DALTON
FULL PAPER

Heterometallic metal carbonyl compounds derived from (η^6-arene)-tricarbonylchromium bearing propargyl units

Osvaldo L. Casagrande, Jr.,*[a] **Elton L. S. Gomes,**[a] **Jairton Dupont,**[a] **Robert Burrow**[b] **and Alan J. Lough**[c]

[a] *Laboratório de Catálise Molecular, Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500, Porto Alegre, RS, 91509-900, Brazil. E-mail: osvaldo@iq.ufrgs.br*
[b] *Departamento de Química, UFSM, Santa Maria, RS, 97105-900, Brazil*
[c] *Department of Chemistry, University of Toronto, M5S 3H6, Canada*

Received 30th November 2000, Accepted 26th March 2001
First published as an Advance Article on the web 1st May 2001

The compounds $[Co_2(CO)_8]$ and $[Mo_2Cp_2(CO)_4]$ readily react with (η^6-arene)tricarbonylchromium complexes containing propargyl (prop-2-ynyl) **1a**–**c** units to give new heterotrimetallic complexes $[Cr\{(\eta^6\text{-}C_6H_5C{\equiv}CC(H)(R)Y)Co_2(CO)_6\}(CO)_3]$ (**2a**, R = Me and Y = NMe_2; **2b**, R = H and Y = NMe_2; **2c**, R = H and Y = OH) and $[Cr\{(\eta^6\text{-}C_6H_5C{\equiv}CCH_2NMe_2)Mo_2(Cp)_2(CO)_4\}(CO)_3]$ **3** in moderate to good yield (51–80%). Compounds **2a** and **3** have been characterised by X-ray crystallography. Structural data reveal that the $Cr(CO)_3$ unit adopts a nearly staggered conformation in **2a** and eclipsed in **3**.

Introduction

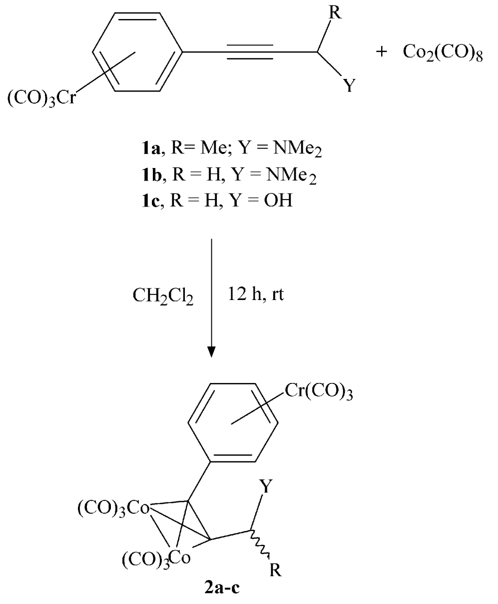
The (η^6-arene)tricarbonylchromium complexes have been studied extensively in recent years due to their prominent role in organic and organometallic chemistry.[1] A particular area of interest is the synthesis of heterometallic complexes derived from (η^6-arene)tricarbonylchromium fragments due to their unique structural and electronic properties.[2] These mixed metal compounds may be expected to exhibit interesting synergistic effects and should display unprecedented reactivity towards organic and organometallic reactions. Recently, the Pfeffer group has demonstrated that the $Cr(CO)_3$ moiety establishes a stereocontrol upon addition of organolithium to cyclomanganated (η^6-arene)tricarbonylchromium compounds.[3]

In the course of our studies concerning the reactivity of propargyl (prop-2-ynyl) amines and thioethers using palladium, platinum, and ruthenium compounds,[4] we have recently demonstrated a facile method to prepare heterobimetallic cyclopalladated compounds *via* chloropalladation reaction of (η^6-arene)tricarbonylchromium complexes bearing a propargyl amine moiety.[5] In order to extend our investigations toward the synthesis of novel heterometallic complexes, we decided to undertake a study of the reactivity of (η^6-arene)tricarbonylchromium complexes containing propargyl amine with binuclear compounds such as $[Co_2(CO)_8]$ and $[Mo_2Cp_2(CO)_6]$ which are of known ability to coordinate to alkyne ligands.[6] Herein, we report the synthesis and structural characterisation of heterotrimetallic complexes derived from (η^6-arene)tricarbonylchromium incorporating propargyl units.

Results and discussion

Synthesis and characterisation of heterotrimetallic compounds derived from (η^6-arene)tricarbonylchromium bearing propargyl units

The (η^6-arene)tricarbonylchromium compounds **1a**–**c** reacted with an equimolar amount of $[Co_2(CO)_8]$ in CH_2Cl_2 at 25 °C to give, after work-up, the heterotrimetallic derivatives $[Cr\{(\eta^6\text{-}C_6H_5C{\equiv}CC(H)(R)Y)Co_2(CO)_6\}(CO)_3]$ (**2a**, R = Me and Y = NMe_2; **2b**, R = H and Y = NMe_2; **2c**, R = H and Y = OH) as dark red solids in 62–80% yields (eqn. 1). The structures of **2a**–**c** were assigned based on elemental analysis, IR, multinuclear (^1H, ^{13}C) NMR data and by the X-ray structural determination carried out for **2a**.



(1)

The characterisation of **2a**–**c** was first provided by the IR ν(CO) spectra. In the solid state, complexes **2a**–**c** show eight bands for the carbonyl stretching frequencies. The five at higher frequencies were attributed to the carbonyls bonded to cobalt atoms.[7] In the case of the (η^6-arene)$Cr(CO)_3$ unit, three bands are expected: the A_1 band at higher frequency and the E band, split due to the deviation from idealised C_{3v} symmetry.[8] In addition, the spectra showed the vibration modes of the C≡C unit at 1560–1568 cm^{-1}, indicating a weakening of the C≡C bond upon coordination of the dicobalt compound.[9] From IR data we can assume that the $Co_2(CO)_6$ moiety coordinated to the propargyl unit acts as an electron-withdrawing substituent.

Comparison of the carbonyl stretching E absorption wavenumbers of **1a**–**c**[5,10] and those of the corresponding heterotrimetallic compounds **2a**–**c** suggests a slight electron density

1634 *J. Chem. Soc.*, *Dalton Trans.*, 2001, 1634–1638 DOI: 10.1039/b009591p

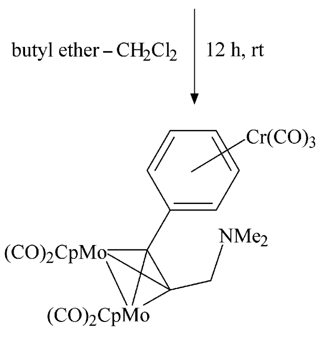
This journal is © The Royal Society of Chemistry 2001

transfer from the chromium fragment to the dicobalt–alkyne unit. This is indicated by the positive values of the parameter $\Delta\nu_M$ calculated for the E-mode carbonyl absorption bands ($\Delta\nu_M$ in the range of 2 to 5 cm^{-1}).[11]

The ^{1}H NMR spectrum of **2a** exhibits characteristic peaks related to methyl groups, and the methine proton is shifted upfield. The most noteworthy feature is related to the protons of the arene ligand which appear as a set of five resonances in a 1 : 1 : 1 : 1 : 1 ratio indicating a restricted arene rotation. This result agrees with that observed by ^{13}C-{^{1}H} NMR in which the arene carbons appear as a set of 6 peaks in the region between δ 100 and 86. As expected, the ^{1}H NMR spectra of **2b,c** showed the usual set of three resonances in the range of δ 5.93–5.28 attributable to aromatic protons. The spectra of **2a–c** showed a low frequency shift of the aromatic proton with respect to those of the corresponding arenetricarbonylchromium complexes **1a–c** as a result of the electron-withdrawing characteristic of the $Co_2(CO)_6$ fragment. The ^{13}C-{^{1}H} NMR spectra of **2a–c** show a sharp peak at δ 232.6 attributable to the carbonyl groups bound to chromium and a typical broad resonance around δ 199.0 corresponding to the two equivalent sets of carbonyl ligands coordinated to the cobalt centres.

The heterotrimetallic complex [Cr{(η^6-$C_6H_5C{\equiv}CCH_2NMe_2$)-$Mo_2(Cp)_2(CO)_4$}$(CO)_3$] **3** was obtained in 51% yield from the reaction of **1b** with [$Mo_2Cp_2(CO)_4$] in di-*n*-butyl ether–CH_2Cl_2 (eqn. 2). The compound **3** has been characterised by elemental analysis, IR, multinuclear (^{1}H, ^{13}C) NMR data, and by an X-ray structural determination.

1b + $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (2)



3

The IR spectrum of **3** shows six ν(CO) bands in the range 1990–1868 cm^{-1} corresponding to the terminal CO groups coordinated to molybdenum and chromium atoms, and a lower-wavenumber band at 1852 cm^{-1} assigned to a semi-bridging carbonyl group. In this case the value of the parameter $\Delta\nu_M$ cannot be calculated due to difficulty in assigning precisely the carbonyl stretching E band related to the $Cr(CO)_3$ fragment.

The ^{1}H NMR spectrum of **3** shows two singlets at δ 3.81 and 2.37 attributable to the methylene and methyl protons respectively, three sets of resonances in the region δ 5.77–5.19 corresponding to arene protons, and a singlet centred at δ 5.29 assigned to cyclopentadienyl protons. The low frequency shift of the aromatic proton with respect to those of the corresponding arenetricarbonylchromium complex **1b** also indicates, as found for **2a–c**, a flow of electron density from the arene ligand to the "$Mo_2Cp_2(CO)_4$" fragment.

The ^{13}C-{^{1}H} NMR spectrum displays one singlet at δ 234.1 attributable to the carbonyl groups coordinated to chromium and two weak singlets at δ 229.1 and 229.9 corresponding to carbonyl groups bonded to molybdenum indicating a fluxional process of these ligands. It is interesting that the CO ligands coordinated to the Cr atom in **3** appear at a slightly higher frequency (δ 234.1) than those in complex **2a** (δ 232.6), suggesting that the "$Mo_2Cp_2(CO)_4$" fragment seems to withdraw less electron density from the (η^6-arene)$Cr(CO)_3$ unit.[12]

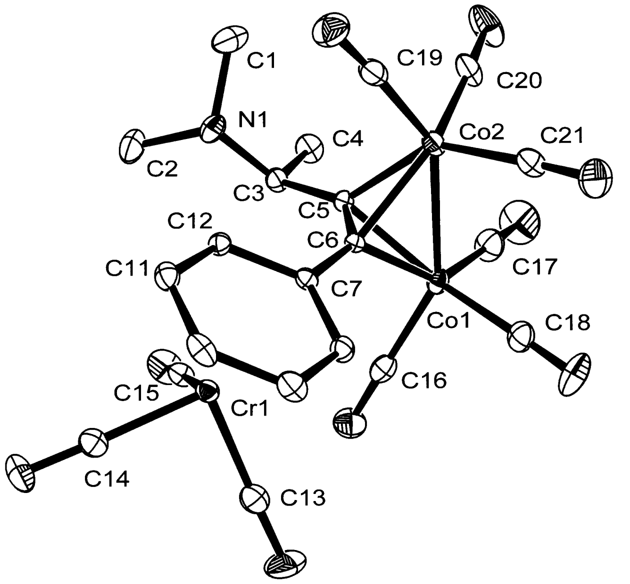


Fig. 1 Molecular structure of complex **2a** (H atoms omitted) with thermal ellipsoids at the 30% probability level.

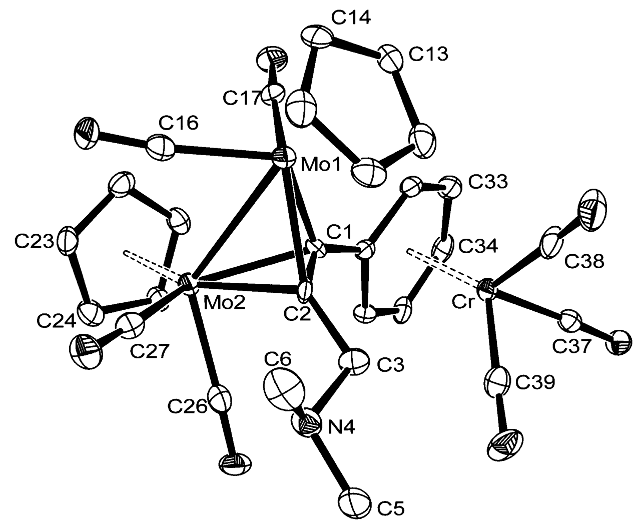


Fig. 2 Molecular structure of complex **3**. Details as in Fig. 1.

Molecular structures of 2a and 3

Selected bond distances and angles for **2a** and **3** are listed in Tables 1 and 2; Figs. 1–3 show the molecular structures. From a hexane solution of **2a** (−20 °C) crystals suitable for an X-ray crystal diffraction study have been obtained. The complex crystallises in the monoclinic space group $P2_1/c$ as two structural sub-units $Cr(CO)_3(\eta^6\text{-}C_6H_5)$ and $Co_2(CO)_6(\eta^2\text{-}\mu\text{-}C{\equiv}CCH(Me)\text{-}NMe_2)$ as indicated by spectroscopic data. The bond angles OC–Cr–CO (88.60° average) and Cr–C distances (1.843 Å average) are comparable to those of (η^6-arene)tricarbonylchromium complexes [$Cr(\eta^6\text{-}C_6H_5C{\equiv}CCH_2Y)(CO)_3$] (Y = NMe_2, 88.4°, 1.841 Å; Y = N(Me)(CH_2Ph), 88.8°, 1.840 Å). The chromium–centroid distance (1.710 Å) is in the expected range.[13] As a general trend, the cluster core "$Co_2(C{\equiv}C)$" of **2a** shows the common tetrahedron geometry where the alkyne unit is almost perpendicular to the Co–Co bond. The coordination around the cobalt centre is distorted octahedral and two tricarbonylcobalt moieties are eclipsed. The Co(1)–Co(2) bond distance is 2.4701(6) Å, which may be considered typical compared to those of analogous cobalt complexes.[14] Both cobalt centres are further connected to C(5) [Co(1,2)–C(5) 1.991(3), 1.961(3) Å],

Table 1 Selected bond lengths (Å) and angles (°) for compound **2a**

Cr(1)–C(7)	2.237(3)	Cr(1)–C(8)	2.213(3)
Cr(1)–C(9)	2.212(3)	Cr(1)–C(10)	2.207(3)
Cr(1)–C(11)	2.213(3)	Cr(1)–C(12)	2.212(3)
Cr(1)–C(13)	1.841(4)	Cr–C(14)	1.852(3)
Cr(1)–C(15)	1.837(3)	C(5)–C(6)	1.345(4)
Co(1)–Co(2)	2.4701(6)	Co(1)–C(16)	1.797(4)
Co(1)–C(17)	1.810(4)	Co(1)–C(18)	1.810(4)
Co(2)–C(19)	1.808(4)	Co(2)–C(20)	1.828(4)
Co(2)–C(21)	1.821(3)		
C(13)–Cr(1)–C(14)	90.99(14)	C(13)–Cr(1)–C(15)	87.29(14)
C(14)–Cr(1)–C(15)	87.51(13)	C(16)–Co(1)–C(17)	102.1(2)
C(16)–Co(1)–C(18)	98.60(14)	C(17)–Co(1)–C(18)	103.8(2)
C(19)–Co(2)–C(20)	102.3(2)	C(19)–Co(2)–C(21)	97.7(2)
C(20)–Co(2)–C(21)	105.03	C(5)–C(6)–C(7)	142.4(2)
C(3)–C(5)–Co(1)	131.8(2)	C(7)–C(6)–Co(1)	137.3(2)
C(3)–C(5)–Co(2)	139.4(2)	C(7)–C(6)–Co(2)	129.6(2)
C(5)–C(3)–N(1)	108.9(2)	C(3)–C(5)–C(6)	140.1(3)

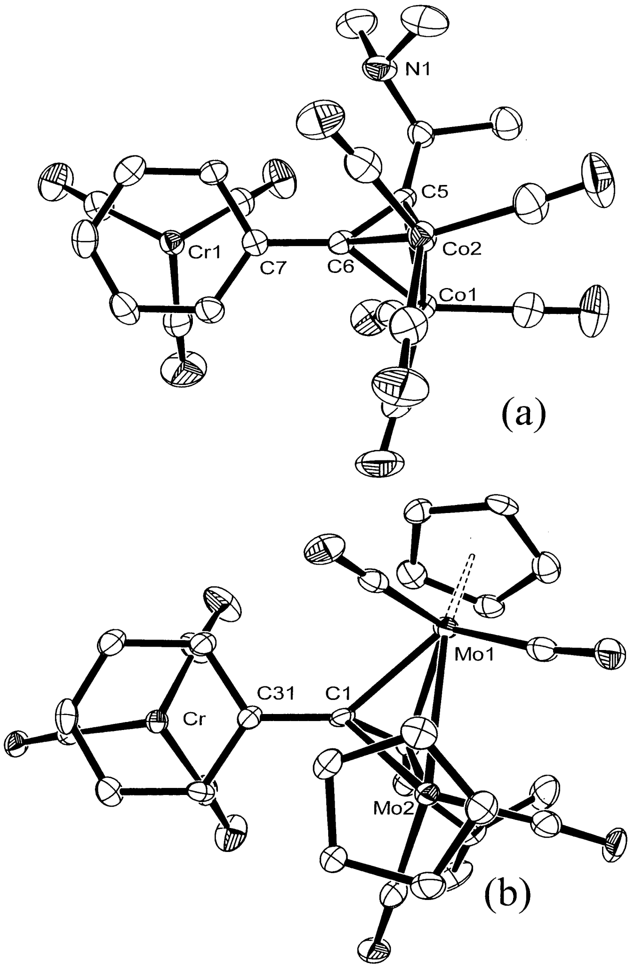


Fig. 3 Top view of the molecular structures of complexes **2a** (a) and **3** (b).

Table 2 Selected bond lengths (Å) and angles (°) for **3**

Cr(1)–C(31)	2.303(7)	Cr(1)–C(32)	2.241(7)
Cr(1)–C(33)	2.229(8)	Cr(1)–C(34)	2.211(8)
Cr(1)–C(35)	2.228(8)	Cr(1)–C(36)	2.214(7)
Cr(1)–C(37)	1.835(8)	Cr(1)–C(38)	1.827(9)
Cr(1)–C(39)	1.840(9)	Mo(1)–Mo(2)	2.9733(9)
Mo(1)–C(16)	1.959(8)	Mo(1)–C(17)	1.969(8)
Mo(2)···C(16)	2.837(8)	Mo(2)–C(27)	1.999(9)
Mo(2)–C(26)	1.996(9)	Mo(1)–C(2)	2.177(7)
Mo(1)–C(1)	2.187(7)	Mo(2)–C(2)	2.211(7)
Mo(2)–C(1)	2.195(7)	C(1)–C(31)	1.449(10)
C(1)–C(2)	1.381(10)	Mo(2)–Ct(02)	1.991(3)
Mo(1)–Ct(01)	2.017(3)		
C(37)–Cr–C(38)	91.2(3)	C(37)–Cr–C(39)	86.3(3)
C(38)–Cr–C(39)	88.2(4)	C(16)–Mo(1)–C(17)	89.5(3)
C(16)–Mo(1)–Ct(1)	115.9(3)	C(17)–Mo(1)–Ct(1)	115.74
C(1)–Mo(1)–C(2)	36.9(3)	Mo(2)–Mo(1)–C(1)	47.39(18)
Mo(2)–Mo(1)–C(2)	47.83(18)	Ct(1)–Mo(1)–Mo(2)	157.45(10)
(C26)–Mo(2)–C(27)	82.5(3)	C(26)–Mo(2)–Ct(2)	110.67
C(27)–Mo(2)–Ct(2)	118.1(3)	C(1)–Mo(2)–C(2)	36.5(3)
Mo(1)–Mo(2)–C(1)	47.15(19)	Mo(1)–Mo(2)–C(2)	46.87(19)
Ct(2)–Mo(2)–Mo(1)	120.69(11)	Mo(1)–C(16)–O(16)	171.02(10)

C(6) [Co(1,2)–C(6) 1.950(3), 1.969(3) Å]. Upon coordination, the C≡C bond is elongated by *ca.* 0.16 Å when compared with that in **1b** (1.187(3)),[5] indicating an increase of sp^2 character of the two acetylene carbons. Furthermore, the substituted alkyne ligand folds in upon coordination to the cluster core; for instance, the bond angles C(3)–C(5)–C(6) and C(5)–C(6)–C(7) change from 180° in the free alkyne to 140.1(3) and 142.4(2)° respectively. As a result, the NMe$_2$ and arene groups of the coordinated alkyne come closer in a well defined rigid geometry (N(1)···C(12) 3.449 Å).

A single crystal of **3** was grown from a hexane solution at −20 °C. The complex crystallises in the orthorhombic system, and the lattice fits the $P2_12_12_1$ symmetry group. The compound consists of two organometallic fragments $Cr(CO)_3(\eta^6\text{-}C_6H_5)$ and $Mo_2Cp_2(CO)_4(\eta^2\text{-}\mu\text{-}C{\equiv}CCH_2NMe_2)$. The distance between the chromium atom and the mean plane of the η^6-arene (1.7388(10) