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Polynuclear metal complexes linked by conjugated pyridines

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Abstract

The alkyne entity in 4,4′-dipyridylbutadiyne (DPB), 1,4-bis(4′-pyridylethynyl)benzene (BPEB), (4-aminophenyl)-4′-pyridylacetylene (APPA), ferrocenyl-4-pyridylacetylene (FPA) and 1,6-diferrocenyl-3-ene-1,5-hexadiyne (DFEHD) can be readily ligated to $Cp_2Mo_2(CO)_4$ and '$Co_2(CO)_6$', derived from $Co_2(CO)_8$. Both alkyne and pyridine entities in DPB or BPEB can be ligated to metal carbonyls, and (μ_4-$\eta^{1:1:2:2}$-DPB)$[W(CO)_5]_2[Cp_2Mo_2(CO)_4]$ (**11**), (μ_4-$\eta^{1:1:2:2}$-BPEB)$[W(CO)_5]_2[Cp_2Mo_2(CO)_4]$ (**12**), (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)$[W(CO)_5]_2[Cp_2Mo_2(CO)_4]_2$ (**13**), (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)$[W(CO)_5]_2[Co_2(CO)_6]_2$ (**14**), and (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)$[W(CO)_5]_2[Cp_2Mo_2(CO)_4][Co_2(CO)_6]$ (**15**) were isolated. There exist semibridging carbonyl ligands in complexes which contain $Cp_2Mo_2(CO)_4$ moiety. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Polynuclear; Metal complexes; Conjugated pyridines

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1. Introduction

Metals in close proximity have potential to exhibit a cooperative effect which is useful in catalysis [1]. While quite a few ligands, such as phosphido, sulfido and amino, are capable of bringing two metal fragments closer [2], construction of polynuclear complexes is generally facilitated by the use of polydentate ligands [3]. Polydentate ligands containing alkyne entities have been successfully used to assemble several metal moieties [4] exploiting the ligating capability of alkynes [5]. It also appears to be interesting that the electronic communication between two metal centers, linked by the conjugated chain containing alkyne entity, is not quenched upon ligation of the alkyne entity to metal carbonyls ([4]a). Recently, we are interested in conjugated pyridyl ligands incorporating an alkyne entity [6] owing to their usefulness in the preparation of organometallics nonlinear optical materials [7] and organometallic polymers [8]. Since metal pyridine [9] complexes are popular among coordination compounds, such conjugated pyridines should be useful building blocks for polynuclear multi-metal complexes. In this report, we will describe several multi-metal complexes assembled by conjugated pyridyl ligands. Some complexes derived from conjugated biferrocene are also included for spectroscopic comparison.

2. Experimental section

2.1. Materials and apparatus

All reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by adoping standard procedures. Column chromatography was performed under N_2 with the use of silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column of 35 cm length and 2.5 cm diameter. 4-Ethynylpyridine [10], 4,4′-dipyridylbutadiyne (DPB) [6], 1,4-bis(4′-pyridylethynyl)benzene (BPEB) [6], (4-aminophenyl)-4′-pyridylacetylene (APPA) [6], ferro-

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cenyl-4-pyridylacetylene (FPA) [6], and $Cp_2Mo_2(CO)_4$ [11] were prepared by published procedures. IR measurements were measured on a Perkin-Elmer 880 spectrometer. The NMR spectra were measured by using Bruker AC200 and AC300 spectrometers. Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer.

2.2. *(μ_2-$\eta^{2:2}$-DPB)[$Cp_2Mo_2(CO)_4$]* (**1**)

To a flask containing a mixture of $Cp_2Mo_2(CO)_4$ (1.00 g, 2.30 mmol) and DPB (0.47 g, 2.30 mmol) was added 200 ml of CH_2Cl_2, and the solution refluxed for 24 h. The solvent was removed in vacuum, and the residue was chromatographed. Elution with CH_2Cl_2/hexane (1:3) gave a purple band from which the powder **1** was isolated in 74% yield (1.09 g) after removal of the solvent. MS (FAB): *m/e* 637 (M^+). Anal. Found: C, 52.65; H, 2.60; N, 4.26. $C_{28}H_{18}N_2O_4Mo_2$. Calc.: C, 52.68; H, 2.84; N, 4.39%.

2.3. *(μ_2-$\eta^{2:2}$-PY)[$Cp_2Mo_2(CO)_4$]* (**2**, *L = APPA;* **3**, *L = FPA)*

Complexes **2** and **3** were synthesized by the same procedure as used for **1** except that APPA and FPA were used instead of DPB.

Purple complex **2** was eluted with THF/hexane (1:3) in a 46% yield. MS (FAB): *m/e* 627 (M^+). Anal. Found: C, 51.38; H, 3.02; N, 4.32. $C_{27}H_{20}N_2O_4Mo_2$. Calc.: C, 51.61; H, 3.21; N, 4.46%.

Orange complex **3** was eluted with THF/CH_2Cl_2 (1:9) in a 35% yield. MS (FAB): *m/e* 720 (M^+). Anal. Found: C, 51.40; H, 3.11; N, 1.72. $C_{31}H_{23}NO_4FeMo_2$. Calc.: C, 51.62; H, 3.21; N, 1.94%.

2.4. *(μ_2-$\eta^{2:2}$-BPEB)[$Cp_2Mo_2(CO)_4$]* (**4**) *and (μ_4-$\eta^{2:2:2:2}$-BPEB)[$Cp_2Mo_2(CO)_4$]$_2$* (**5**)

Complexes **4** and **5** were synthesized by the same procedure used for **1** except that BPEB was used instead of DPB. Elution of the residue with THF/CH_2Cl_2 (1:9) gave an red band from which the powder **4** was

Table 1
Crystal data for compounds **1**, **2**·THF, **9** and **13**

	1	**2**·THF	**9**	**13**
Formula	$C_{28}H_{18}N_2O_4Mo_2$	$C_{31}H_{28}N_2O_5Mo_2$	$C_{40}H_{30}O_2Fe_2Mo_2$	$C_{29}H_{16}NO_9Mo_2W$
Formula weight	638.33	699.44	878.25	898.18
a (Å)	8.809(2)	9.026(1)	14.243(2)	8.597(2)
b (Å)	9.280(1)	9.915(6)	9.498(1)	29.746(7)
c (Å)	16.237(3)	16.878(5)	25.178(2)	11.7181(9)
α (°)	85.31(2)	87.83(4)	—	—
β (°)	75.65(2)	79.36(2)	101.386(8)	94.09(1)
γ (°)	72.52(1)	72.75(2)	—	—
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z	2	2	4	4
V (Å^3)	1226.5(4)	1418(1)	3339.1(6)	2989(1)
$D_{calc.}$ (g cm^{-3})	1.729	1.639	1.747	1.996
Crystal size (mm)	$0.20 \times 0.14 \times 0.28$	$0.10 \times 0.14 \times 0.28$	$0.38 \times 0.22 \times 0.25$	$0.38 \times 0.09 \times 0.16$
Radiation Mo–K$_\alpha$ (Å)	$\lambda = 0.7107$	$\lambda = 0.7107$	$\lambda = 0.7107$	$\lambda = 0.7107$
μ (mm^{-1})	1.01	0.87	1.61	4.78
Transmission factors (max–min)	1.00–0.93	1.00–0.86	1.00–0.94	1.00–0.69
2θ range (°)	2.0–45	2.0–50	2.0–45	2.0–45
Octants	$-8 \le h \le 9$, $0 \le k \le 9$, $-17 \le l \le 17$)	$-9 \le h \le 9$), $0 \le k \le 10$, $-17 \le l \le 18$	$-15 \le h \le 15$, $0 \le k \le 10$), $0 \le l \le 27$	$-9 \le h \le 9$, $0 \le k \le 32$, $0 \le l \le 12$
No. of unique reflections	3211	3694	4350	4565
No. of reflections with $I > n\sigma$	2597 ($n = 2$)	2859 ($n = 2$)	3557 ($n = 2.5$)	3107 ($n = 2$)
No. of variables	326	318	433	379
R^a, Rw^b	0.026, 0.028	0.047, 0.055	0.027, 0.033	0.036, 0.037
GOF	1.43	2.70	1.60	1.50
Max Δ/σ	0.002	0.001	0.121	0.004

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $Rw = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$. For **1** $k = 0.00005$, **2**·THF $k = 0.00005$, **9** $k = 0.0001$ and **13** $k = 0.0001$.

