, 62.68; H, 5.06; N, 2.71%.

2.2.5. $Co(NO)(CO)(Ph_2PCH_2CHCH_2)_2$ (**5**)

The procedure for the synthesis of **4** was followed, except that allyl bromide was used instead of methyl iodide, and the eluent for the chromatography was CH_2Cl_2 :hexane (1:7 by volume). Complex **5** was obtained as reddish-brown powders (67%) Anal. Found: C, 65.07; H, 5.33; N, 2.38. $C_{31}H_{30}NO_2P_2Co$ calc.: C, 65.30; H, 5.31; N, 2.46%.

2.2.6. $Co(NO)(CO)(Ph_2PCH_2CCH)_2$ (**6**)

The procedure for the synthesis of **4** was followed except that propargyl bromide was used instead of methyl iodide. The first band eluted with CH_2Cl_2 :hexane (1:7 by volume) was not characterized. The orange-red, second band eluted with CH_2Cl_2 :hexane (1:4 by volume) provided **6** (31%) after removal of the

Table 6
Atomic coordinates for **6**

Atom	x	y	z	B_{iso} ($\text{\AA}^2$)
Co	0.08324(11)	0.33596(5)	0.24096(6)	3.70(5)
P(1)	−0.02023(21)	0.41497(10)	0.31605(11)	3.33(9)
P(2)	0.20179(20)	0.40380(10)	0.16039(11)	3.13(8)
N	−0.0383(7)	0.2863(3)	0.1839(4)	4.6(3)
O(1)	0.2980(7)	0.2668(3)	0.3487(4)	7.6(4)
O(2)	−0.1189(7)	0.2486(3)	0.1462(4)	7.2(3)
C(1)	0.2134(9)	0.2961(3)	0.3068(5)	3.4(4)
C(2)	0.0980(7)	0.4610(4)	0.3968(4)	3.9(4)
C(3)	0.1611(8)	0.4133(4)	0.4615(5)	4.1(4)
C(4)	0.2152(10)	0.3764(5)	0.5129(5)	6.0(5)
C(5)	0.0931(8)	0.4464(4)	0.0728(4)	3.7(3)
C(6)	0.0138(8)	0.3939(4)	0.0205(4)	3.8(4)
C(7)	−0.0490(10)	0.3518(5)	−0.0200(5)	5.6(5)
C(11)	−0.1089(8)	0.4887(4)	0.2606(5)	3.7(4)
C(12)	−0.2074(9)	0.4744(4)	0.1933(5)	4.7(4)
C(13)	−0.2767(9)	0.5273(5)	0.1475(5)	5.7(5)
C(14)	−0.2491(11)	0.5955(5)	0.1661(6)	6.4(5)
C(15)	−0.1543(12)	0.6114(5)	0.2313(6)	7.2(6)
C(16)	−0.0826(11)	0.5591(4)	0.2773(5)	6.1(5)
C(21)	−0.1642(8)	0.3812(4)	0.3762(4)	3.8(4)
C(22)	−0.2299(9)	0.4238(4)	0.4315(5)	4.6(4)
C(23)	−0.3385(10)	0.3990(5)	0.4754(5)	5.8(5)
C(24)	−0.3839(11)	0.3327(6)	0.4648(6)	7.3(6)
C(25)	−0.3233(12)	0.2902(5)	0.4093(8)	9.6(7)
C(26)	−0.2116(11)	0.3140(5)	0.3649(6)	7.6(6)
C(31)	0.3425(8)	0.3624(4)	0.1056(4)	3.6(3)
C(32)	0.4369(9)	0.3998(4)	0.0630(5)	4.9(4)
C(33)	0.5402(10)	0.3681(6)	0.0197(6)	6.5(5)
C(34)	0.5506(11)	0.2965(6)	0.0203(7)	7.4(6)
C(35)	0.4554(13)	0.2580(5)	0.0611(8)	9.5(7)
C(36)	0.3519(11)	0.2906(5)	0.1051(6)	6.9(5)
C(41)	0.2959(8)	0.4790(4)	0.2093(4)	3.4(3)
C(42)	0.2582(10)	0.5470(4)	0.1945(5)	5.5(5)
C(43)	0.3285(12)	0.6023(4)	0.2371(7)	7.4(6)
C(44)	0.4365(12)	0.5879(6)	0.2955(6)	6.9(6)
C(45)	0.4788(9)	0.5212(6)	0.3120(5)	5.7(5)
C(46)	0.4077(9)	0.4661(4)	0.2697(5)	4.6(4)

