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Synthesis and characterization of new transition metal diynyl complexes

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Abstract

The reaction of (η^5-C_5H_5)Mo(CO)(dppe)Cl with $LiC\equiv CC\equiv CSiMe_3$ yielded (η^5-C_5H_5)(CO)(dppe)$MoC\equiv CC\equiv CSiMe_3$ (**1b**) and, as a by-product (η^5-C_5H_5)Mo(CO)(dppe)Br (**1a**). Treatment of **1b** with 0.2 equivalents of tetrabutylammonium fluoride or (η^5-C_5H_5)Mo(CO)(dppe)Cl with $HC\equiv CC\equiv CH$ gave the terminal butadiyne complex (η^5-C_5H_5)(CO)(dppe)$MoC\equiv CC\equiv CH$ (**2**). Complex **2** was deprotonated with *sec*-BuLi or lithium diisopropylamide, and the resulting anion (η^5-C_5H_5)(CO)(dppe)$MoC\equiv CC\equiv CLi$ (**3**) was trapped with Me_3SiCl to regenerate **1b**. The synthesis of $Co_2(CO)_4L_2$(μ-η^2-$Me_3SiC_2C\equiv CSiMe_3$) (L_2 = dppa **4**, $2PPh_2Me$ **5**) compounds can be achieved by two methods: from $Co_2(CO)_6$(μ-dppa) by reaction with $Me_3SiC\equiv CC\equiv CSiMe_3$ in 1:1 ratio to yield **4**, or from $Co_2(CO)_6$(μ-η^2-$Me_3SiC_2C\equiv CSiMe_3$) by reaction with dppa (1:1 ratio) and PPh_2Me (1:2 ratio) to yield **4** and **5**, respectively. When the $Co_2(CO)_4$(μ-dppa)(μ-η^2-$Me_3SiC_2C\equiv CSiMe_3$) complex was treated with more $Co_2(CO)_6$(μ-dppa) the green di-substituted complex $[Co_2(CO)_4(\mu\text{-dppa})]_2$($\mu$-$\eta^2$:$\mu$-$\eta^2$-$Me_3SiC_2C_2SiMe_3$) (**6**) was obtained. Desilylation of **4** with Bu_4NF gave $Co_2(CO)_4$(μ-dppa)(μ-η^2-$Me_3SiC_2C\equiv CH$) (**7**). All compounds synthesized have been characterized by analytical and spectroscopic data (IR, ^1H-, ^{31}P-, ^{13}C-NMR, MS). In addition, compounds **1a** and **4** were characterized by X-ray structure analysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl; Molybdenum; Cobalt; Butadiynyl; Carbonyl complexes

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1. Introduction

Complexes in which sp carbon chains span transition metal endgroups are attracting increasing attention [1–4]. These wire-like, unsaturated linear assemblies offer aesthetic appeal, a variety of interesting fundamental properties, and intriguing possibilities for molecular-level devices [5]. Specific properties of transition metal complexes result primarily from the ability of the metal to participate in π-delocalization, as well as the potential for interaction of the transition metal d-orbitals with the conjugated π-orbitals of the unsaturated carbon chains [6–9].

Linear coordinated carbon chains stabilized by organometallic building blocks, $L_nMC_xM'L'_{n'}$, are now available for $x = 1$–20 [2b], and a few of them have been prepared for different oxidation states of the metal termini, providing 'consanguineous' families of molecules $[L_nMC_xML_n]^{n+}$. Two series of these compounds, with rhenium [2d] and iron [3a], were isolated and fully characterized for three different oxidation states.

On the other hand, polyynes incorporating metal clusters have received considerable attention [1] as possible molecular connectors or bridges as they promote the formation of linear (molecular-wire) arrays [10] and their complexes with $Co_2(CO)_6$ units are well known [9].

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In this work, we report the synthesis and characterization of σ- and π-acetylene organometallic complexes of molybdenum and cobalt containing 1,3-diyne units.

2. Experimental

2.1. Reagents and general techniques

All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free Ar. All solvents for synthetic use were reagent grade. Diethyl ether, hexane and tetrahydrofuran (THF) were dried and distilled over sodium in the presence of benzophenone under an Ar atmosphere. Also under Ar, CH_2Cl_2 (DCM), toluene and CCl_4 were dried and distilled over CaH_2, Na and $MgSO_4$, respectively. Methanol was stored over molecular sieves (4 Å) under Ar. All solvents were bubbled with Ar for 1 h after distillation and then stored under Ar, or degassed by means of at least 3 freeze–pump–thaw cycles after distillation and before use. Column chromatography was performed by using Alfa neutral alumina at activity II. Me_3SiCl (Aldrich) was dried and stored over molecular sieves (4 Å) and distilled under Ar. $Mo(CO)_6$, NaH, 1,2-bis(diphenilphosphine)ethane (dppe), 1,4-bis(trimethylsilyl)butadiyne ($Me_3SiC{\equiv}CC{\equiv}CSiMe_3$), pyridine, $Fe_2(SO_4)_3(H_2O)_n$, glacial acetic acid and $Cu(OAc)_2$ (Fluka) and MeLi–LiBr, tetrabutylammonium fluoride (FTBA) and PCy_3 were used as received (Aldrich). *n*-BuLi and *sec*-BuLi (Aldrich) were standardized [11] before use. Me_3NO was sublimed prior to use and stored under Ar. The compounds, $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ [12], $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ [13], $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ [12], $(\eta^5\text{-}C_5H_5)Mo(CO)(dppe)Cl$ [14], $Co_2(CO)_6(\mu\text{-dppa})$ [15] and $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$ [16] were prepared according to literature procedures and were purified by TLC. All reagents were used without further purification unless otherwise noted. The ^{1}H-NMR spectra were recorded on a Bruker AMX-300 and 500 instrument. Chemical shifts were measured relative either to an internal reference of tetramethylsilane or to residual protons of the solvents. Infrared spectra were measured on a Perkin–Elmer 1650 infrared spectrometer. Elemental analyses were performed by the microanalytical laboratory of the University Autónoma of Madrid on a Perkin–Elmer 240 B microanalyzer. Electronic spectra were recorded on a Pye Unicam SP 8-100 UV–Vis spectrophotometer. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB or AIE by the mass laboratory of the University Autónoma of Madrid.

2.2. Synthesis of $(\eta^5\text{-}C_5H_5)(CO)(dppe)MoC{\equiv}CC{\equiv}CSiMe_3$ (**1b**)

A solution of complex $(\eta^5\text{-}C_5H_5)Mo(CO)(dppe)Cl$ (1.60 g, 2.57 mmol) in THF (50 ml) was treated at −80°C with a solution of $LiC{\equiv}CC{\equiv}CSiMe_3$ [17], prepared in situ from $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ and MeLi–LiBr at −80°C in THF (50 ml). The reaction mixture was gradually warmed to ambient temperature overnight. The reaction was monitored by FT-IR spectroscopy until the ν(C≡C) bands of the parent

Table 1
Crystal data and structure refinement

Compound	**1a**	**4**
Empirical formula	$C_{32}H_{29}BrMoOP_2$	$C_{38}H_{39}Co_2NO_4P_2Si_2$
Formula weight	667.34	809.68
Temperature (K)	150.0(1)	173.0(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
Unit cell dimensions		
a (Å)	13.878(3)	21.0122(8)
b (Å)	17.338(4)	13.4485(5)
c (Å)	23.456(5)	30.5942(9)
α (°)	90	90
β (°)	90	105.590(2)
γ (°)	90	90
V (Å^3)	5644.0(20)	8327.3(5)
Z	8	8
$D_{\text{calc.}}$ (Mg cm^{-3})	1.571	1.292
Absorption coefficient (mm^{-1})	2.018	0.968
F(000)	2688	3344
Crystal size (mm)	0.35 × 0.30 × 0.20	0.10 × 0.15 × 0.12
Theta range for data collection (°)	4.10–26.37	4.10–26.42
Index ranges	$0 \le h \le 17$, $0 \le k \le 21$, $0 \le l \le 29$	$0 \le h \le 26$, $0 \le k \le 16$, $-38 \le l \le 36$
Reflections collected	42 018	62 585
Independent reflections	5730 [$R_{\text{int}} = 0.070$]	16873 [$R_{\text{int}} = 0.112$]
Independent reflections [$I > 2\sigma(I)$]	4610	9510
Absorption correction	Denzo-SMN	Denzo-SMN
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5730/3/339	16873/0/897
Goodness-of-fit on F^2	1.063	0.985
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0459$, $wR_2 = 0.1245$	$R_1 = 0.0569$, $wR_2 = 0.1420$
R indices (all data)	$R_1 = 0.0604$, $wR_2 = 0.1384$	$R_1 = 0.1106$, $wR_2 = 0.1637$
Extinction coefficient	0.0001(2)	0.00024(12)
Largest difference peak and hole (e Å^{-3})	1.267 and −1.448	0.715 and −0.544
Position of largest difference peak	1.20(1) Å from Br	2.97(1) Å from H(53A)