Table 2
Atomic coordinates for complex **1**

Atom	x	y	z	B_{iso}
Mo1	0.39833(5)	0.91391(5)	0.78425(3)	2.71(2)
Mo2	0.10838(5)	1.15009(5)	0.74811(3)	2.40(2)
O1	0.6282(5)	0.9789(5)	0.8862(3)	6.7(3)
O2	0.1862(6)	0.8587(5)	0.9629(2)	6.6(3)
O3	0.2660(5)	1.0945(4)	0.5554(2)	5.3(2)
O4	0.0241(5)	0.8447(4)	0.7748(3)	5.6(2)
N1	0.3167(6)	1.4036(5)	1.0192(3)	4.5(3)
N2	0.9264(7)	1.3876(7)	0.4285(3)	6.2(3)
C1	0.5440(7)	0.9556(6)	0.8492(4)	4.2(3)
C2	0.2615(7)	0.8834(6)	0.8987(3)	3.8(3)
C3	0.2078(7)	1.1096(6)	0.6273(3)	3.4(3)
C4	0.0706(6)	0.9509(6)	0.7652(3)	3.7(3)
C5	0.4050(7)	1.4072(6)	0.9403(4)	4.5(3)
C6	0.3973(6)	1.3329(6)	0.8724(3)	3.3(3)
C7	0.2904(5)	1.2452(5)	0.8852(3)	2.3(2)
C8	0.1959(6)	1.2400(5)	0.9671(3)	3.3(3)
C9	0.2113(7)	1.3211(6)	1.0299(3)	3.9(3)
C10	0.2867(5)	1.1558(5)	0.8155(3)	2.3(2)
C11	0.3662(5)	1.1408(5)	0.7307(3)	2.4(2)
C12	0.4790(6)	1.1991(5)	0.6718(3)	2.5(2)
C13	0.5742(6)	1.2433(5)	0.6168(3)	3.0(3)
C14	0.6923(6)	1.2940(5)	0.5538(3)	2.7(2)
C15	0.8300(7)	1.1929(6)	0.5073(3)	3.9(3)
C16	0.9416(8)	1.2439(8)	0.4471(4)	5.6(4)
C17	0.7956(9)	1.4841(7)	0.4731(5)	6.5(4)
C18	0.6762(7)	1.4445(6)	0.5364(4)	4.8(3)
C19	0.5652(8)	0.6688(6)	0.7678(4)	4.9(3)
C20	0.6432(7)	0.7597(7)	0.7074(4)	5.5(3)
C21	0.5477(9)	0.8175(6)	0.6489(3)	5.0(3)
C22	0.4112(8)	0.7636(6)	0.6712(4)	4.8(3)
C23	0.4199(8)	0.6740(6)	0.7453(4)	4.6(3)
C24	−0.0220(7)	1.4108(6)	0.7649(5)	5.0(3)
C25	−0.0807(7)	1.3585(7)	0.7047(4)	4.5(3)
C26	−0.1639(6)	1.2560(7)	0.7452(4)	4.3(3)
C27	−0.1583(6)	1.2455(6)	0.8317(3)	4.0(3)
C28	−0.0709(7)	1.3402(7)	0.8438(4)	4.6(3)

isolated in a 37% yield after removal of the solvent. MS (FAB): *m/e* 713 (M^+). Anal. Found: C, 56.79; H, 2.99; N, 3.75. $C_{34}H_{22}N_2O_4Mo_2$ Calc.: C, 57.16; H, 3.10; N, 3.92%. Further elution with THF/CH_2Cl_2 (3:2) gave a purple band from which the powder **5** was isolated in an 11% yield, again after removal of the solvent. MS (FAB): *m/e* 1147 (M^+). Anal. Found: C, 50.14; H, 3.27; N, 2.40. $C_{48}H_{32}N_2O_8Mo_2$. Calc.: C, 50.20; H, 3.01; N, 2.44%.

2.5. (μ_4-$\eta^{2:2:2:2}$-BPEB)[$Co_2(CO)_6$]$_2$ (6)

A solution of $Co_2(CO)_8$ (241 mg, 0.71 mmol) in hexane (50 ml) was added slowly to a solution of BPEB (200 mg, 0.35 mmol) in 100 ml of CH_2Cl_2. The resulting solution was stirred at room temperature (r.t.) for 24 h and the solvent was removed in vacuo. The residue was chromatographed using THF/CH_2Cl_2 (1:15) as eluant. The brown band collected was pumped to dryness and the residue recrystallized from CH_2Cl_2/hexane to give complex **6** as brown powder in a 43% yield (262 mg). MS (FAB): *m/e* 851 (M^+). Anal. Found: C, 45.25; H, 1.29; N, 3.45. $C_{32}H_{12}N_2O_{12}Co_4$. Calc.: C, 45.10; H, 1.15; N, 3.29%.

2.6. (μ_4-$\eta^{2:2:2:2}$-BPEB)[$Cp_2Mo_2(CO)_4$][$Co_2(CO)_6$] (7)

Complex **7** was synthesized by the same procedure as used for **6** except that complex **4** was used instead of BPEB. Dark brown complex **7** was eluted with THF/CH_2Cl_2 (2:3), resulting in an 18% yield. Anal. Found: C, 47.82; H, 2.14; N, 2.77. $C_{40}H_{22}N_2O_{10}Co_2Mo_2$. Calc.: C, 48.03; H, 2.22; N, 2.80%.

2.7. 1,6-Diferrocenyl-3-ene-1,5-hexadiyne (DFEHD) (8)

Complex **8** was isolated as a minor product (10%)