Table 7

Selected bond distances (Å) and angles (°) for **1** and **3–6**

	1	3	4	5	6
<i>Bond distances</i>					
Co(1)–P(1)	2.188(2)				
Co(1)–P(2)	2.202(2)				
Co(1)–C(1)	1.722(9)				
Co(1)–N	1.653(8)				
Co(2)–P(3) or Co(2)–P(3a)	2.185(2)				
Co(2)–C/N(3) or Co(2)–C/N(3a)	1.696(9)				
Mn–P or Mn–Pa		2.246(2)			
Mn–N		1.734(8)			
Mn–C(1) or Mn–C(1a)		1.796(5)			
Co–P or Co–Pa			2.2076(8)		
Co–C/N or Co–C/N(a)			1.694(3)		
Co–P(1)				2.201(3)	2.202(2)
Co–P(2)				2.212(3)	2.194(2)
Co–N					1.687(7)
Co–C(1)					1.718(8)
Co–C/N(1)				1.70 (1)	
Co–C/N(2)				1.69 (1)	
N(1)–(1)					
C/N(3)–O(3)	1.15(1)				
N–O(2)	1.16(1)	1.17(1)			1.170(9)
C/N–O			154(4)		
C(1)–O(1)	1.13(1)	1.142(6)			1.14(1)
C(2)–O(2)					
C(3)–O(3)					
C/N(1)–O(1)				1.16(1)	
C/N(2)–O(2)				1.17(1)	
P(1)–C(2)				1.85(1)	1.851(7)
P(2)–C(5)				1.841(9)	1.851(7)
C(2)–C(3)				1.51(2)	1.47(1)
C(3)–C(4)				1.26(2)	1.16(1)
C(5)–C(6)				1.50(1)	1.46(1)
C(6)–C(7)				1.28(2)	1.16(1)
P–H		1.38(3)			
<i>Bond angles</i>					
P(1)–Co(1)–P(2)	101.95(9)				
P(1)–Co(1)–N	109.3(3)				
P(1)–Co(1)–C(1)	104.9(3)				
P(2)–Co(1)–N	114.8(2)				
P(2)–Co(1)–C(1)	99.0(4)				
N–Co(1)–C(1)	124.2(4)				
P(3)–Co(2)–P(3a)	96.9(1)				
P(3)–Co(2)–C/N(3)	110.9(3)				
P(3)–Co(2)–C/N(3a)	108.9(3)				
C/N(3)–Co(2)–C/N(3a)	118.3(4)				
P–Mn–Pa		175.18(8)			
P–Mn–N or Pa–Mn–N		92.41(5)			
P–Mn–C(1) or Pa–Mn–C(1a)		87.6(2)			
P–Mn–C(1a) or Pa–Mn–C(1)		89.7(2)			
N–Mn–C(1) or N–Mn–C(1a)		124.0(2)			
C(1)–Mn–C(1a)		111.9(2)			
P–Co–Pa			99.63(4)		
P–Co–C/N or Pa–Co–C/N(a)			109.12(8)		
P–Co–C/N(a) or Pa–Co–C/N			106.4(1)		
C/N–Co–C/N(a)			123.5(1)		
P(1)–Co–P(2)				102.0(1)	100.87(8)
P(1)–Co–N					112.0(2)
P(1)–Co–C(1)					106.6(2)
P(2)–Co–N					111.1(2)
P(2)–Co–C(1)					104.9(2)
P(1)–Co–C/N(1)				106.9(3)	
P(1)–Co–C/N(2)				107.5(3)	

Table 7 (continued)