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1a**

	x	y	z	U_{eq}[a]
Mo	4546(1)	1476(1)	3309(1)	19(1)
Br	2730(1)	1849(1)	3109(1)	38(1)
C(1)	4160(3)	1270(3)	4073(2)	23(1)
O(1)	3954(4)	1073(3)	4554(2)	41(1)
Br*2	4163(10)	883(8)	4381(6)	88(4)
C(1*2)	3337	1739	3508	59
O(1*2)	2591	1897	3676	122
C(2)	4094(3)	615(3)	2562(2)	32(1)
C(3)	4864(4)	1068(3)	2367(2)	33(1)
C(4)	5662(4)	910(3)	2731(2)	36(1)
C(5)	5366(4)	361(3)	3143(2)	35(1)
C(6)	4396(4)	182(3)	3037(2)	33(1)
P(1)	4697(1)	2879(1)	3095(1)	21(1)
P(2)	5988(1)	1882(1)	3821(1)	22(1)
C(7)	5908(3)	3262(3)	3289(2)	27(1)
C(8)	6624(3)	2603(3)	3393(2)	28(1)
C(21)	4636(3)	3103(2)	2332(2)	24(1)
C(22)	3812(4)	3397(3)	2077(2)	31(1)
C(23)	3801(4)	3565(3)	1497(2)	40(1)
C(24)	4613(4)	3419(3)	1165(2)	44(1)
C(25)	5426(4)	3121(3)	1409(2)	43(1)
C(26)	5453(4)	2965(3)	1991(2)	32(1)
C(31)	3926(3)	3620(2)	3410(2)	24(1)
C(32)	3266(3)	3448(3)	3838(2)	28(1)
C(33)	2735(4)	4027(3)	4095(2)	35(1)
C(34)	2851(4)	4785(3)	3922(2)	37(1)
C(35)	3490(4)	4965(3)	3498(2)	35(1)
C(36)	4044(3)	4389(3)	3246(2)	29(1)
C(41)	6886(3)	1147(3)	3994(2)	25(1)
C(42)	7789(3)	1128(3)	3744(2)	31(1)
C(43)	8447(3)	546(3)	3895(2)	36(1)
C(44)	8196(4)	−5(3)	4296(2)	34(1)
C(45)	7300(4)	15(3)	4541(2)	33(1)
C(46)	6646(3)	586(3)	4394(2)	30(1)
C(51)	5918(3)	2416(3)	4495(2)	28(1)
C(52)	6772(4)	2589(3)	4795(2)	36(1)
C(53)	6740(5)	3071(3)	5263(2)	47(1)
C(54)	5884(5)	3390(3)	5440(2)	47(1)
C(55)	5041(5)	3221(3)	5156(2)	44(1)
C(56)	5059(4)	2731(3)	4686(2)	34(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Bond lengths (Å) and bond angles (°) for **1a**

Bond lengths (Å)			
Mo–C(1)	1.906(5)	C(2)–C(6)	1.406(7)
Mo–C(5)	2.277(4)	C(3)–C(4)	1.425(7)
Mo–C(4)	2.279(4)	C(4)–C(5)	1.417(7)
Mo–C(6)	2.341(4)	C(5)–C(6)	1.404(7)
Mo–C(3)	2.360(4)	P(1)–C(31)	1.828(5)
Mo–C(2)	2.385(4)	P(1)–C(21)	1.832(5)
Mo–P(2)	2.4371(12)	P(1)–C(7)	1.864(5)
Mo–P(1)	2.4928(12)	P(2)–C(41)	1.827(4)
Mo–Br	2.6445(8)	P(2)–C(8)	1.830(4)
C(1)–O(1)	1.214(7)	P(2)–C(51)	1.837(5)
C(2)–C(3)	1.404(7)	C(7)–C(8)	1.534(6)
Bond angles (°)			
C(1)–Mo–C(5)	98.2(2)	C(31)–P(1)–C(7)	100.3(2)
C(1)–Mo–C(4)	132.0(2)	C(21)–P(1)–C(7)	101.8(2)
C(1)–Mo–C(6)	92.9(2)	C(31)–P(1)–Mo	123.71(15)
C(1)–Mo–C(3)	151.3(2)	C(21)–P(1)–Mo	113.56(14)
C(1)–Mo–C(2)	119.9(2)	C(7)–P(1)–Mo	111.95(15)
C(1)–Mo–P(2)	79.71(14)	C(41)–P(2)–C(8)	105.6(2)
C(1)–Mo–P(1)	113.33(15)	C(41)–P(2)–C(51)	101.3(2)
P(2)–Mo–P(1)	75.46(4)	C(8)–P(2)–C(51)	98.8(2)
C(1)–Mo–Br	86.78(14)	C(41)–P(2)–Mo	117.94(15)
P(2)–Mo–Br	143.07(3)	C(8)–P(2)–Mo	108.8(2)
P(1)–Mo–Br	78.80(3)	C(51)–P(2)–Mo	121.80(15)
O(1)–C(1)–Mo	173.9(5)	C(8)–C(7)–P(1)	111.0(3)
C(31)–P(1)–C(21)	102.7(2)	C(7)–C(8)–P(2)	106.5(3)

compound had disappeared. After 15 h the resulting solution was evaporated under reduced pressure, and the residue was purified by TLC using DCM/hexane (1:2) as eluent. The first red-band, by-product, was identified as (η^5-C_5H_5)Mo(CO)(dppe)Br (**1a**) (1.35 g, 75% yield) in comparison with an authentic sample. The second red-band yielded a reddish–brown solid **1b** (0.14 g, 7% yield). **1a**: FT-IR (CH_2Cl_2, cm^{-1}): ν(CO) 1855 (vs). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.43 (m, *o*-H, 8H, Ph); 7.37 (m, *m*- and *p*-H, 12H, Ph); 4.45 (d, $J_{HP} = 2.42$ Hz, Cp); 2.70 (m, 2H, CH_2); 1.70 (m, 2H, CH_2). ^{31}P-NMR ($CDCl_3$): δ 92.83 (d, $J_{PP} = 38.61$ Hz, 1P); 67.87 (d, $J_{PP} = 38.67$ Hz, 1P). **1b**: FT-IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2185 (w), 2065 (w); ν(CO) 1856 (vs). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.44 (m, *o*-H, 8H, Ph); 7.35 (m, *m*- and *p*-H, 12H, Ph); 4.51 (d, $J_{HP} = 2.42$ Hz, Cp); 2.97 (m, 2H, CH_2); 1.50 (m, 2H, CH_2); 0.15 (s, 9H, $SiMe_3$). ^{31}P-NMR ($CDCl_3$): δ 92.83 (d, $J_{PP} = 38.61$ Hz, 1P); 67.87 (d, $J_{PP} = 38.67$ Hz, 1P). ^{13}C-NMR ($CDCl_3$): δ 141.5 (d, $J_{CP} = 34$ Hz, *i*-Ph); 137.0 (d, $J_{CP} = 32$ Hz, C≡CC≡CSiMe$_3$); 136.2 (d, $J_{CP} = 40$ Hz, *i*-Ph); 134.1 (d,

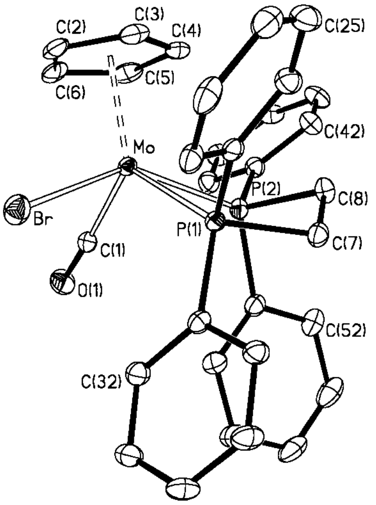


Fig. 1. ORTEP diagramar of (η^5-C_5H_5)Mo(CO)(dppe)Br, **1a**, with 30% ellipsoids. H atoms on the cyclopentadienyl and phenyl groups have been removed for clarity.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **4**