Table 3
Atomic coordinates for complexes 2·THF

Atom	x	y	z	B_{iso}
Mo1	0.20080(8)	0.74240(8)	0.86493(4)	4.32(4)
Mo2	0.4376(1)	0.89782(7)	0.81978(4)	4.39(4)
O1	0.208(1)	0.9057(9)	1.0156(4)	11.6(6)
O2	−0.0485(8)	1.0039(8)	0.8138(4)	9.1(4)
O3	0.7583(8)	0.7807(8)	0.7037(5)	8.2(5)
O4	0.617(1)	0.7147(7)	0.9455(4)	8.7(5)
N1	0.205(1)	0.8928(7)	0.5134(4)	5.1(4)
N2	0.815(1)	0.1562(7)	0.6631(4)	8.1(5)
C1	0.217(1)	0.852(1)	0.9555(6)	7.3(6)
C2	0.044(1)	0.909(1)	0.8338(5)	5.9(5)
C3	0.641(1)	0.821(1)	0.7440(6)	5.4(5)
C4	0.554(1)	0.7789(9)	0.8980(6)	5.5(5)
C5	0.334(1)	0.903(1)	0.5324(5)	5.8(6)
C6	0.375(1)	0.8769(9)	0.6079(5)	5.1(5)
C7	0.2766(8)	0.8359(6)	0.6683(4)	2.8(3)
C8	0.1379(9)	0.8266(8)	0.6489(5)	4.2(4)
C9	0.109(1)	0.8554(9)	0.5725(6)	5.3(5)
C10	0.3136(8)	0.8028(7)	0.7486(4)	3.0(3)
C11	0.4195(8)	0.6958(7)	0.7797(4)	2.9(3)
C12	0.5310(8)	0.5589(7)	0.7491(4)	3.1(3)
C13	0.529(1)	0.5083(7)	0.6739(5)	4.3(4)
C14	0.625(1)	0.3765(8)	0.6455(5)	4.8(4)
C15	0.726(1)	0.2917(8)	0.6902(5)	4.7(4)
C16	0.731(1)	0.3430(8)	0.7651(5)	5.8(5)
C17	0.634(1)	0.4741(8)	0.7935(5)	4.8(4)
C18	0.020(2)	0.643(1)	0.9392(9)	8.8(8)
C19	0.037(2)	0.601(1)	0.8607(9)	8.1(8)
C20	0.190(2)	0.516(1)	0.8368(8)	8.3(8)
C21	0.264(2)	0.504(1)	0.902(1)	9.3(9)
C22	0.161(2)	0.579(2)	0.9658(8)	10(1)
C23	0.509(2)	1.097(1)	0.833(1)	10(1)
C24	0.449(2)	1.112(1)	0.7582(9)	8.8(9)
C25	0.290(2)	1.1218(9)	0.7816(8)	8.0(8)
C26	0.246(2)	1.1156(9)	0.8663(8)	8.4(8)
C27	0.388(2)	1.100(1)	0.896(1)	11(1)
O5	0.922(3)	0.601(3)	0.362(2)	19.0(9)
C28	0.806(5)	0.556(3)	0.383(2)	24(1)
C29	0.743(4)	0.581(4)	0.464(2)	23(1)
C30	0.770(4)	0.695(4)	0.486(2)	24(1)
C31	0.848(4)	0.721(4)	0.422(3)	23(1)

Table 4
Atomic coordinates for complexes **9**

Atom	*x*	*y*	*z*	B_{iso}
Mo1	0.83715(3)	0.87747(4)	0.07382(2)	2.57(2)
Mo2	0.80401(3)	0.59125(4)	0.02603(2)	2.90(2)
Fe1	0.64795(4)	0.54175(7)	0.18043(3)	2.60(3)
Fe2	0.65277(5)	0.98612(8)	−0.19532(3)	3.54(3)
O1	0.6675(3)	1.0730(4)	0.0866(2)	5.7(2)
O2	0.8042(3)	1.0128(5)	−0.0417(2)	5.7(2)
O3	0.9545(3)	0.4629(5)	0.1198(2)	7.0(2)
O4	0.9691(3)	0.7392(4)	−0.0158(2)	5.3(2)
C1	0.7287(4)	0.9977(5)	0.0820(2)	3.6(2)
C2	0.8110(3)	0.9581(6)	−0.0008(2)	3.6(2)
C3	0.8994(4)	0.5117(6)	0.0857(2)	4.4(3)
C4	0.9072(4)	0.6953(6)	0.0044(2)	3.9(3)
C5	0.7644(3)	0.6870(5)	0.0974(2)	2.6(2)
C6	0.7075(3)	0.7398(4)	0.0522(2)	2.4(2)
C7	0.6037(3)	0.7554(5)	0.0388(2)	2.8(2)
C8	0.5476(3)	0.8174(5)	−0.0028(2)	3.1(2)
C9	0.5731(3)	0.8899(5)	−0.0471(2)	3.3(2)
C10	0.5804(3)	0.9563(5)	−0.0862(2)	3.6(2)
C11	0.9513(3)	0.8335(6)	0.1535(2)	3.9(2)
C12	0.9111(4)	0.9664(6)	0.1565(2)	4.0(3)
C13	0.9370(4)	1.0516(6)	0.1160(2)	4.9(3)
C14	0.9916(4)	0.9680(7)	0.0866(2)	4.9(3)
C15	1.0022(3)	0.8352(6)	0.1108(2)	4.1(3)
C16	0.7308(6)	0.3754(7)	−0.0002(3)	6.3(4)
C17	0.6653(4)	0.4767(7)	−0.0194(2)	5.2(3)
C18	0.6949(5)	0.5568(7)	−0.0571(2)	5.0(3)
C19	0.7810(5)	0.5099(8)	−0.0647(3)	6.2(4)
C20	0.8085(5)	0.3958(8)	−0.0275(3)	7.3(4)
C21	0.7496(3)	0.6624(5)	0.1526(2)	2.6(2)
C22	0.16882(3)	0.7475(4)	0.1790(2)	2.7(2)
C23	0.6961(3)	0.7002(5)	0.2328(2)	3.4(2)
C24	0.7619(3)	0.5862(5)	0.2408(2)	3.5(2)
C25	0.7936(3)	0.5634(5)	0.1922(2)	3.1(2)
C26	0.5632(4)	0.4401(6)	0.1169(2)	4.0(2)
C27	0.5076(3)	0.5274(6)	0.1436(2)	3.9(2)
C28	0.5189(3)	0.4833(5)	0.19752(2)	3.7(2)
C29	0.5834(4)	0.3683(5)	0.2048(2)	3.7(2)
C30	0.6105(4)	0.3408(5)	0.1552(2)	4.0(3)
C31	0.5814(4)	1.0358(5)	−0.1353(2)	3.7(2)
C32	0.6459(4)	1.1452(5)	−0.1424(2)	4.2(3)
C33	0.6182(4)	1.1944(6)	−0.1960(2)	4.9(3)
C34	0.5387(4)	1.1138(7)	−0.2222(2)	5.1(3)
C35	0.5162(3)	1.0168(6)	−0.1849(2)	4.3(3)
C36	0.7602(7)	0.84691)	−0.1709(3)	7.6(5)
C37	0.7891(5)	0.9450(9)	−0.2014(5)	7.4(5)
C38	0.7340(8)	0.9448(8)	−0.2506(4)	7.1(5)
C39	0.6645(6)	0.839(1)	−0.2515(4)	8.4(5)
C40	0.6843(8)	0.7810(7)	−0.2003(5)	8.1(6)

during the synthesis of ferrocenylbutadiyne following the known procedure [12]. MS (FAB): *m*/*e* 444 (M^+). Anal. Found: C, 70.32; H, 4.31. $C_{26}H_{20}Fe_2$. Calc.: C, 70.31; H, 4.54%.

2.8. (μ_2-$\eta^{2:2}$-DFEHD)[$Cp_2Mo_2(CO)_4$] (**9**)

Complex **9** was synthesized by the same procedure used in the synthesis of **1** except that DFEHD was used instead of DPB. Dark purple complex **7** was eluted with CH_2Cl_2/hexane (1:3) in a 36% yield. MS (FAB): *m*/*e* 877 (M^+). Anal. Found: C, 54.38; H, 3.54. $C_{40}H_{30}O_4Fe_2Mo_2$. Calc.: C, 54.71; H, 3.44%.

2.9. (μ_4-$\eta^{2:2:2:2}$-DFEHD)[$Cp_2Mo_2(CO)_4$][$Co_2(CO)_6$] (**10**)

Complex **10** was synthesized by the same procedure used in the synthesis of **7** except that complex **9** was used instead of complex **4**. Dark green complex **7** was eluted with CH_2Cl_2/hexane (1:9) in a 40% yield. MS (FAB): *m*/*e* 1163 (M^+). Anal. Found: C, 47.02; H, 2.50. $C_{46}H_{30}O_{10}Co_2Fe_2Mo_2$. Calc.: C, 47.46; H, 2.60%.