	1	3	4	5	6
Bond angles					
P(2)–Co–C/N(1)				111.1(3)	
P(2)–Co–C/N(2)				109.6(3)	
N–Co–C(1)					119.6(3)
C/N(1)–Co–C/N(2)				118.2(4)	
P(1)–C(2)–C(3)				114.5(7)	112.6(5)
C(2)–3–C(4)				127 (1)	178.0(9)
P(2)–C(5)–C(6)				113.5(6)	110.7(5)
C(5)–C(6)–C(7)				124 (1)	179.1(8)
Co(1)–C(1)–O(1)	178.8(8)				
Co(1)–N–O(2)	177.6(6)				
Co(2)–C/N(3)–O(3)	173.9(8)				
Mn–N–O(2)		180.0			
Mn–C(1)–O(1) or Mn–C(1a)–O(1a)		179.1(5)			
Co–C/N–O			178.0(2)		
Co–N–O(2)					176.3(6)
Co–C(1)–O(1)					176.9(6)
Co–C/N(1)–O(1)				175.2(8)	
Co–C/N(2)–O(2)				177.1(8)	

solvent. Anal. Found: C, 65.64; H, 4.61; N, 2.48. $C_{31}H_{26}NO_2P_2Co$ calc.: C, 65.85; H, 4.64; N, 2.48%.

2.3. Crystallographic studies

Crystals of **1** were grown by cooling a concentrated solution of **1** in hexane at -5°C for several days, and

crystals of **3–6** were grown by cooling a concentrated solution of relevant complexes in CH_2Cl_2 :hexane (1:5) at -5°C for several days. Crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf–Nonious CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda =$

Table 8
IR Spectra and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compounds

Complex	$\nu(\text{CO}), \nu(\text{NO}); \nu(\text{PH})^a$ (cm^{-1})	$\delta^{b,c}$ (ppm)	$\delta^{b,d}$ (ppm)
1	1967s, 1723s; 2319vw, 2312vw	Ph (7.60–7.60, m, 20H); PH (6.20, d, 2H, $^1J(\text{P–H}) = 340$ Hz)	P (35.1, br)
2	1724m, 1673s; 2313vw, 2287vw	Ph (7.53–7.26, m, 20H); PH (6.45, d, 2H, $^1J(\text{P–H}) = 392$ Hz)	P (37.4)
3	1954m, 1867vs, 1660s; 2324vw, 2324vw	Ph (7.84–7.48, m, 20H); PH (7.38, d, 2H, $^1J(\text{P–H}) = 362$ Hz)	P (55.8)
4	1939s, 1701s	Ph (7.49–7.37, m, 20 H); Me (1.49, d, 6H, $^2J(\text{R–H}) = 6.6$ Hz)	P (43.2, br)
5	1943s, 1700s	Ph (7.46–7.34, m, 20H); $\text{CH}=\text{CH}_2$ (5.39, m, 2H); $\text{CH}=\text{CHaHb}$ (4.78, d, 2H, $^3J(\text{H–H}) = 6.8$ Hz); $\text{CH}=\text{CHaHb}$ (4.61, d, 2H, $^3J(\text{H–H}) = 11.2$ Hz); PCHaHb (2.80, m, 2H); PCHaHb (2.58, m, 2H)	P (52.5, br)
6	1943s, 1700s	Ph (7.34–7.23, m, 20 H); PCHaHb (2.67, ddd, 2H, $^2J(\text{H–H}) = 16.5$, $^2J(\text{P–H}) = 7.0$ Hz, $^4J(\text{H–H}) = 2.5$ Hz), PCHaHb (2.65, ddd, 2H, $2J(\text{H–H}) = 16.5$ Hz, $^2J(\text{P–H}) = 7.0$ Hz, $^4J(\text{H–H}) = 2.5$ Hz); CCH (1.87, m, 2H)	P (52.5, br)
7	2041s, 1989vs, 1770s; 2284vw		
8	2013m, 1765m, 1720s; 2336vw		
9	2038s, 1975m, 1926s, 1715s; 2300vw		
$\text{Co}(\text{NO})(\text{CO})_3$	2104m, 2034s, 1801s		
$\text{Fe}(\text{NO})_2(\text{CO})_2$	2067s, 2018s, 1824s, 1764s		
$\text{Mn}(\text{NO})(\text{CO})_4$	2101w, 2028vs, 1974vs, 1758s		

^a Measured in CH_2Cl_2 (**3–6**, **8**), hexane (**1**, **7**, $\text{Co}(\text{NO})(\text{CO})_3$) or CH_3CN (**h2**, **9**, $\text{Fe}(\text{NO})_2(\text{CO})_2$, $\text{Mn}(\text{NO})(\text{CO})_4$) solution.