	x	y	z	U_{eq}
Co(1A)	226(1)	3645(1)	4247(1)	32(1)
Co(2A)	407(1)	2846(1)	3566(1)	33(1)
Si(1A)	−242(1)	5234(1)	3303(1)	37(1)
Si(2A)	−2524(1)	2236(1)	3381(1)	54(1)
P(1A)	286(1)	2271(1)	4653(1)	35(1)
P(2A)	566(1)	1337(1)	3847(1)	33(1)
N(1A)	425(2)	1262(3)	4365(1)	39(1)
O(11A)	1439(2)	4814(3)	4549(1)	66(1)
O(12A)	−677(2)	4837(3)	4607(1)	60(1)
O(13A)	1755(2)	3537(3)	3658(2)	78(1)
O(14A)	21(2)	2385(3)	2601(1)	67(1)
C(1A)	−651(3)	5010(4)	2695(2)	68(2)
C(2A)	−784(3)	6021(4)	3553(2)	72(2)
C(3A)	574(3)	5817(4)	3368(2)	68(2)
C(4A)	−108(2)	4036(3)	3603(1)	33(1)
C(5A)	−428(2)	3198(3)	3691(1)	33(1)
C(6A)	−1083(2)	2854(3)	3594(1)	36(1)
C(7A)	−1650(2)	2580(4)	3509(2)	44(1)
C(8A)	−3014(3)	3112(7)	2952(2)	105(3)
C(9A)	−2617(3)	940(6)	3170(3)	100(3)
C(10A)	−2784(3)	2369(6)	3909(2)	89(2)
C(11A)	973(2)	4326(4)	4442(2)	41(1)
C(12A)	−314(2)	4363(4)	4482(2)	41(1)
C(13A)	1230(3)	3267(4)	3624(2)	50(1)
C(14A)	169(2)	2563(4)	2985(2)	44(1)
C(21A)	910(2)	2090(3)	5192(1)	38(1)
C(22A)	1564(3)	2405(4)	5231(2)	53(1)
C(23A)	2058(3)	2178(4)	5609(2)	65(2)
C(24A)	1925(3)	1665(4)	5968(2)	65(2)
C(25A)	1301(3)	1358(5)	5939(2)	69(2)
C(26A)	789(3)	1565(4)	5553(2)	53(1)
C(31A)	−461(2)	1965(4)	4811(1)	40(1)
C(32A)	−848(3)	1140(4)	4643(2)	51(1)
C(33A)	−1410(3)	922(5)	4779(2)	63(2)
C(34A)	−1591(3)	1548(5)	5086(2)	63(2)
C(35A)	−1230(3)	2383(5)	5246(2)	61(2)
C(36A)	−663(3)	2582(4)	5118(2)	51(1)
C(41A)	74(2)	320(3)	3533(1)	35(1)
C(42A)	286(3)	−660(4)	3593(2)	49(1)
C(43A)	−97(3)	−1400(4)	3336(2)	62(2)
C(44A)	−685(3)	−1193(4)	3032(2)	55(1)
C(45A)	−903(3)	−228(4)	2979(2)	50(1)
C(46A)	−530(2)	529(4)	3225(2)	41(1)
C(51A)	1409(2)	849(3)	3935(2)	37(1)
C(52A)	1635(3)	651(5)	3553(2)	58(2)
C(53A)	2263(3)	310(5)	3597(2)	67(2)
C(54A)	2690(3)	158(4)	4021(2)	65(2)
C(55A)	2478(3)	362(4)	4396(2)	57(1)
C(56A)	1841(2)	714(4)	4354(2)	46(1)
Co(1B)	4890(1)	3733(1)	800(1)	32(1)
Co(2B)	4765(1)	2929(1)	1497(1)	32(1)
Si(1B)	5282(1)	5401(1)	1707(1)	35(1)
Si(2B)	7628(1)	2187(1)	1649(1)	43(1)
P(1B)	4925(1)	2364(1)	407(1)	33(1)
P(2B)	4588(1)	1442(1)	1194(1)	33(1)
N(1B)	4833(2)	1347(3)	710(1)	37(1)
O(11B)	3583(2)	4639(3)	516(1)	62(1)
O(12B)	5653(2)	5088(3)	398(1)	58(1)
O(13B)	3484(2)	3647(3)	1575(2)	86(2)
O(14B)	5335(2)	2379(3)	2440(1)	65(1)
C(1B)	5609(3)	5252(4)	2333(2)	66(2)
C(2B)	5847(3)	6199(4)	1485(2)	63(2)
C(3B)	4437(3)	5942(4)	1565(2)	64(2)
C(4B)	5232(2)	4175(3)	1439(1)	33(1)
C(5B)	5583(2)	3363(3)	1356(1)	30(1)
C(6B)	6228(2)	3021(3)	1453(1)	32(1)
C(7B)	6789(2)	2700(3)	1539(2)	39(1)
C(8B)	8166(3)	2659(5)	2182(2)	75(2)
C(9B)	7550(3)	809(4)	1680(2)	72(2)
C(10B)	7975(2)	2557(4)	1175(2)	53(1)
C(11B)	4086(2)	4263(4)	620(2)	41(1)
C(12B)	5343(2)	4545(4)	544(2)	41(1)
C(13B)	3977(3)	3345(4)	1530(2)	50(1)
C(14B)	5098(2)	2591(3)	2063(2)	42(1)
C(21B)	4332(2)	2114(3)	−142(1)	39(1)
C(22B)	3692(3)	2458(4)	−221(2)	54(1)
C(23B)	3217(3)	2201(4)	−619(2)	56(1)
C(24B)	3382(3)	1610(4)	−942(2)	47(1)
C(25B)	4022(3)	1282(4)	−867(2)	49(1)
C(26B)	4491(2)	1525(4)	−471(2)	43(1)
C(31B)	5701(2)	2145(3)	270(1)	39(1)
C(32B)	6111(2)	1339(4)	446(2)	43(1)
C(33B)	6685(3)	1182(4)	312(2)	55(1)
C(34B)	6864(3)	1832(4)	9(2)	58(1)
C(35B)	6466(3)	2639(4)	−155(2)	55(1)
C(36B)	5886(3)	2789(4)	−31(2)	48(1)
C(41B)	5023(2)	396(3)	1521(1)	35(1)
C(42B)	4735(2)	−535(4)	1523(2)	44(1)
C(43B)	5091(3)	−1299(4)	1793(2)	53(1)
C(44B)	5711(3)	−1146(4)	2054(2)	51(1)
C(45B)	6014(3)	−222(4)	2052(2)	50(1)
C(46B)	5669(2)	543(3)	1786(1)	39(1)
C(51B)	3732(2)	1011(3)	1041(2)	37(1)
C(52B)	3402(2)	984(4)	1385(2)	51(1)
C(53B)	2753(2)	644(4)	1286(2)	59(2)
C(54B)	2432(3)	348(4)	854(2)	67(2)
C(55B)	2752(3)	392(4)	519(2)	59(2)
C(56B)	3400(2)	725(4)	610(2)	47(1)

$J_{CP} = 10$ Hz, o-Ph); 133.5 (d, $J_{CP} = 10$ Hz, o-Ph); 131–128 (m, m-, p-Ph); 100.2 (s, C≡CC≡CSiMe$_3$); 94.3 (s, Cp); 87.9 (s, C≡CC≡CSiMe$_3$); 70.5 (s, C≡CC≡CSiMe$_3$); 0.9 (s, SiMe$_3$). Anal. Calc. for $C_{39}H_{38}OP_2SiMo$: C, 65.90; H, 5.39. Found: C, 65.95; H, 5.41.

*2.3. Synthesis of (η^5-C$_5$H$_5$)(dppe)(CO)MoC≡CC≡CH (**2**)*

2.3.1. Method A

A solution of Bu$_4$NF (1.0 M, 0.42 ml, 0.42 mmol) in THF was added to a solution of **1b** (0.20 g, 0.28 mmol) in THF (50 ml). The solution was stirred overnight at room temperature (r.t.). The reaction was monitored by FT-IR spectroscopy. After removal of the solvent under vacuum, the residue was washed with hexane and the remaining solid was extracted with diethyl ether. Solvent was then evaporated from the extract to give 0.11 g of the orange–yellow complex **2** (65% yield). FT-IR (CH$_2$Cl$_2$, cm^{-1}): ν(≡CH) 3325 (w); ν(C≡C) 1981 (w), 1968 (w); ν(CO) 1847 (vs). ^{1}H-NMR (300 MHz,

$CDCl_3$): δ 7.43 (m, *o*-H, 8H, Ph); 7.33 (m, *m*- and *p*-H, 12H, Ph); 4.52 (d, $J_{HP} = 2.28$ Hz, Cp); 2.98 (m, 2H, CH_2); 2.34 (s, 1H, CH); 1.42 (m, 2H, CH_2). ^{31}P-NMR ($CDCl_3$) δ: 92.80 (d, $J_{PP} = 38.56$ Hz, 1P); 67.80 (d, $J_{PP} = 38.60$ Hz, 1P). ^{13}C-NMR ($CDCl_3$): δ 141.4 (d, $J_{CP} = 39$ Hz, *i*-Ph); 141.1 (d, $J_{CP} = 35$ Hz, *i*-Ph); 136.7 (d, $J_{CP} = 21$ Hz, C≡CC≡CH); 136.2 (d, $J_{CP} = 30$ Hz, *i*-Ph); 135.9 (d, $J_{CP} = 40$ Hz, *i*-Ph); 133.8 (d, $J_{CP} = 20$ Hz, *o*-Ph); 133.6 (d, $J_{CP} = 10$ Hz, *o*-Ph); 133.3 (d, $J_{CP} = 10$ Hz, *o*-Ph); 133.1 (d, $J_{CP} = 9$ Hz, *o*-Ph); 131–127 (m, *m*-, *p*-Ph); 94.5 (s, C≡CC≡CH); 93.9 (s, Cp); 71.9 (s, C≡CC≡CH); 59.9 (s, C≡CC≡CH). MS (FAB^+) *m*/*z*: 639.4 (M^+); 611.0 ($M^+ - CO$). Anal. Calc. for $C_{36}H_{30}OP_2Mo$: C, 67.70; H, 4.74. Found: C, 67.73; H, 4.78.

2.3.2. Method B

A solution of complex (η^5-C_5H_5)Mo(CO)(dppe)Cl (1.60 g, 2.57 mmol) in THF (20 ml) and $NHEt_2$ (50 ml) was treated at −80°C with CuI (75 mg, 0.39 mmol) and a solution of HC≡CC≡CH (ca. 4.0 mmol) in THF (50 ml), prepared in situ from ClCC≡CCCl and KOH at −80°C [17a]. The reaction mixture was gradually warmed to ambient temperature and a rapid change of color, from red to orange–yellow, was observed. Upon removal of the solvent under reduced pressure, an orange solid was obtained, and the product was extracted with hexane (25% yield).

2.4. Synthesis of (η^5-C_5H_5)(dppe)(CO)MoC≡CC≡CLi (3)

A solution of lithium diisopropylamide, prepared in situ from *n*-BuLi and diisopropylamine, was added dropwise to a solution of **2** (0.10 g, 0.16 mmol) in THF (20 ml) at −70°C. After 4 h the reaction mixture turned reddish–brown. FT-IR (THF, cm^{-1}): ν(C≡C) 2200 (w), 2090 (w); ν(CO) 1858 (vs).

The resulting anion **3** can be trapped by reaction with Me_3SiCl to regenerate **1b** in 70% yield.

2.5. Synthesis of $Co_2(CO)_4$(μ-dppa)(μ-η^2-Me_3SiC_2C≡$CSiMe_3$) (4)

2.5.1. Method A

A solution of Me_3SiC≡CC≡$CSiMe_3$ (0.29 g, 1.48 mmol) in THF (80 ml) was added to a suspension of $Co_2(CO)_6$(μ-dppa) [15] (1.00 g 1.48 mmol) in the same solvent (30 ml). The reaction mixture was stirred at 60°C for 18 h and then at r.t. overnight. Upon filtration and removal of the solvent under reduced pressure, a red solid was obtained, which was extracted with hexane and purified by column chromatography on Al_2O_3 packed in hexane. Hexane/CH_2Cl_2 (1:1) eluted a red band which yielded **4** as red crystals (1.14 g, 95% yield). FT-IR (CH_2Cl_2, cm^{-1}): ν(NH) 3329 (m); ν(C≡C) 2112 (w); ν(CO) 2027 (s), 2000 (vs), 1973 (s) 1966 (sh, w); ν(C–C) 1520 (m, coordinated acetylene);. ^1H-NMR ($CDCl_3$): δ 7.47 (m, *o*-H, 8H, Ph); 7.36 (m, *m*- and *p*-H, 12H, Ph); 3.78 (t, 1H, NH); 0.33 (s, 9H, Me_3SiC–); 0.11 (s, 9H, ≡$CSiMe_3$). ^{31}P-NMR ($CDCl_3$): δ 93.45 (s, 2P). ^{13}C-NMR ($CDCl_3$): δ 141.4 (d, $J_{CP} = 21$ Hz, *i*-Ph); 141.2 (d, $J_{CP} = 21$ Hz, *i*-Ph); 139.7 (d, $J_{CP} = 23$ Hz, *i*-Ph); 139.5(d, $J_{CP} = 24$ Hz, *i*-Ph); 131.5 (d, $J_{CP} = 7$ Hz, *o*-Ph); 131.4 (d, $J_{CP} = 7$ Hz, *o*-Ph); 130.2 (d, $J_{CP} = 6$ Hz, *p*-Ph); 128.8 (d, $J_{CP} = 5$ Hz, *p*-Ph); 128.7 (d, $J_{CP} = 5$ Hz, *p*-Ph); 128.6 (d, $J_{CP} = 5$ Hz, *p*-Ph); 128.5 (d, $J_{CP} = 5$ Hz, *p*-Ph); 106.8 (s, C(3) $Me_3SiC_4SiMe_3$); 100.0 (s, C(4) $Me_3SiC_4SiMe_3$); 77.5 (s, C(2) $Me_3SiC_4SiMe_3$); 68.3 (s, C(1) $Me_3SiC_4SiMe_3$); 1.43(s, Me_3SiC–); 0.11 (s, 9H, ≡$CSiMe_3$). MS (FAB^+) *m*/*z*: 810.2 (M^+); 781.7 ($M^+ - CO$); 753.7 ($M^+ - 2CO$); 725.7 ($M^+ - 3CO$); 697.7 ($M^+ - 4CO$); 625.2 ($M^+ - 4CO\text{-}SiMe_3$); 503.1 ($M^+ - 4CO\text{-}(Me_3SiC{\equiv}C)_2$). Anal. Calc. for $C_{38}H_{39}Co_2O_4P_2NSi_2$: C, 56.37; H, 4.85; N, 1.73; Co, 14.58. Found: C, 56.41; H, 4.85; N, 1.77; Co, 14.67.

2.5.2. Method B

A solution of dppa (0.80 g, 2.08 mmol) in THF (50 ml) was added to a solution of $Co_2(CO)_6$(μ-η^2-Me_3SiC_2C≡$CSiMe_3$) [16] (1.00 g, 2.08 mmol) in the same solvent. The reaction mixture was stirred at 40°C overnight. Complex **4** was isolated in 98% yield, in the same manner used in Section 2.5.1.

2.6. Synthesis of $Co_2(CO)_4(PPh_2Me)_2$(μ-η^2-Me_3SiC_2C≡$CSiMe_3$) (5)

A solution of PPh_2Me (0.60 ml, 3.18 mmol) in toluene (20 ml) was added to a solution of $Co_2(CO)_6$(μ-η^2-Me_3SiC_2C≡$CSiMe_3$) [16] (0.76 g, 1.58 mmol) in the same solvent (40 ml). The reaction mixture was stirred at 90°C for 3 h. Upon filtration and removal of the solvent under reduced pressure, a red solid was obtained, which was extracted with hexane and purified by column chromatography on Al_2O_3 packed in hexane. Hexane/CH_2Cl_2 (2:1) eluted a red band which yielded **5** as red crystals (1.14 g, 95% yield). FT-IR (CH_2Cl_2, cm^{-1}): ν(C≡C) 2109 (w); ν(CO) 2020 (vs), 1982 (sh), 1966 (s) 1945 (sh, w); ν(C–C) 1549 (m, coordinated acetylene). ^1H-NMR ($CDCl_3$): δ 7.57 (m, *o*-H, 8H, Ph); 7.37 (m, *m*- and *p*-H, 12H, Ph); 1.98 (s, 6H, PMe); 0.31 (s, 9H, Me_3SiC–); 0.1 (s, 9H, ≡$CSiMe_3$). ^{31}P-NMR ($CDCl_3$): δ 25.8 (s, 2P).

2.7. Synthesis of $[Co_2(CO)_4(\mu\text{-dppa})]_2$(μ-$\eta^2$:μ-$\eta^2$-$Me_3SiC_2C_2SiMe_3$) (6)

2.7.1. Method A

A solution of Me_3SiC≡CC≡$CSiMe_3$ (0.29 g, 1.48 mmol) in THF (30 ml) was added to a suspension of $Co_2(CO)_6$(μ-dppa) (2.00 g, 2.96 mmol) in the same

Table 5
Bond lengths (Å) and bond angles (°) for **4**

Bond lengths (Å)			
Co(1A)–C(11A)	1.777(5)	Co(1B)–C(12B)	1.763(5)
Co(1A)–C(12A)	1.782(5)	Co(1B)–C(11B)	1.780(5)
Co(1A)–C(5A)	1.969(4)	Co(1B)–C(5B)	1.981(4)
Co(1A)–C(4A)	1.976(4)	Co(1B)–C(4B)	1.982(4)
Co(1A)–P(1A)	2.2114(13)	Co(1B)–P(1B)	2.2102(13)
Co(1A)–Co(2A)	2.4620(8)	Co(1B)–Co(2B)	2.4658(8)
Co(2A)–C(14A)	1.755(5)	Co(2B)–C(14B)	1.744(5)
Co(2A)–C(13A)	1.784(5)	Co(2B)–C(13B)	1.777(5)
Co(2A)–C(5A)	1.951(4)	Co(2B)–C(5B)	1.969(4)
Co(2A)–C(4A)	1.952(4)	Co(2B)–C(4B)	1.974(4)
Co(2A)–P(2A)	2.1927(13)	Co(2B)–P(2B)	2.1939(13)
Si(1A)–C(4A)	1.838(5)	Si(1B)–C(4B)	1.833(5)
Si(1A)–C(3A)	1.848(5)	Si(1B)–C(2B)	1.858(5)
Si(1A)–C(1A)	1.852(5)	Si(1B)–C(3B)	1.859(5)
Si(1A)–C(2A)	1.862(5)	Si(1B)–C(1B)	1.865(5)
Si(2A)–C(7A)	1.832(5)	Si(2B)–C(8B)	1.831(6)
Si(2A)–C(10A)	1.848(5)	Si(2B)–C(7B)	1.838(5)
Si(2A)–C(9A)	1.851(7)	Si(2B)–C(10B)	1.856(4)
Si(2A)–C(8A)	1.856(7)	Si(2B)–C(9B)	1.865(6)
P(1A)–N(1A)	1.686(4)	P(1B)–N(1B)	1.691(4)
P(1A)–C(31A)	1.810(4)	P(1B)–C(31B)	1.814(5)
P(1A)–C(21A)	1.827(4)	P(1B)–C(21B)	1.834(4)
P(2A)–N(1A)	1.691(3)	P(2B)–N(1B)	1.699(3)
P(2A)–C(41A)	1.825(5)	P(2B)–C(41B)	1.823(5)
P(2A)–C(51A)	1.840(5)	P(2B)–C(51B)	1.828(4)
O(11A)–C(11A)	1.150(5)	O(11B)–C(11B)	1.136(5)
O(12A)–C(12A)	1.135(5)	O(12B)–C(12B)	1.148(5)
O(13A)–C(13A)	1.138(6)	O(13B)–C(13B)	1.154(6)
O(14A)–C(14A)	1.157(5)	O(14B)–C(14B)	1.163(5)
C(4A)–C(5A)	1.375(6)	C(4B)–C(5B)	1.377(6)
C(5A)–C(6A)	1.406(6)	C(5B)–C(6B)	1.387(6)
C(6A)–C(7A)	1.207(6)	C(6B)–C(7B)	1.215(6)
Bond angles (°)			
C(11A)–Co(1A)–C(12A)	100.7(2)	C(12B)–Co(1B)–C(11B)	101.2(2)
C(11A)–Co(1A)–C(5A)	142.73(18)	C(12B)–Co(1B)–C(5B)	100.19(19)
C(12A)–Co(1A)–C(5A)	98.20(19)	C(11B)–Co(1B)–C(5B)	141.57(18)
C(11A)–Co(1A)–C(4A)	104.08(18)	C(12B)–Co(1B)–C(4B)	98.95(19)
C(12A)–Co(1A)–C(4A)	99.52(19)	C(11B)–Co(1B)–C(4B)	104.30(18)
C(5A)–Co(1A)–C(4A)	40.80(17)	C(5B)–Co(1B)–C(4B)	40.68(17)
C(11A)–Co(1A)–P(1A)	109.24(15)	C(12B)–Co(1B)–P(1B)	100.01(16)
C(12A)–Co(1A)–P(1A)	99.88(16)	C(11B)–Co(1B)–P(1B)	109.46(15)
C(5A)–Co(1A)–P(1A)	98.68(13)	C(5B)–Co(1B)–P(1B)	97.71(13)
C(4A)–Co(1A)–P(1A)	137.19(13)	C(4B)–Co(1B)–P(1B)	136.85(13)
C(11A)–Co(1A)–Co(2A)	100.72(15)	C(12B)–Co(1B)–Co(2B)	148.27(15)
C(12A)–Co(1A)–Co(2A)	146.98(15)	C(11B)–Co(1B)–Co(2B)	97.48(15)
C(5A)–Co(1A)–Co(2A)	50.77(12)	C(5B)–Co(1B)–Co(2B)	51.16(11)
C(4A)–Co(1A)–Co(2A)	50.76(13)	C(4B)–Co(1B)–Co(2B)	51.28(12)
P(1A)–Co(1A)–Co(2A)	96.41(4)	P(1B)–Co(1B)–Co(2B)	97.60(4)
C(14A)–Co(2A)–C(13A)	100.0(2)	C(14B)–Co(2B)–C(13B)	99.0(2)
C(14A)–Co(2A)–C(5A)	103.0(2)	C(14B)–Co(2B)–C(5B)	98.9(2)
C(13A)–Co(2A)–C(5A)	143.4(2)	C(13B)–Co(2B)–C(5B)	143.2(2)
C(14A)–Co(2A)–C(4A)	103.0(2)	C(14B)–Co(2B)–C(4B)	103.5(2)
C(13A)–Co(2A)–C(4A)	105.8(2)	C(13B)–Co(2B)–C(4B)	103.4(2)
C(5A)–Co(2A)–C(4A)	41.26(17)	C(5B)–Co(2B)–C(4B)	40.90(17)
C(14A)–Co(2A)–P(2A)	99.70(16)	C(14B)–Co(2B)–P(2B)	99.15(16)
C(13A)–Co(2A)–P(2A)	102.32(16)	C(13B)–Co(2B)–P(2B)	104.87(17)
C(5A)–Co(2A)–P(2A)	101.44(13)	C(5B)–Co(2B)–P(2B)	103.68(13)
C(4A)–Co(2A)–P(2A)	139.85(12)	C(4B)–Co(2B)–P(2B)	140.13(12)
C(14A)–Co(2A)–Co(1A)	152.24(16)	C(14B)–Co(2B)–Co(1B)	149.84(16)
C(13A)–Co(2A)–Co(1A)	98.28(18)	C(13B)–Co(2B)–Co(1B)	103.26(18)
C(5A)–Co(2A)–Co(1A)	51.43(12)	C(5B)–Co(2B)–Co(1B)	51.59(12)
C(4A)–Co(2A)–Co(1A)	51.61(12)	C(4B)–Co(2B)–Co(1B)	51.60(12)

Table 5 (Continued)

P(2A)–Co(2A)–Co(1A)	96.60(4)	P(2B)–Co(2B)–Co(1B)	94.57(4)
N(1A)–P(1A)–C(31A)	104.0(2)	N(1B)–P(1B)–C(31B)	103.73(19)
N(1A)–P(1A)–C(21A)	100.5(2)	N(1B)–P(1B)–C(21B)	101.73(19)
C(31A)–P(1A)–C(21A)	101.1(2)	C(31B)–P(1B)–C(21B)	101.0(2)
N(1A)–P(1A)–Co(1A)	111.73(13)	N(1B)–P(1B)–Co(1B)	110.50(12)
C(31A)–P(1A)–Co(1A)	114.69(16)	C(31B)–P(1B)–Co(1B)	115.14(15)
C(21A)–P(1A)–Co(1A)	122.54(15)	C(21B)–P(1B)–Co(1B)	122.49(15)
N(1A)–P(2A)–C(41A)	103.32(19)	N(1B)–P(2B)–C(41B)	101.33(18)
N(1A)–P(2A)–C(51A)	104.2(2)	N(1B)–P(2B)–C(51B)	105.15(19)
C(41A)–P(2A)–C(51A)	101.3(2)	C(41B)–P(2B)–C(51B)	102.1(2)
N(1A)–P(2A)–Co(2A)	112.04(14)	N(1B)–P(2B)–Co(2B)	112.35(14)
C(41A)–P(2A)–Co(2A)	118.87(15)	C(41B)–P(2B)–Co(2B)	117.92(15)
C(51A)–P(2A)–Co(2A)	115.28(15)	C(51B)–P(2B)–Co(2B)	116.10(15)
P(1A)–N(1A)–P(2A)	122.7(2)	P(1B)–N(1B)–P(2B)	121.5(2)
C(5A)–C(4A)–Si(1A)	143.0(4)	C(5B)–C(4B)–Si(1B)	145.7(3)
C(5A)–C(4A)–Co(2A)	69.3(3)	C(5B)–C(4B)–Co(2B)	69.4(3)
Si(1A)–C(4A)–Co(2A)	134.7(2)	Si(1B)–C(4B)–Co(2B)	133.9(2)
C(5A)–C(4A)–Co(1A)	69.4(2)	C(5B)–C(4B)–Co(1B)	69.6(2)
Si(1A)–C(4A)–Co(1A)	134.1(2)	Si(1B)–C(4B)–Co(1B)	132.3(2)
Co(2A)–C(4A)–Co(1A)	77.63(16)	Co(2B)–C(4B)–Co(1B)	77.12(16)
C(4A)–C(5A)–C(6A)	136.8(4)	C(4B)–C(5B)–C(6B)	139.8(4)
C(4A)–C(5A)–Co(2A)	69.4(2)	C(4B)–C(5B)–Co(2B)	69.7(2)
C(6A)–C(5A)–Co(2A)	139.4(3)	C(6B)–C(5B)–Co(2B)	135.7(3)
C(4A)–C(5A)–Co(1A)	69.8(2)	C(4B)–C(5B)–Co(1B)	69.7(2)
C(6A)–C(5A)–Co(1A)	134.3(3)	C(6B)–C(5B)–Co(1B)	135.9(3)
Co(2A)–C(5A)–Co(1A)	77.80(15)	Co(2B)–C(5B)–Co(1B)	77.25(15)
C(7A)–C(6A)–C(5A)	178.6(5)	C(7B)–C(6B)–C(5B)	178.6(5)
C(6A)–C(7A)–Si(2A)	176.8(5)	C(6B)–C(7B)–Si(2B)	177.8(4)
O(11A)–C(11A)–Co(1A)	175.6(4)	O(11B)–C(11B)–Co(1B)	177.0(4)
O(12A)–C(12A)–Co(1A)	175.9(4)	O(12B)–C(12B)–Co(1B)	176.8(4)
O(13A)–C(13A)–Co(2A)	179.6(5)	O(13B)–C(13B)–Co(2B)	175.9(5)
O(14A)–C(14A)–Co(2A)	178.9(4)	O(14B)–C(14B)–Co(2B)	178.2(4)

solvent (80 ml). The reaction mixture was stirred at 60°C for 8 h. After removal of the solvent under vacuum the residue was eluted with hexane/CH_2Cl_2 (1:1) on an alumina column. The green band yielded crystals of **6** (1.49 g, 98% yield). FT-IR (CH_2Cl_2, cm^{-1}): ν(NH) 3329 (w); ν(CO) 2027 (s), 2000 (vs) 1972 (vs); ν(C–C) 1523 (m, coordinated acetylene). ^{1}H-NMR ($CDCl_3$): δ 7.49 (m, *o*-H, 16H, Ph); 7.37 (m, *m*- and *p*-H, 24H, Ph); 3.84 (t, 2H, NH); 0.40 (s, 18H, Me_3SiC–). ^{31}P-NMR ($CDCl_3$): δ 89.83 (s, 4P). MS (FAB^+) *m*/*z*: 1366.1 ($M^+ - 2CO$); 892.1 ($M^+ - 8CO$-4Ph); 697.1 ($M^+ - 8CO$-4Ph-($Me_3SiC{\equiv}C)_2$). Anal. Calc. for $C_{66}H_{60}Co_4O_8P_4N_2Si_2$: C, 55.62; H, 4.25; N, 1.97; Co, 16.50. Found: C, 55.66; H, 4.26; N, 2.02; Co, 16.58.

2.7.2. Method B

A suspension of $Co_2(CO)_6$(μ-dppa) (0.20 g, 0.30 mmol) in THF (30 ml) was added to a solution of **4** (0.24 g, 0.30 mmol) in the same solvent (20 ml). Complex **4** was isolated in 94% yield, in the same manner used in Section 2.7.1.

2.8. Synthesis of $Co_2(CO)_4(\mu$-dppa$)(\mu$-η^2-Me_3Si-$C_2C{\equiv}CH)$ (7)

A solution of Bu_4NF (1.0 M, 0.86 ml, 0.86 mmol) in THF was added to a solution of **4** (0.69 g, 0.85 mmol) in THF/MeOH (1:5) (80 ml). The solution was refluxed at 70°C for a period of 8 h. The reaction was stopped when all the starting material had been consumed (FT-IR spectroscopy). Upon filtration and removal of the solvent under reduced pressure, a red solid was obtained which was washed with hexane, extracted with DCM and purified by column chromatography on Al_2O_3 packed in hexane and using hexane/DCM (1:1) as eluent. Solvent was evaporated to give 0.60 g of the red complex **7** (95% yield). FT-IR ($CDCl_3$, cm^{-1}): ν(C≡C) 2070 (w); ν(CO) 2036 (s), 1995 (s), 1970 (s); ν(C–C) 1523 (m, coordinated acetylene). ^{1}H-NMR ($CDCl_3$): δ 7.47 (m, *o*-H, 8H, Ph); 7.38 (m, *m*- and *p*-H, 12H, Ph); 3.74 (t, 1H, NH); 3.20 (s, 1H, ≡CH); 0.34 (s, 9H, Me_3SiC–). ^{31}P-NMR ($CDCl_3$): δ 93.96 (s, 2P). ^{13}C-NMR ($CDCl_3$): δ 140.8 (d, $J_{CP} = 21$ Hz, *i*-Ph); 140.5 (d, $J_{CP} = 21$ Hz, *i*-Ph); 139.0 (d, $J_{CP} = 24$ Hz, *i*-Ph); 138.7 (d, $J_{CP} = 23$ Hz, *i*-Ph); 131.1 (d, $J_{CP} = 7$ Hz, *o*-Ph); 131.0 (d, $J_{CP} = 7$ Hz, *o*-Ph); 130.5 (d, $J_{CP} = 7$ Hz, *o*-Ph); 130.0 (d, $J_{CP} = 7$ Hz, *o*-Ph); 129.8 (s, *p*-Ph); 128.4 (d, $J_{CP} = 5$ Hz, *m*-Ph); 128.3 (d, $J_{CP} = 5$ Hz, *m*-Ph); 128.0 (d, $J_{CP} = 5$ Hz, *m*-Ph); 127.9 (d, $J_{CP} = 5$ Hz, *m*-Ph); 84.8 (s C(3) Me_3SiC_4H); 82.9 (s, s C(4) Me_3SiC_4H); 77.1 (s, s C(2) Me_3SiC_4H); 67.9 (s, s C(1) Me_3SiC_4H); 0.96 (s, Me_3SiC–). MS (FAB^+) *m*/*z*: 709.0 ($M^+ - CO$); 625.1 ($M^+ - 4CO$); 503.0 ($M^+ - 4CO$-$Me_3SiC{\equiv}CC{\equiv}CH$);

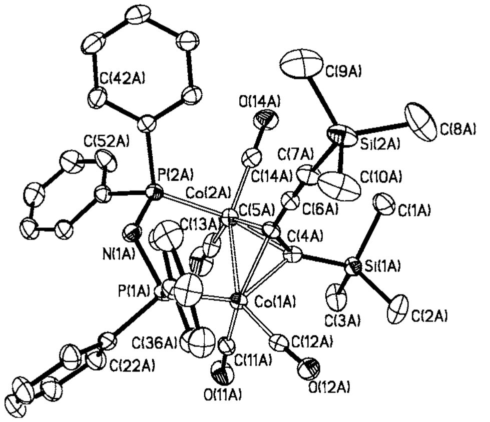


Fig. 2. ORTEP diagram of $Co_2(CO)_4(dppa)_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$, **4**, (molecule 1) with 30% ellipsoids. H atoms have been removed for clarity.

426.0 ($M^+ - 4CO\text{-}Me_3SiC{\equiv}CC{\equiv}CH\text{-}Ph$); 348.9 ($M^+ - 4CO\text{-}Me_3SiC{\equiv}CC{\equiv}CH\text{-}2Ph$). Anal. Calc. for $C_{35}H_{31}Co_2O_4P_2NSi$: C 57.00; H 4.24; N 1.90; Co 15.98. Found: C 57.05; H 4.26; N 1.92; Co 15.90.

2.9. X-ray crystallography

Dark red, block-shaped crystals of (η^5-C_5H_5)-Mo(CO)(dppe)Br (**1a**), are obtained by recrystallization of the complex from CH_2Cl_2/hexane mixtures. Red block-shaped crystals of $Co_2(CO)_4(dppa)_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$ (**4**), are obtained by recrystallization of the complex from CH_2Cl_2/hexane mixtures. A summary of selected crystallographic data for both complexes is given in Table 1. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package [18].

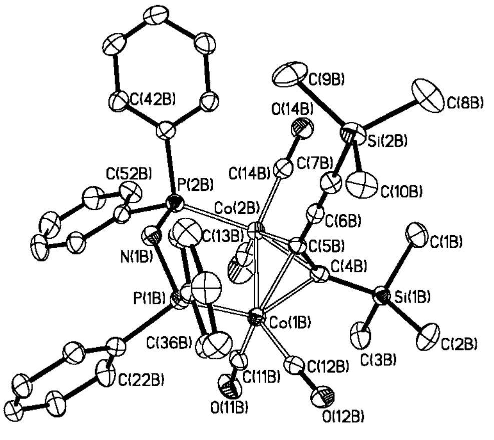
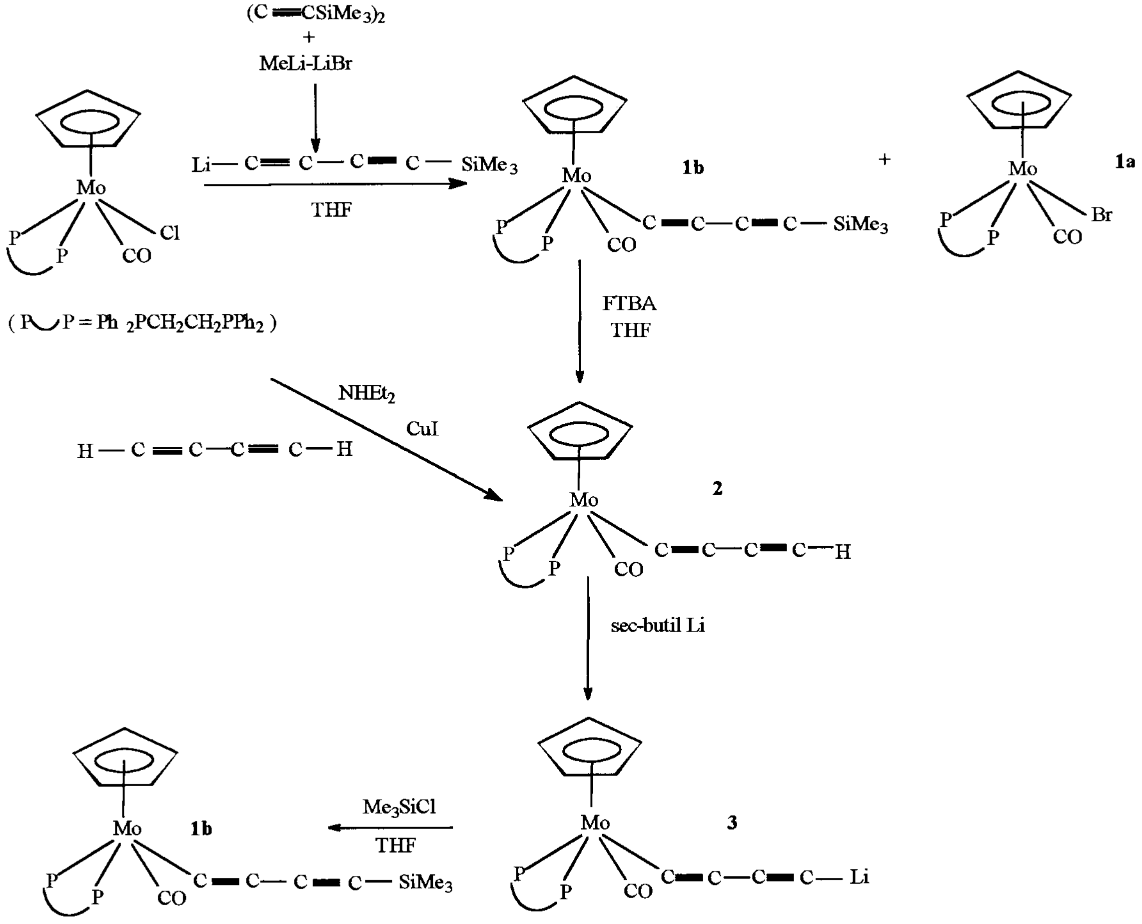


Fig. 3. ORTEP diagram of $Co_2(CO)_4(dppa)_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$, **4**, (molecule 2) with 30% ellipsoids. H atoms have been removed for clarity.

The structures were solved and refined using the SHELXTL\PC V5.1 package [19]. The position of the Mo atom, in **1a**, was deduced by the Patterson method and the remaining non-H atoms were located by successive difference Fourier syntheses. Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). The H atom positions were calculated and the atoms were constrained as riding atoms with U isotropic 20% larger than the corresponding C-atoms. As the refinement converged, it became apparent that a minor disorder resulting from interchange of the Br and CO ligands existed. The atoms Br*1, C1*2 and O1*2 refined to a site occupancy of 0.12(3) which were fixed to 0.10 in subsequent cycles of refinement. Distance restraints were applied to Mo–Br*1 and Mo–C1*2–O1*2 in the final cycles of refinement. Final positional parameters for **1a** are given in Table 2. Views of the disorder model, anisotropic thermal parameters, hydrogen atom parameters and structure amplitudes are available as supplementary material. Table 3 contains selected bond distances and angles for **1a**. Fig. 1 presents a molecular diagram of **1a**.

The structure of **4** was solved by direct methods and refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). The H atom positions were calculated and the atoms were constrained as riding atoms with U isotropic 20% larger than the corresponding C-atoms for the phenyl H atoms and the N–H atom, and 50% larger for the methyl H atoms. After examination of difference Fourier maps it became obvious that there were partial occupancy disordered solvent molecules in the crystal lattice. The crystals prepared for the X-ray analysis were grown from CH_2Cl_2/hexane mixtures and therefore these were the only possible choices. The pattern of the peaks in the difference Fourier map did not correspond with any ordered orientation of CH_2Cl_2/hexane molecules. Accordingly, the contribution of the density of the disordered solvent molecules was subtracted from the measured structure factors using the SQUEEZE [20] option in PLATON [21]. Subsequent refinement converged with a lower R-factor than when attempts were made to model the disordered solvent. There were no significant changes to the geometry of the cobalt-containing molecules. Final positional parameters for **4** are given in Table 4. Anisotropic thermal parameters, hydrogen atom parameters and structure amplitudes are available as supplementary material. Table 5 contains selected bond distances and angles for **1a**. Figs. 2 and 3 presents molecular diagrams of **4** molecules 1 and 2, respectively.



Scheme 1.

3. Results and discussion

3.1. Synthesis and characterization of the butadiynyl molybdenum complexes $(\eta^5\text{-}C_5H_5)(CO)(dppe)MoC\equiv CC\equiv CR$ ($R = SiMe_3$, H, Li)

Following a known procedure [22], the complex $(\eta^5\text{-}C_5H_5)(CO)(dppe)MoC\equiv CC\equiv CSiMe_3$ (**1b**) was obtained from reaction of the corresponding molybdenum halide $(\eta^5\text{-}C_5H_5)Mo(CO)(dppe)Cl$ [14] with $LiC\equiv CC\equiv CSiMe_3$ [17] in THF at r.t. The butadiynyl compound was isolated after purification by column chromatography as a reddish–brown powder in low yield (7%) (Scheme 1). $(\eta^5\text{-}C_5H_5)Mo(CO)$-(dppe)Br (**1a**) has been obtained as a by-product in this reaction. The spectroscopic and X-ray data support the identity of this compound.

Removal of the TMS protecting group from **1b** was easily accomplished by treatment with 0.2 equivalents of Bu_4NF in THF at r.t. to give the terminal butadiyne complex $(\eta^5\text{-}C_5H_5)(CO)(dppe)MoC\equiv CC\equiv H$ (**2**), isolated as an orange–yellow solid in 65% yield. Complex **2** can also be prepared by CuI-catalyzed direct reaction between $(\eta^5\text{-}C_5H_5)(CO)(dppe)Cl$ and buta-1,3-diyne in the presence of diethylamine and THF which serves both to generate the active diynylcopper intermediate and to remove the HCl as diethylammonium chloride.

Complex **2** can be deprotonated by lithium diisopropylamide or by *sec*-BuLi at r.t. to generate the anion $(\eta^5\text{-}C_5H_5)(CO)(dppe)MoC\equiv CC\equiv CLi$ (**3**). This reaction is another example in which the terminal proton of a transition metal alkynyl complex is deprotonated with a base [22]. The resulting anion can be trapped by reaction with Me_3SiCl to regenerate **1** in 70% yield.

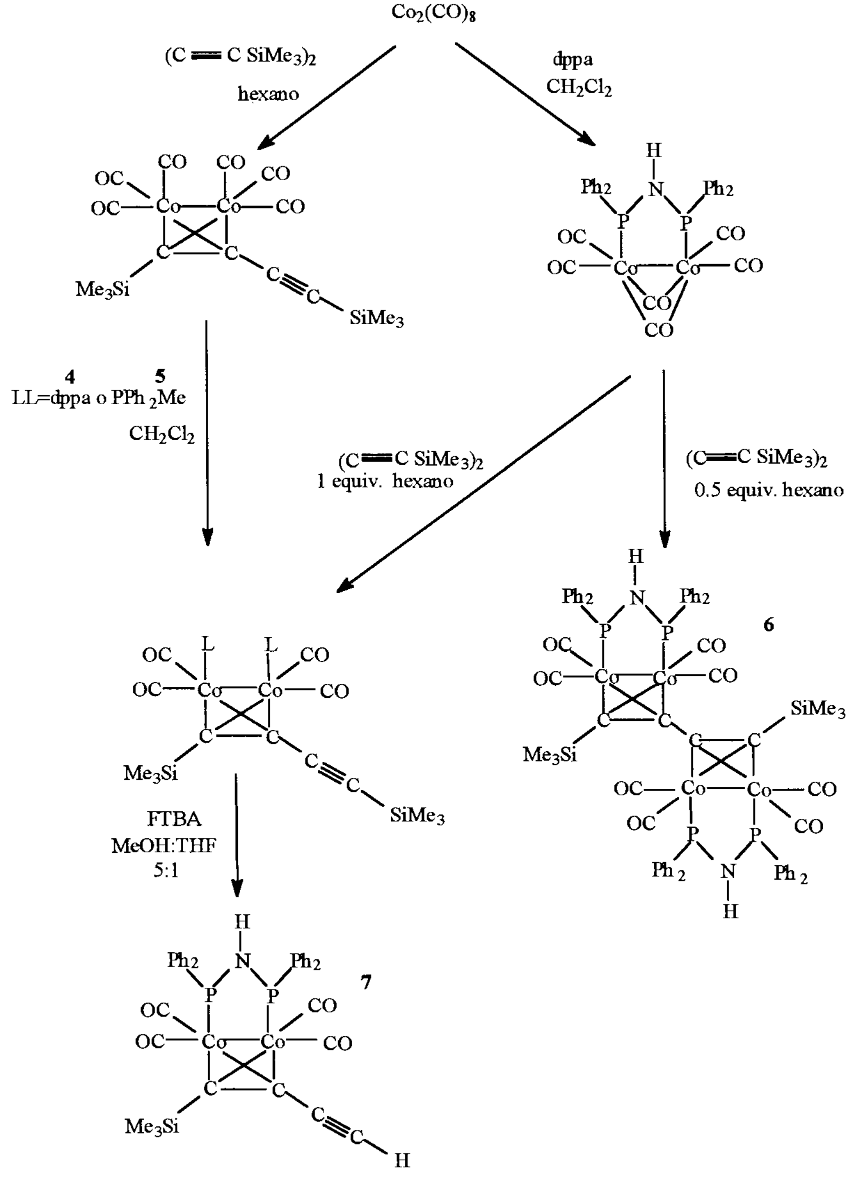
The novel mononuclear and analytically pure compounds **1b** and **2** were characterized by IR, ^1H-, ^{13}C- and ^{31}P-NMR, MS data and by elemental analysis (see Section 2). The IR spectra of **1b**, **2**, and **3** complexes in THF display a typical single absorption band at ca. 1856 cm^{-1} associated with terminal Mo–CO stretching ($\nu(CO)$) modes. This frequency in $(\eta^5\text{-}C_5H_5)(CO)(dppe)MoC\equiv CC\equiv CR$ ($R = SiMe_3$, H, Li) complexes apparently is weakly sensitive to the electronic properties of the R group of the acetylide ligand. Furthermore, these compounds **1b**, **2** and **3** exhibit two $\nu(C\equiv C)$ bands. As expected, the $\nu(C\equiv C)$ values of complex **2** with a proton at the end of the butadiynyl ligand are lower than those of the corresponding terminal TMS. The IR spectrum of complex **2** also exhibits a medium ν(C–H) band at 3325 cm^{-1}.

The ^{1}H-NMR data of compounds **1b** and **2** (see Section 2) show a doublet at ca. δ 4.56 ppm attributed to the cyclopentadienyl ligand and two other singlets at δ 0.20 and 1.25 ppm, attributed to the TMS group and H atom, respectively. The ^{31}P-NMR spectra for these compounds can be found at ca. δ 68 and 94 ppm, which is consistent with a *cis* arrangement of the dppe ligand. The ^{13}C-NMR data exhibit four resonances of the -C_4- chain. All carbon resonances can be unequivocally assigned on the basis of the J_{CH} and J_{CP} coupling constants (see Section 2). Thus, substitution of TMS group by a H atom results in variation of the chemical shifts of the carbon atoms of the chain mainly at Cγ and Cδ (87.9, 70.5 and 71.9, 59.9, respectively). This can be taken as an indication of good communication between the end groups and the butadiyne system. This fact has been previously observed in (η^5-C_5H_5)-$(CO)_2$FeC≡CC≡CR complexes [3b].

Crystals of (η^5-C_5H_5)Mo(CO)(dppe)Br (**1a**), contain discrete molecules of the complex. As shown in Fig. 1, the Mo atom has a four-legged piano stool arrangement of an η^5-Cp ligand, with Br, CO, and dppe ligands. The bond length and angles in **1a** are comparable to those reported for similar structures [23].

3.2. Synthesis and characterization of butadiynyl cobalt complexes

It is known that $Co_2(CO)_8$ decomposes at ca. 60°C to give $Co_4(CO)_{12}$ or during prolonged storage at r.t., for this reason all the reactions were carried out at temper-



Scheme 2.

atures lower than 60°C and all products were stored at -20°C. Reaction of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ with $Co_2(CO)_6(\mu\text{-dppa})$ in equimolar quantity at 60°C in THF afforded the expected monosubstituted unsymmetrical complex $Co_2(CO)_6(\mu\text{-dppa})(\mu-\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$ (**4**) as sole product in high yield (95%). This stable red complex is readily converted to the green di-substituted complex **6** on treatment with more $Co_2(CO)_6(\mu\text{-dppa})$ or by direct reaction in 1:2 ratio at 60°C. Both reactions are characteristic of terminal acetylenic cobalt complexes (Scheme 2).

No reaction was observed when the $Co_2(CO)_6(PPh_2Me)_2$ complex was treated with the same alkyne under thermal conditions, but the analogous $Co_2(CO)_4(PPh_2Me)_2)(\mu-\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$ (**5**) can be readily prepared by thermal substitution reaction [16] of two carbonyl ligands on $Co_2(CO)_6(\mu-\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$ by PPh_2Me.

Desilylation of **4** was performed with Bu_4NF in THF/MeOH (1:5) to yield the terminal butadiyne complex **7** as stable deep red crystals.

All these compounds were readily characterized by the usual methods, details of which are given in Section 2 and **7** has also been characterized by X-ray crystallography. The compounds **4**, **5**, **7** and **8** contain an uncomplexed C≡C triple bond, which gives a ν(C≡C) absorption at 2112 (**4**), 2109 (**5**) and 2070 cm^{-1} (**7**) (as expected the ν(C≡C) value of **7** is lower than **4**), and a complexed one, which gives a ν(C–C) absorption at ca. 1520 cm^{-1}. In addition, these complexes exhibit three ν(CO) bands at ca. 2060–1970 cm^{-1} assignable to terminal stretching modes (ν(CO)).

The ^1H-, ^{31}P- and ^{13}C-NMR spectra of **4**–**7** are consistent with the proposed structures (Scheme 2). The ^{13}C-NMR resonances of the -C_4- chain were easily observed, and the chemical shifts of the carbon atoms proved to be sensitive to the nature of the terminal groups. The carbon resonances of the butadiynyl ligand can be assigned on the basis of coupling constant, chemical shifts and in comparison with analogous complexes [24]. As in the molybdenum compounds the substitution of the TMS group by a H atom results in variation of chemical shifts at Cγ and Cδ (see Section 2).

The electrochemical study of **4**, **5** and **6** in different solvents is currently in progress.

3.3. Description of the crystal and molecular structure of $Co_2(CO)_4(\mu\text{-dppa})(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$ (4)

The single-crystal X-ray structure determination of $Co_2(CO)_4(dppa)_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$ (**4**) confirmed the structure presented in Scheme 2. The bimetallic Co complex **4** has two terminal CO ligands on each Co atom, a bridging 1,3-diyne ligand, $Me_3SiC_4SiMe_3$, and bridging dppa ligands. This geometry has been observed in other cobalt–carbonyl bimetallic complexes possessing a bridging acetylene ligand [25]. The geometric parameters for **4** have been summarized in Table 5 and Figs. 2 and 3 present views of the two molecules in the asymmetric unit of the crystal together with the atom-labeling scheme.

The ligands around the Co centers can be considered to adopt a highly distorted tetrahedral geometry, if the second Co atom and the two acetylene C atoms are considered as a 'cyclopropene-type' ligand occupying the fourth coordination site. Thus, the angles subtended at Co(1A) between the centroid of the Co(2A), C(4A) and C(5A) ring, and C(11A), C(12A) and P(1A) are 116.3(2), 118.2(2) and 110.9(2)°. The other three angles subtended at Co(1A) are 100.7(2), 109.2(2) and 99.9(2)°. Similar angles are observed at the other three Co centers. The Co–Co distances in the two independent molecules **4**, 2.4628(8) and 2.4658(8) Å, are equivalent. A comparable Co–Co distance of 2.459(2) Å is reported for the related compound $Co_2(CO)_4(PPPh_2(C_2Ph))_2(\mu\text{-}\eta^2\text{-}MeC{\equiv}CMe_3)$ [23].

The C(4)–C(5) distances in the ligand, 1.375(6) and 1.377(6) Å, are much longer than the C(6)–C(7) triple bond values, 1.203(6) and 1.215(6) Å, and this reflects the loss of triple bond character as a result of coordination of the acetylenic moiety to the Co_2 fragment. The C(4)–C(5) values are longer than 1.302(11) Å reported for the unconjugated system $Co_2(CO)_4(PPPh_2(C_2Ph))_2(\mu\text{-}\eta^2\text{-}MeC{\equiv}CMe_3)$ [23]. The C(5)–C(6) distances, 1.406(6) and 1.387(6), are shorter than normal C–C singles bonds as a result of conjugation. The change in hybridization at C(4) and C(5) is also reflected in the C(4)–C(5)–C(6) angles, 136.8(4) and 139.8(4)°. The C(5)–C(6)–C(7) angles are 178.6(5) and 178.6(5)°.

The average P–N distance of the bridging $(Ph_2P)_2NH$ ligand, 1.692(5) Å, is normal; the P–N bond lengths are statistically equivalent. The P–N–P angles are 122.7(2) and 121.5(2)°. These values are comparable with the average found for bridging $(Ph_2P)_2NR$ ligands of 119.3(7)° [2]. All other bond lengths and angles in **4** are comparable to those reported for similar structures [23].

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