2.10. (μ_4-$\eta^{1:1:2:2}$-DPB)[$W(CO)_5$]$_2$[$Cp_2Mo_2(CO)_4$] (**11**)

A THF solution (180 ml) of $W(CO)_5$(THF) prepared in situ from $W(CO)_6$ (551 mg, 0.78 mmol) was trans-

Table 5
Atomic coordinates for complexes **13**

Atom	*x*	*y*	*z*	B_{iso}
W	0.38888(5)	0.20707(1)	0.2285393)	3.62(2)
Mo1	0.67931(9)	0.04220(3)	0.77553(7)	3.24(4)
Mo2	0.92452(9)	0.11261(3)	0.77580(7)	3.57(4)
N	0.5163(9)	0.1649(3)	0.3663(6)	3.4(3)
O1	0.4320(9)	0.1184(3)	0.7899(7)	6.4(4)
O2	0.800(1)	0.0605(3)	1.0274(6)	7.3(5)
O3	1.163(1)	0.0440(3)	0.8915(7)	7.1(4)
O4	1.1614(9)	0.1169(3)	0.5870(8)	7.5(5)
O5	0.436(1)	0.2901(3)	0.3947(6)	6.4(4)
O6	0.696(1)	0.2323(3)	0.1094(7)	8.0(5)
O7	0.348(1)	0.1267(3)	0.0524(7)	9.1(6)
O8	0.055(1)	0.1876(4)	0.3119(9)	9.5(6)
O9	0.209(1)	0.2697(3)	0.0516(7)	8.6(5)
C1	0.525(1)	0.0907(4)	0.7876(9)	4.4(5)
C2	0.764(1)	0.0575(4)	0.9300(9)	4.9(5)
C3	1.074(1)	0.0686(4)	0.8480(9)	4.8(6)
C4	1.076(1)	0.1153(4)	0.6562(9)	4.7(5)
C5	0.418(1)	0.2598(4)	0.3358(9)	4.0(5)
C6	0.587(1)	0.2236(4)	0.1550(8)	4.7(5)
C7	0.366(2)	0.1552(4)	0.1181(9)	5.3(6)
C8	0.177(1)	0.1929(4)	0.2848(9)	5.6(6)
C9	0.277(1)	0.2463(4)	0.1162(8)	5.1(6)
C10	0.445(1)	0.1349(4)	0.4260(9)	4.6(5)
C11	0.512(1)	0.1104(3)	0.5162(8)	4.0(4)
C12	0.6680(9)	0.1162(3)	0.5515(7)	3.0(4)
C13	0.743(1)	0.1477(4)	0.489(1)	6.0(6)
C14	0.664(1)	0.1703(4)	0.399(1)	6.2(6)
C15	0.745(1)	0.0910(3)	0.6468(7)	3.2(5)
C16	0.854(1)	0.0575(3)	0.6578(7)	3.1(4)
C17	0.9302(9)	0.0289(3)	0.5778(7)	3.2(4)
C18	0.886(1)	0.0295(3)	0.4612(8)	4.2(5)
C19	1.046(1)	−0.0019(4)	0.6143(8)	4.5(5)
C21	0.491(2)	−0.0121(4)	0.806(2)	7.3(9)
C22	0.623(3)	−0.0277(5)	0.855(1)	8.3(9)
C23	0.728(2)	−0.0356(5)	0.773(3)	11(2)
C24	0.643(4)	−0.0234(8)	0.672(2)	13(2)
C25	0.506(2)	−0.0103(5)	0.694(2)	8.7(10)
C26	0.793(1)	0.1592(4)	0.903(1)	5.2(6)
C27	0.950(2)	0.1563(4)	0.945(1)	6.1(6)
C28	1.037(1)	0.1756(5)	0.859(1)	7.2(8)
C29	0.938(2)	0.1910(4)	0.76991)	6.7(7)
C30	0.784(1)	0.1806(4)	0.796(1)	5.6(6)

Table 6
Selected bond distances (Å) and angles (°) for complexes **1**, **2**·THF, **9**, and **13**

	1	**2**·THF	**9**	**13**
Bond length (Å)				
Mo1–Mo2	2.9735(8)	2.965(2)	2.9727(6)	2.971(1)
Mo1–C1	1.986(6)	1.96(1)	1.964(5)	1.97(1)
Mo1–C2	1.998(6)	1.958(9)	1.994(6)	1.96(1)
Mo1–C4	2.894(5)		2.781(5)	
Mo2–C1		2.86(1)		
Mo2–C2				2.86(1)
Mo2–C3	1.956(6)	1.99(1)	1.967(6)	1.98(1)
Mo2–C4	1.960(6)	1.97(1)	1.936(6)	1.98(1)
Mo1–C5			2.223(4)	
Mo1–C6			2.240(4)	
Mo2–C5			2.186(4)	
Mo2–C6			2.161(4)	
Mo1–C10	2.209(4)	2.187(7)		
Mo1–C11	2.176(4)	2.154(7)		
Mo2–C10	2.140(4)	2.189(7)		
Mo2–C11	2.194(4)	2.198(7)		
W–C5				2.01(1)
W–C6				2.02(1)
W–C7				2.01(1)
W–C8				2.02(1)
W–C9				1.96(1)
C5–C6			1.357(6)	
C7–C8			1.325(6)	
C9–C10			1.192(8)	
C10–C11	1.379(6)	1.363(9)		
C1–O1	1.14(8)	1.14(1)	1.151(7)	1.15(1)
C2–O2	1.136(7)	1.14(1)	1.140(7)	1.16(1)
C3–O3	1.155(7)	1.12(1)	1.141(7)	1.15(1)
C4–O4	1.162(7)	1.13(1)	1.178(7)	1.14(1)
C5–O5				1.14(1)
C6–O6				1.14(1)
C7–O7				1.15(2)
C8–O8				1.13(2)
C9–O9				1.16(1)
C12–C13	1.201(7)			
Mo1–C15				2.195(9)
Mo1–C16				2.159(8)
Mo2–C15				2.180(9)
Mo2–C16				2.202(9)
Bond angle (°)				
Mo1–C1–O1	179.6(5)	168(1)	177.1(4)	176.8(9)
Mo1–C2–O2	176.6(5)	177.5(9)	172.9(4)	168.5(9)
Mo2–C3–O3	176.0(4)	176.5(8)	178.6(5)	178.1(9)
Mo2–C4–O4	169.6(5)	177.2(7)	167.6(4)	179.5(8)
C1–Mo1–C2	84.7(2)	88.9(4)	82.6(2)	88.4(5)
C3–Mo2–C4	91(2)	83.1(4)	87.8(2)	83.7(4)
C5–W–C6				90.2(4)
C5–W–C7				177.8(4)
C5–W–C8				92.0(4)
C5–W–C9				89.4(4)
C6–W–C7				87.6(4)
C6–W–C8				173.3(4)
C6–W–C9				87.4(4)
C7–W–C8				90.1(5)
C7–W–C9				90.2(4)
C8–W–C9				86.3(5)
Mo1–C5–C6			73.0(3)	
Mo1–C6–C5			71.6(3)	
Mo2–C5–C6			70.8(2)	
Mo2–C6–C5			72.8(3)	
Mo1–C10–C11	70.4(3)	70.4(4)		
Mo1–C11–C10	73.0(3)	73.0(4)		
Mo2–C10–C11	73.6(3)	72.3(4)		
Mo2–C11–C10	69.3(3)	71.5(4)		
Mo1–C15–C16				70.3(5)
Mo1–C16–C15				73.1(5)
Mo2–C15–C16				72.7(5)
Mo2–C16–C15				70.9(5)
C21–C5–C6			133.0(4)	
C5–C6–C7			129.9(4)	
C6–C7–C8			130.8(4)	
C7–C8–C9			129.1(4)	
C8–C9–C10			170.2(5)	
C9–C10–C31			175.5(5)	
C7–C10–C11	133.7(4)	134.5(6)		
C10–C11–C12	138.8(4)	135.4(6)		
C11–C12–C13	175.2(5)			
C12–C13–C14	177.5(5)			
C12–C15–C16				135.6(8)
C15–C16–C17				134.6(8)