^b Measured in acetone- d_6 except for **6** (CD_2Cl_2). ^c Reported in parts per million relative to $\delta(\text{Me}_4\text{Si})$ 0 ppm. ^d Reported in parts per million relative to δ (85% H_3PO_4) 0 ppm. Abbreviations; s, singlet; d, doublet; t, triplet; m, multiplet.

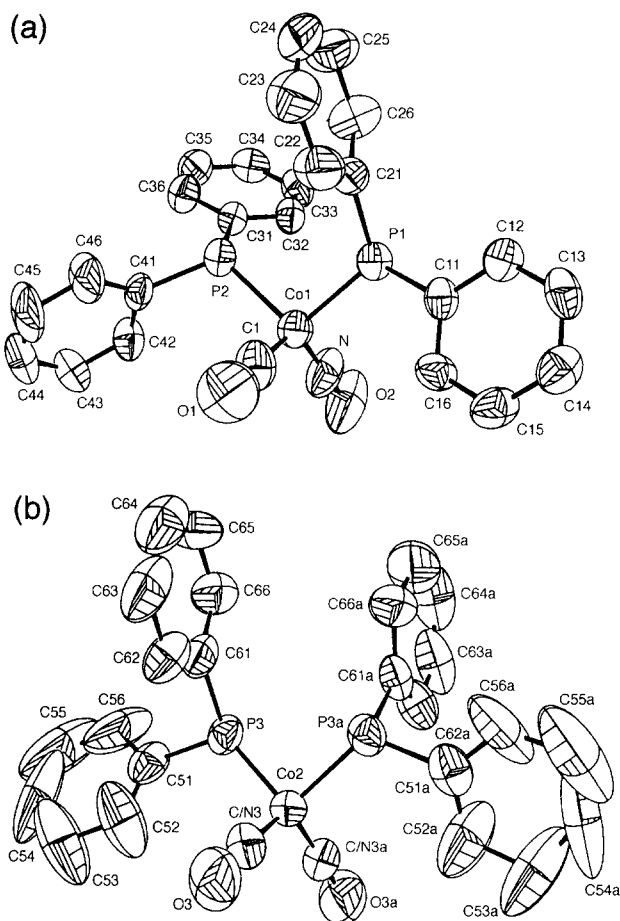


Fig. 1. ORTEP drawing of $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PH})_2$ (**1**). Thermal ellipsoids are drawn with 30% probability boundaries.

0.7107 Å) or Cu K α radiation ($\lambda = 1.5406$ Å) with the θ - 2θ scan mode. Unit cells were determined by centering 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 1. All data reduction and refinements were carried out on DecAl-

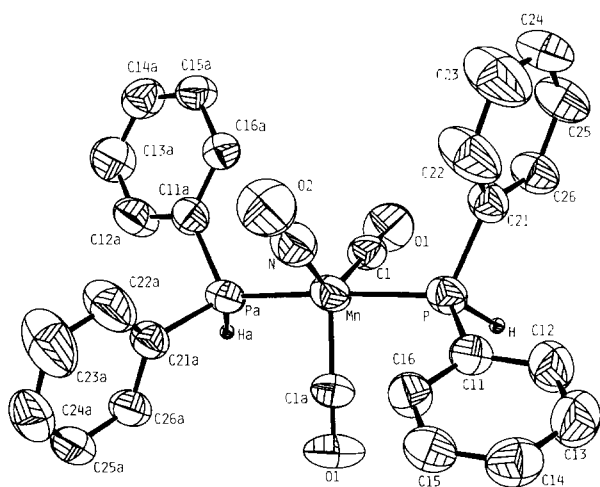


Fig. 2. ORTEP drawing of $\text{Mn}(\text{NO})(\text{CO})_2(\text{Ph}_2\text{PH})_2$ (**3**). Thermal ellipsoids are drawn with 30% probability boundaries.

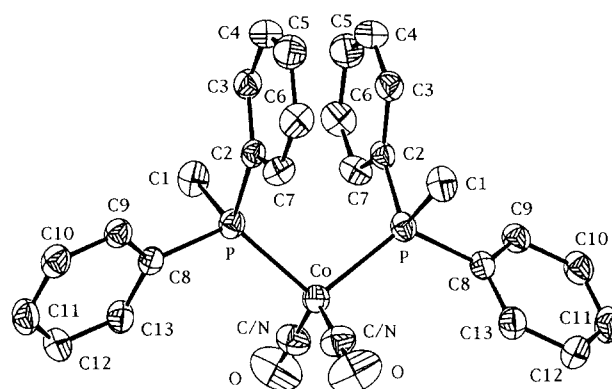
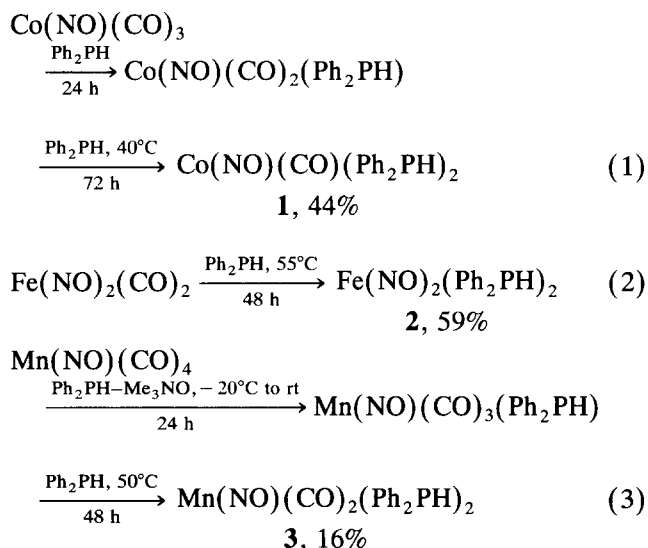


Fig. 3. ORTEP drawing of $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PMe})_2$ (**4**). Thermal ellipsoids are drawn with 30% probability boundaries.

pha 3000/400 computer using NRCVAX programs [11]. Intensities were collected and corrected for decay, absorption (empirical and ψ scan) and Lorentz-polarization effects. Each structure was solved by direct methods [12] and refined on F using full-matrix least-squares techniques. An E map from the starting set with the highest combined figure of merit revealed coordinates for metal atoms. The remaining non-H atoms were located from successive difference Fourier maps. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the structure factor calculation in idealized positions with $d_{\text{C-H}} = 0.98 \text{ \AA}$. The final positional parameters are listed in Tables 2–6 and selected interatomic distances and bond angles are given in Table 7.

3. Results and discussion

Complexes $\text{Co(NO)(CO)(Ph}_2\text{PH)}_2$ (1), $\text{Fe(NO)}_2\text{-(Ph}_2\text{PH)}_2$ (2) and $\text{Mn(NO)(CO)}_2\text{(Ph}_2\text{PH)}_2$ (3) were synthesized from ligand substitution of Co(NO)-(CO)_3 , $\text{Fe(NO)}_2\text{(CO)}_2$ and Mn(NO)(CO)_4 respectively as follows:



The IR monitoring of the reactions suggested that $\text{Co}(\text{NO})(\text{CO})_2(\text{Ph}_2\text{PH})$ (**7**), $\text{Fe}(\text{NO})_2(\text{CO})(\text{Ph}_2\text{PH})$ (**8**) and $\text{Mn}(\text{NO})(\text{CO})_3(\text{Ph}_2\text{PH})$ (**9**) formed as intermediates (Table 4), although they were not isolated pure. As expected, the ligation of the second phosphine requires more vigorous conditions than that of the first phosphine. The low yield for **3** is mainly due to its air sensitivity and extensive decomposition during chromatography.

The spectroscopic properties of **1–3** (Table 8) are consistent with their formulation. The presence of ligated Ph_2PH is evident from the observation of two weak $\nu(\text{P–H})$ bands at about 2300 cm^{-1} and a large one-bond P–H coupling (350–400 Hz) in both ^1H and ^{31}P NMR spectra. Both $\nu(\text{NO})$ and $\nu(\text{CO})$ decrease when an additional CO ligand is displaced by a phosphine ligand. According to the prediction of Rossi and Hoffmann [13] for a pentacoordinated metal atom with d^8 electronic configuration and trigonal bipyramidal geometry, the two better σ -donating ligands, Ph_2PH , should reside in the apical positions, whereas the better π -accepting ligands, CO and NO, prefer to be in the equatorial sites for **3**. Complex **3** indeed has a structure (vide infra) which is consistent with the postulate of Rossi and Hoffmann and, as expected, it has a medium and a strong CO stretchings in the IR spectra and two magnetically equivalent Ph_2PH ligands in both ^1H and ^{31}P NMR spectra (Table 8).

The lithiated phosphine complex $[\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PLi})_2]$ is likely to be generated upon treating **1** with two equivalents of BuLi. Reactions of this thermally unstable anion with methyl iodide, allyl bromide and propargyl bromide provide the complexes $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PMe})_2$ (**4**), $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CHCH}_2)_2$ (**5**) and $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CCH})_2$ (**6**) respectively. The

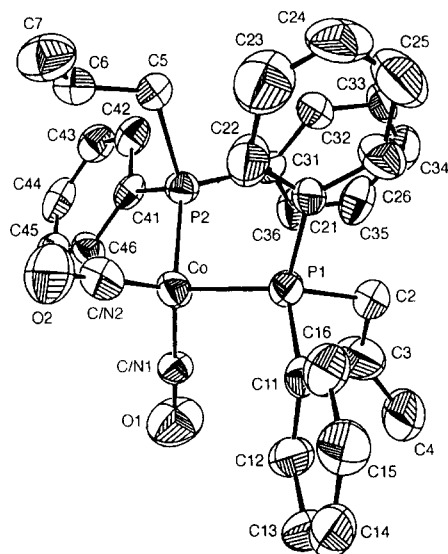


Fig. 4. ORTEP drawing of $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CHCH}_2)_2$ (**5**). Thermal ellipsoids are drawn with 30% probability boundaries.

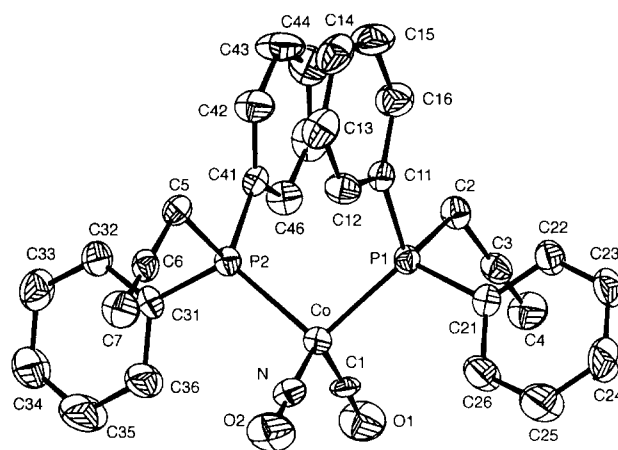


Fig. 5. ORTEP drawing of $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CCH})_2$ (**6**). Thermal ellipsoids are drawn with 30% probability boundaries.

characteristic $\nu(\text{P–H})$ bands in IR absorption and one-bond P–H coupling in NMR spectra found in **1** disappeared in **4–6** (Table 8). Both $\nu(\text{CO})$ and $\nu(\text{NO})$ in **4–6** are significantly lower than those in **1**, implying that substitution of methyl, allyl and propargyl for hydrogen in Ph_2PH significantly enhances the σ -donating ability, or suppresses the π -accepting ability of the phosphine ligand. The two methylene protons of the phosphine ligands in **5** and **6** appear to be diastereotopic since no plane of symmetry bisecting these groups is possible in both complexes. Complex **6** is likely to be useful for construction of polynuclear metal complexes such as $[\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CCH})_2][\text{Co}_2(\text{CO})_6]_2$ via ligation of the alkyne entities [14], or for synthesizing organometallic polymers via polymerization of the alkyne entities [15]. Use of the two available diphenylphosphine for heterodinuclear complexes bridged by two phosphide ligands and phosphide-bridged heterotrinnuclear complexes will be pursued in future.

3.1. Crystal structure of $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PH})_2$ (**1**), $\text{Mn}(\text{NO})(\text{CO})_2(\text{Ph}_2\text{PH})_2$ (**3**), $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PMe})_2$ (**4**), $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CHCH}_2)_2$ (**5**) and $\text{Co}(\text{NO})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CCH})_2$ (**6**)

The ORTEP drawings of **1**, **3**, **4**, **5** and **6** are shown in Figs. 1, 2, 3, 4 and 5 respectively. Important interatomic distances and angles are listed in Table 7. The coordination geometries of **1** and **4–6** are distorted tetrahedras about the cobalt center. There are two crystallographically independent molecules, A and B, for **1**. The two molecules have approximately similar structures except that the nitrosyl and the carbonyl ligands of molecule B are disordered owing to the presence of a twofold symmetry axis which passes the cobalt atom and bisects the angles P–Co–P and C–Co–N. Such a twofold axis also exists in **4** and renders the nitrosyl and the carbonyl

ligands disordered. In **5** the nitrogen atom of NO and the carbon atom of CO are disordered and both sites have 50% N and 50% C. The location of the NO ligand in other complexes was distinguished from that of the CO ligand by conspicuous discrepancies in the thermal parameters for the N and C atoms when incorrectly assigned [16]. Albano et al. [17] and Mingos and Ibers [18] suggested that, in tetrahedral Co, Pt and Ir complexes of general formula $ML_nL'_{4-n}$ ($L = CO$ or NO ; $L' =$ tertiary phosphine), the good π -accepting abilities of NO and CO would result in non-bonding repulsions and cause the N–M–C angle to deviate significantly from the ideal value of 109.48° . Indeed, **1** ($124.2(4)^\circ$; $18.3(4)^\circ$), **4** ($123.5(1)^\circ$), **5** ($118.2(4)^\circ$) and **6** ($119.6(3)^\circ$) all have large N–Co–C angles, similar to that of $Co(NO)(CO)(PPh_3)_2$ ($120.0(4)^\circ$) [17a]. The P–Co–P angles in $Co(NO)(CO)(PPh_3)_2$ ($114.1(2)^\circ$) is larger than those in **1** ($101.95(9)^\circ$; $96.9(1)^\circ$), **4** ($99.63(4)^\circ$), **5** ($102.0(1)^\circ$) and **6** ($100.87(8)^\circ$), apparently owing to the greater steric crowdedness of PPh_3 . The structure of **3** is similar to that of $Mn(NO)(CO)_2(PPh_3)_2$ [19] which has a trigonal bipyramidal geometry with apical phosphine ligands and with NO in an equatorial position. The two carbonyls and the two phosphines are symmetry related owing to the presence of a twofold axis which is on the equatorial plane and bisects the angle spanned by the two carbonyls. The two phosphine ligands are slightly bent away from the NO group with a P–Mn–Pa angle of $175.18(8)^\circ$. Other relevant crystal data for **1** and **3–6** appear to be normal. Neither carbonyl nor nitrosyl ligands deviate significantly from linearity. The metal–N distances lie in the range 1.57–2.03 Å reported for metal nitrosyls, and the N–O distances ($1.154(4)$ – $1.17(1)$ Å) compare well with other N–O distances ranging from 1.1 to 1.26 Å [20]. The sp^2 carbon–carbon distance (average, $1.27(1)$ Å) in the two allyl entities of **5** and the sp carbon–carbon distance (average, $1.16(1)$ Å) in the two propargyl entities of **6** are not abnormal. The average Co–P distances in **1** ($2.19(1)$ Å), **4** ($2.2076(8)$ Å), **5** ($2.206(8)$ Å) and **6** ($2.20(1)$ Å) are shorter than those in $Co(NO)(CO)_2(PPh_3)_2$ ($2.224(3)$ Å) and $Co(NO)(CO)(PPh_3)_2$ ($2.224(3)$ Å) [17a]. Complex **3** also appears to have a shorter Mn–P distance ($2.246(2)$ Å) than $Mn(NO)(CO)_3(PPh_3)_2$ ($2.305(4)$ Å) and $Mn(NO)(CO)_2(PPh_3)_2$ ($2.278(1)$ Å) [21]. These observations could be attributed to the larger cone angle of PPh_3 .

4. Supplementary materials available

All bond distances and angles (Table S1; **1**, 2 pages; **3**, 1 page; **4**, 1 page; **5**, 2 pages; **6**, 2 pages), anisotropic thermal parameters and isotropic thermal parameters (Table S2; **1**, 2 pages; **3**, 1 page; **4**, 1 page; **5**, 2 pages;

6, 2 pages) and positional parameters for calculated hydrogen atoms (Table S3; **1**, 1 page; **3**, 1 page; **4**, 1 page; **5**, 1 page; **6**, 1 page), are available from the authors.

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