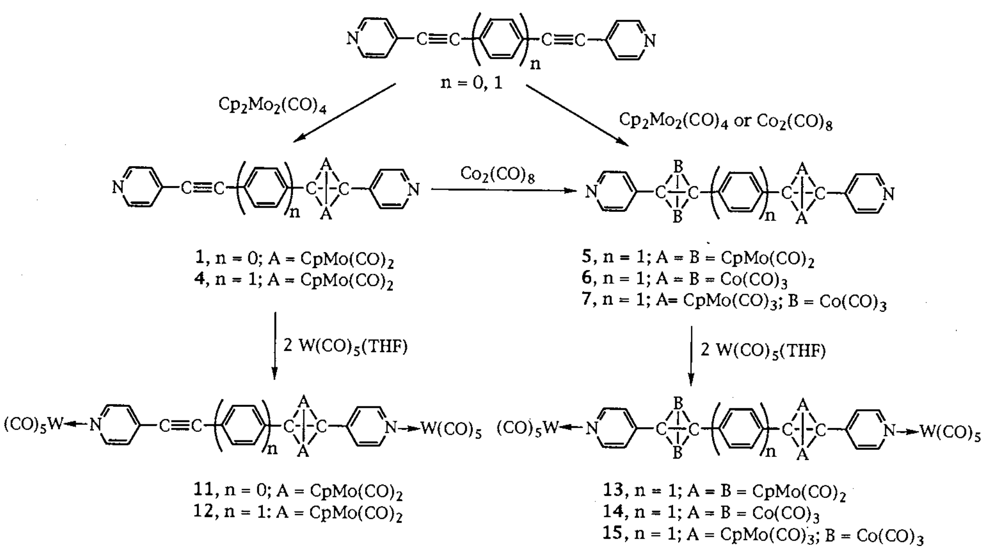
ferred to a flask containing complex **1** (500 mg, 0.78 mmol). The solution was stirred at r.t. for 24 h, and the solvent removed under vacuum. The residue was chromatographed using CH_2Cl_2/hexane (1:3) as eluent. The deep red band collected was pumped dry and the residue recrystallized from CH_2Cl_2/hexane to give complex **11** as a deep red powder in a 26% yield (265 mg). MS (FAB): *m/e* 1283 (M^+). Anal. Found: C, 35.57; H, 1.35; N, 2.12. $C_{38}H_{18}N_2O_{14}Mo_2W_2$. Calc.: C, 35.52; H, 1.41; N, 2.06%.

2.11. (μ_4-$\eta^{1:1:2:2}$-BPEB)[W(CO)$_5$]$_2$[Cp$_2$Mo$_2$(CO)$_4$] (**12**)

Complex **12** was synthesized by the same procedure employed in the synthesis of **11** except that complex **4** was used instead of complex **1**. Orange–red complex **12** was eluted with CH_2Cl_2/hexane (1:2) in a 46% yield. Anal. Found: C, 38.55; H, 1.80, N, 2.04. $C_{44}H_{22}N_2O_{14}Mo_2W_2$. Calc.: C, 38.82; H, 1.63; N, 2.06%.

2.12. (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)[W(CO)$_5$]$_2$[Cp$_2$Mo$_2$(CO)$_4$]$_2$ (**13**)

Complex **13** was synthesized by the same procedure employed in the synthesis of **11** except that complex **5** was used instead of complex **1**. Orange–red complex **13** was eluted with CH_2Cl_2/hexane (1:2) in a 44% yield. Anal. Found: C, 38.66; H, 1.70, N, 1.32. $C_{58}H_{32}N_2O_{18}Mo_4W_2$. Calc.: C, 38.80; H, 1.80; N, 1.56%.



Scheme 1.

2.13. $(\mu_6\text{-}\eta^{1:1:2:2:2:2}\text{-BPEB})[W(CO)_5]_2[Co_2(CO)_6]_2$ (**14**)

Complex **13** was synthesized by the same procedure employed in the synthesis of **11** except that complex **6** was used instead of complex **1**. Orange–red complex **14** was eluted with CH_2Cl_2/hexane (1:2) in a 46% yield. Anal. Found: C, 33.42; H, 0.78, N, 1.75. $C_{42}H_{12}N_2O_{22}Co_2W_2$. Calc.: C, 33.65; H, 0.81; N, 1.87%.

2.14. $(\mu_6\text{-}\eta^{1:1:2:2:2:2}\text{-BPEB})[W(CO)_5]_2[Cp_2Mo_2(CO)_4][Co_2(CO)_6]$ (**15**)

Complex **15** was synthesized by the same procedure used in the synthesis of **11** except that complex **7** was used instead of complex **1**. Orange–red complex **13** was eluted with CH_2Cl_2/hexane (1:2) in a 35% yield. Anal. Found: C, 36.31; H, 1.29, N, 1.34. $C_{50}H_{22}N_2O_{20}$-$Co_2Mo_2W_2$. Calc.: C, 36.46; H, 1.35; N, 1.40%.

2.15. Crystallographic studies

Crystals of **1** and **9** were grown by slowly diffusing hexane into a concentrated solution of relevant complexes in CH_2Cl_2. Crystals of **2**·THF were grown by slowly diffusing hexane into a concentrated solution of relevant complex in THF. Crystals of **13** were grown by slowly diffusing hexane into a concentrated solution of complex **13** in ethylacetate. These crystals were then mounted on a thin-walled glass capillaries. Diffraction data were measured using an Enraf-Nonious CAD4 diffractometer employing an $\omega - 2\theta$ scan mode. The unit cell dimensions were determined by centering 25 reflections in an appropriate 2θ range. Other relevant experimental details are listed in Table 1. All data reduction and refinements were performed on a MicroVax 3800 computer employing NRCVAX [13] programs. Intensities were collected and corrected for decay, absorption (empirical, Ψ-scan) and L_P effects. The structures were solved by a combination of direct methods [14] and difference Fourier methods and further refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically, while the H atoms were included in the structure factor calculation in idealized positions with $d_{C-H} = 0.95$ Å. The final positional parameters are listed in Tables 2–5, and the selected interatomic distances and bond angles are given in Table 6. The THF molecule in **2**·THF is disordered. An inversion center is present in the centroid of the benzene ring in **13**.

3. Results and discussion

Being isolobal [15] to an organic alkyne, $Cp_2Mo_2(CO)_4$ and '$Co_2(CO)_6$' have a great tendency to bind an alkyne in a flyover fashion. As expected, one of the alkyne moieties in DPB, BPEB, APPA, FPA, and DFEHD are readily ligated to $Cp_2Mo_2(CO)_4$ and '$Co_2(CO)_6$', derived from $Co_2(CO)_8$. Although the complex $(\mu_4\text{-}\eta^{2:2:2:2}\text{-BPEB})[Cp_2Mo_2(CO)_4]_2$ can be easily obtained from the reaction of BPEB with $Cp_2Mo_2(CO)_4$, $(\mu_4\text{-}\eta^{2:2:2:2}\text{-DPB})[Cp_2Mo_2(CO)_4]_2$ is elusive from the reaction of DPB, even when an excess of $Cp_2Mo_2(CO)_4$ is used. It is interesting to note that the two consecutive alkynes in $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ are both capable of interacting with a metal and form $(\mu_4\text{-}\eta^{2:2:2:2}\text{-}Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)[Cp_2W_2(CO)_4]_2$ ([4]b). We previously demonstrated that ligation of pyridine in DPB and BPEB to '$W(CO)_5$' resulted in the formation of $(\mu\text{-PY})[W(CO)_5]_2$ (PY = DPB, BPEB) ([6]a). Complexation of the alkyne moiety with $Cp_2Mo_2(CO)_4$ or '$Co_2(CO)_6$' does not extinguish the ligating ability of the pyridine in DPB and BPEB. Therefore, complexes (μ_4-$\eta^{1:1:2:2}$-DPB)[W(CO)$_5$]$_2$[Cp$_2$Mo$_2$(CO)$_4$] (**11**), (μ_4-$\eta^{1:1:2:2}$-BPEB)[W(CO)$_5$]$_2$[Cp$_2$Mo$_2$(CO)$_4$] (**12**), (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)[W(CO)$_5$]$_2$[Cp$_2$Mo$_2$(CO)$_4$]$_2$ (**13**), (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)[W(CO)$_5$]$_2$[Co$_2$(CO)$_6$]$_2$ (**14**), and (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)[W(CO)$_5$]$_2$[Cp$_2$Mo$_2$(CO)$_4$][Co$_2$(CO)$_6$] (**15**) have been synthesized easily, as illustrated in Scheme 1.

The spectroscopic properties (Table 7) of these new complexes are consistent with their formulation. For complexes (**1–5** and **9**) which contain only Cp$_2$Mo$_2$(CO)$_4$ metal moiety, three characteristic carbonyl stretching bands at ca. 1990 s, 1930 vs, and 1840 cm^{-1} are observed,

Table 7
IR spectra in the ν(CO) region and ^{1}H-NMR spectra of compounds **1**–**15**

Compound	ν(C≡C),[a] ν(CO) (cm^{-1})	δ (ppm)[b,c] J (Hz)
1	2001 s, 1939 vs, 1849 m	NC*H* (8.49, d, 2 H, ^3J(H–H) = 9.1); NC*H* (8.46, d, 2 H, ^3J(H–H) = 9.1); NCHC*H* (7.34, d, 2 H); NCHC*H* (7.32, d, 2 H), C_5H_5 (5.47, s, 10 H)
2	1984 s, 1924 vs, 1841 m	NC*H* (8.36, d, 2 H, ^3J(H–H) = 5.8); NCHC*H* (7.05, d, 2 H); H$_2$NCC*H* (6.79, d, 2 H, ^3J(H–H) = 8.5); H$_2$NCC*H* (6.51, d, 2 H); C_5H_5 (5.35; s, 10 H); NH_2 (3.65, s, 2 H)
3	1987 s, 1925 vs, 1843 m	NC*H* (8.56, d, 2 H, ^3J(H–H) = 5.9); NCHC*H* (7.71, d, 2 H); C_5H_5 (5.33; s, 10 H); C_5H_4 (4.28, t, 2 H, J(H–H) = 1.8); C_5H_4 (4.20, t, 2 H, J(H–H) = 1.8); C_5H_5 (4.07; s, 5 H)
4	2200 w, 1989 s, 1927 vs, 1845 m	NC*H* (8.60, d, 2 H, ^3J(H–H) = 6.0); NC*H* (8.38, d, 2 H, ^3J(H–H) = 6.0); C_6H_4 (7.45, d, 2 H, ^3J(H–H) = 8.0); NCHC*H* (7.42, d, 2 H, ^3J(H–H) = 6.0); C_6H_4 (7.09, d, 2 H); NCHC*H* (7.01, d, 2 H, ^3J(H–H) = 6.0); C_5H_5 (5.37; s, 10 H)
5	1979 s, 1915 vs, 1836 m	NC*H* (8.33, d, 4 H, ^3J(H–H) = 6.0); NCHC*H* (6.98, d, 4 H); C_6H_4 (6.87, s, 4 H); C_5H_5 (5.34; s, 20 H)
6	2092 m, 2061 vs, 2033 s	NC*H* (8.58, d, 4 H, ^3J(H–H) = 4.8); C_6H_4 (7.55, s, 4 H); NCHC*H* (7.45, d, 4 H)
7	2092 m, 2058 vs, 2029 s, 1998 m, 1937 s, 1850 m	NC*H* (8.59, d, 2 H, ^3J(H–H) = 6.1); NC*H* (8.34, d, 2 H, ^3J(H–H) = 6.1); C_6H_4 (7.51, m, 4 H); NCHC*H* (7.10, d, 2 H, ^3J(H–H) = 6.1); NCHC*H* (7.00, d, 2 H); C_5H_5 (5.38; s, 10 H)
8[d]		=C*H* (6.00, s, 2 H); C_5H_4 (4.47; t, 4 H, J(H–H) = 1.8); C_5H_4 (4.30; t, 4 H, J(H–H) = 1.8); C_5H_5 (4.23, s, 10 H);
9[d]	2160 w, 1982 s, 1918 vs, 1832 s	=C*H* (7.69, d, 1 H, ^3J(H–H) = 11.1); =C*H* (6.14, d, 1 H); C_5H_5 (5.38; s, 10 H); C_5H_4 (4.44, t, 2 H, J(H–H) = 1.8); C_5H_4 (4.29; t, 2 H, J(H–H) = 1.8); C_5H_4 and C_5H_5 (4.24, m, 9 H); C_5H_5 (4.14, s, 5 H)
10[d]	2083 m, 2047 vs, 2019 s, 1984 w, 1927 s, 1835 m	=C*H* (7.93, d, 1 H, ^3J(H–H) = 14.5); =C*H* (7.41, d, 1 H); C_5H_5 (5.41; s, 10 H); C_5H_4 (4.54, t, 2 H, J(H–H) = 1.8); C_5H_4 (4.49; t, 2 H, J(H–H) = 1.8); C_5H_4 (4.38, t, 2 H; J(H–H) = 1.8); C_5H_5 (4.32, s, 5 H); C_5H_4 (4.27, t, 2 H; J(H–H) = 1.8); C_5H_5 (4.20, s, 5 H)
11	2168 w, 2069 m, 2009 w, 1955 sh, 1931 vs, 1903 s, 1863 w	NC*H* (8.90, d, 2 H, ^3J(H–H) = 6.6); NC*H* (8.74, d, 2 H, ^3J(H–H) = 6.6); NCHC*H* (7.43, pseudo triplet, 4 H, ^3J(H–H) = 6.6); C_5H_5 (5.56; s, 10 H)
12	2200 w, 2069 m, 1996 m, 1933 vs, 1901 s, 1859 w	NC*H* (9.01, d, 2 H, ^3J(H–H) = 6.7); NC*H* (8.68, d, 2 H, ^3J(H–H) = 6.7); NCHC*H* (7.53, d, 2 H, ^3J(H–H) = 6.7); C_6H_4 (7.51, d, 2 H, ^3J(H–H) = 8.6); NCHC*H* (7.12, d, 2 H, ^3J(H–H) = 6.7); C_6H_4 (7.10, d, 2 H); C_5H_5 (5.42; s, 10 H)
13	2069 w, 1995 m, 1932 vs, 1900 m, 1853 m	NC*H* (8.63, d, 4 H, ^3J(H–H) = 7.5); NCHC*H* (7.11, d, 4 H); C_6H_4 (6.90, s, 4 H); C_5H_5 (5.37; s, 20 H)
14	2094 m, 2062 s, 2035 s, 1976 w, 1930 vs, 1903 m	NC*H* (8.99, d, 4 H, ^3J(H–H) = 6.4); C_6H_4 (7.73, s, 4 H); NCHC*H* (7.65, d, 4 H)
15	2094 m, 2068 s, 2060 s, 2033 m, 1998 w, 1975 w, 1928 vs, 1901 w, 1856 m	NC*H* (8.97, d, 2 H, ^3J(H–H) = 6.8); NC*H* (8.67, d, 2 H, ^3J(H–H) = 6.8); NCHC*H* (7.61, d, 2 H, ^3J(H–H) = 6.8); C_6H_4 (7.53, d, 2 H, ^3J(H–H) = 8.5); NCHC*H* (7.13, d, 2 H, ^3J(H–H) = 6.8); C_6H_4 (7.10, d, 2 H); C_5H_5 (5.42; s, 10 H)

s, singlet; d, doublet; m, multiplet.

[a] Measured in THF solution except for **6** (in toluene), **7** (in CH$_2$Cl$_2$) and **10** (in CH$_2$Cl$_2$). [b] Measured in acetone-d$_6$ except for **6**, which was measured in CDCl$_3$. [c] Reported in ppm relative to TMS (0 ppm). [d] The signals due to the AA′MM′ spin system in symmetrical Cp ligands are, due to their simple appearance, reported as triplets with coupling constants equal to half of the separation between the two outer lines.

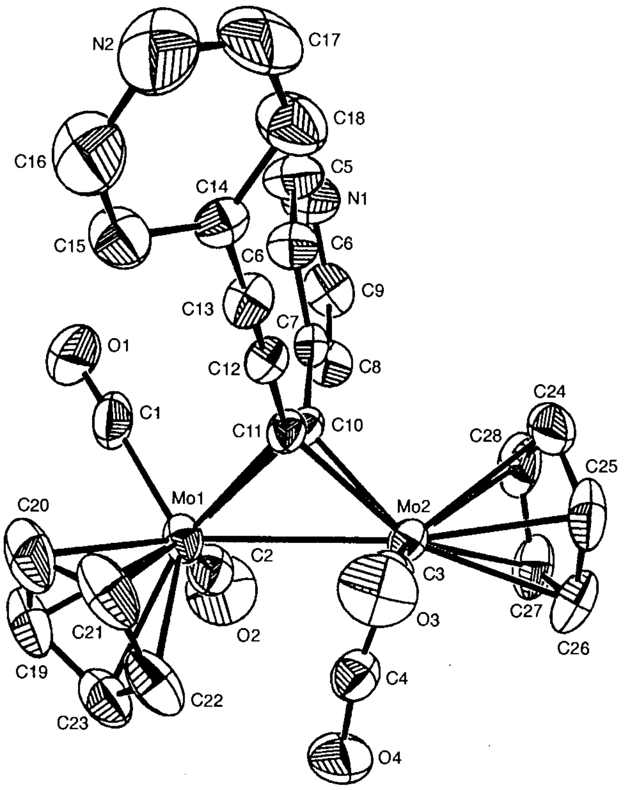


Fig. 1. ORTEP drawing of (μ_2-$\eta^{2:2}$-DPB)[$Cp_2Mo_2(CO)_4$] (**1**). Thermal ellipsoids are drawing in 50% probability boundaries.

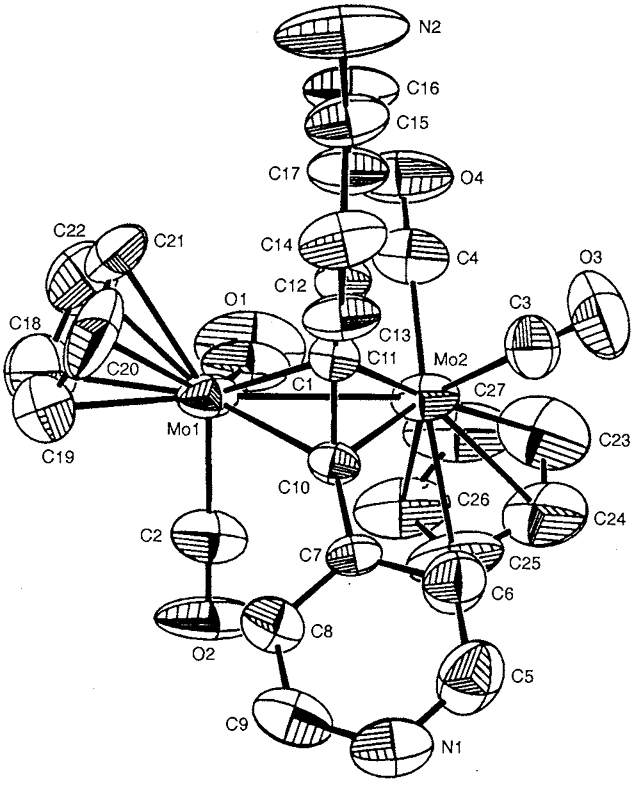


Fig. 2. ORTEP drawing of (μ_2-$\eta^{2:2}$-APPA)[$Cp_2Mo_2(CO)_4$] (**2**). Thermal ellipsoids are drawing in 50% probability boundaries.

similar to the alkyne complexes of $Cp_2Mo_2(CO)_4$. The lower energy stretching bands can be assigned to ν(CO) of the semibridging carbonyl ligand (vide infra) [16]. The carbonyl stretches for $Co_2(CO)_6$ complexed with an alkyne normally appear above 2000 cm^{-1} [17]. Consequently, we are able to distinguish the carbonyl stretches due to $Co_2(CO)_6$ from those due to $Cp_2Mo_2(CO)_4$ in complexes **7** and **10**. For complexes **11**–**13**, the three moderate/strong carbonyl stretches from $W(CO)_5$ moiety are partially overlapping with the three carbonyl stretches from $Cp_2Mo_2(CO)_4$ metal moiety. However, the two sets of carbonyl stretches are discernible by comparison of the spectra of **11**–**13** with those of **1** and **4**, and the presence of the semibridging carbonyl ligand in **11**–**13** is evident. In **14** and **15**, the carbonyl stretches for $Co_2(CO)_6$ appear at the highest frequency and can be distinguished from others. The presence of the semibridging carbonyl ligand in **15** is also evident. A weak ν(C≡C) stretching band is observed at ca. 2200 cm^{-1} in all complexes which contain unligated alkyne moiety.

An interesting feature in the ^{1}H-NMR spectra of these complexes is that ligation of the alkyne moiety has a great influence on the chemical shift of DPB, BPEB, and DFEHD. Complexation of DPB and BPEB with $Cp_2Mo_2(CO)_4$ results in an upfield shift of the nearby pyridyl and phenyl protons by 0.2–0.4 ppm (DPB: $H_\alpha(py) = 8.66$, $H_\beta(py) = 7.53$ ppm; **1**: $H_\alpha(py) =$ 8.49, 8.46, $H_\beta(py) = 7.33$, 7.32 ppm; BPEB: $H_\alpha(py) =$ 8.63, $H_\beta(py) = 7.47$, Ph = 7.66 ppm; **4**, $H_\alpha(py) = 8.38$, $H_\beta(py) = 7.01$, $(Ph)_a = 7.45$ ppm, $(Ph)_b = 7.09$ ppm). In contrast, the pyridyl protons nearby the uncomplexed alkyne have negligible change in chemical shift (**4**: $H'_\alpha(py) = 8.60$, $H'_b(py) = 7.42$ ppm). Complexation of both alkyne entities with $Cp_2Mo_2(CO)_4$ leads to a larger upfield shift of pyridyl and phenyl protons than **4** (**5**: $H_\alpha(py) = 8.31$, $H_\beta(py) = 6.97$, Ph = 6.88 ppm). In **9**, the olefin entity of DFEHD has a *cis* geometry on the basis of the coupling constant, ^3J(H–H), and the structural determination (vide infra). The effect of complexation of the alkyne entity in DFEHD with $Cp_2Mo_2(CO)_4$ or $Co_2(CO)_6$ on the chemical shift of olefinic protons (DFEHD: $\delta = 6.00$; **9**: $\delta = 7.69$, 6.14; **10**: $\delta = 7.93$, 7.41 ppm) is greater than that in DPB and BPEB, albeit in the opposite direction. The spectra of **2** and **3** seem to follow the same trend. However, at this juncture in time, we do not have a rationale for these differences on the basis of the known substituent effects [18]. Pyridyl protons shift to lower field upon ligation to $W(CO)_5$, as expected.

The molecular structures of (μ_2-$\eta^{2:2}$-DPB)[$Cp_2Mo_2(CO)_4$] (**1**), (μ_2-$\eta^{2:2}$-APPA)[$Cp_2Mo_2(CO)_4$] (**2**), (μ_2-$\eta^{2:2}$-DFEHD)[$Cp_2Mo_2(CO)_4$] (**9**), and (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)[$W(CO)_5$]$_2$[$Cp_2Mo_2(CO)_4$]$_2$ (**13**) were established by X-ray diffraction analysis. The ORTEP drawings of **1**, **2**, **9**, and **13** are shown in Figs. 1–4, respectively. A prominent feature of these structures is a significant elongation of the C≡C bond occurs upon coordination of the alkyne. This is accompanied by the deviation of the C–C≡C bond angle from the ideal angle of 180° (Table 8). The other prominent feature in these complexes is that one of the CO ligands (**1**: C_4O_4; **2**: C_1O_1; **9**: C_4O_4; **13**: C_2O_2) in $Cp_2Mo_2(CO)_4$ is coordinated in a semibridged fashion [19]. This can be easily recognized by the characteristic bond angle M–C–O (**1**: semibridging, 169.6(5), others 178(2)°; **2**: semibridging, 168(1),

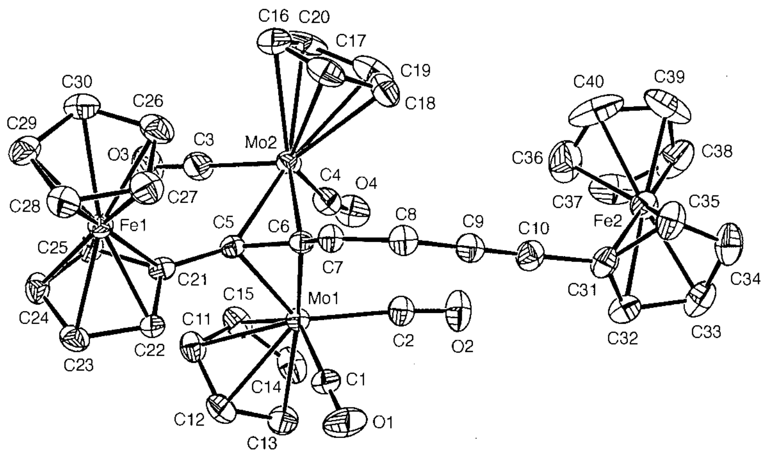


Fig. 3. ORTEP drawing of (μ_2-$\eta^{2:2}$-DFEHD)[$Cp_2Mo_2(CO)_4$] (**9**). Thermal ellipsoids are drawing in 50% probability boundaries.

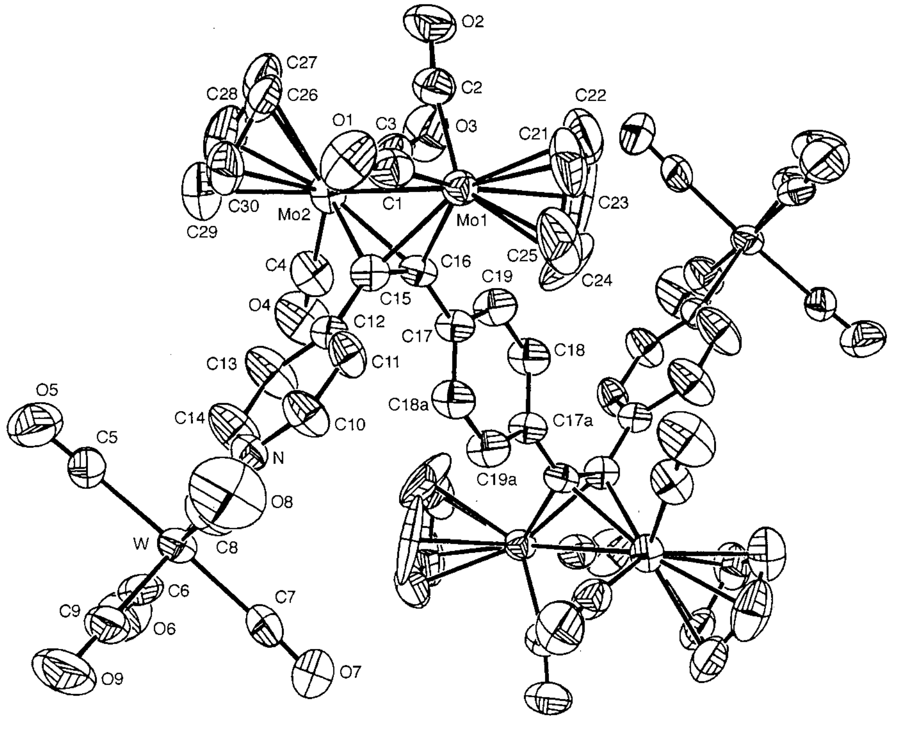


Fig. 4. ORTEP drawing of (μ_6-$\eta^{1:1:2:2:2:2}$-BPEB)[$W(CO)_5]_2[Cp_2Mo_2(CO)_4$] (**13**). Thermal ellipsoids are drawing in 50% probability boundaries.

Table 8
Bond distances (C≡C) and angles (C–C≡C) for alkynes in **1**, **2**, **9** and **13**

Compound	Distances (ligated) (Å)	Distances (unligated) (Å)	Angles (ligated) (°)	Angles (unligated) (°)
1	1.379(6)	1.201(7)	133.7(4), 138.8(4)	175.2(5), 177.5(5)
2	1.37(1)		134.4(6), 135.4(7)	
9	1.357(6)	1.192(8)	133.0(4), 129.9(4)	175.5(5), 170.2(5)
13	1.37(1)		134.6(8), 135.6(8)	

others 177(1)°; **9**: semibridging, 167.6(4), others 176(3)°; **13**: semibridging, 168.5(9), others 178(2)°) where M is the metal to which it is ligated, and the M′–C distance (**1**: 2.894(5); **2**: 2.86(1); **9**: 2.781(5); **13**: 2.86(1) Å) where M′ is the metal to which it is semi-bridged. These values are within the range found in similar complexes ([16]a, [20]). Other relevant crystal data appear to be normal. The Mo–Mo distances, which range from 2.964 (2) to 2.9735(8) Å, are comparable to those of analogous complexes [20]. The tungsten atom in **13** resides in an approximately octahedral environment, and the two olefinic protons in **9** are in a mutually *cis* disposition.

To summarize, we have demonstrated that conjugated pyridyl ligands incorporating alkyne entities can be used to assemble different metal moieties. In complex **13**, up to six metal fragments are accommodated. Our future research aims at designing the ligands with suitable shape to accommodate metal fragments selectively, and designing an organometallic monomer for the construction of polymers.

4. Supplementary material available

Complete crystal data, all bond distances and angles, positional parameters, anisotropic thermal parameters, and isotropic thermal parameters, are available, upon request, from the authors.

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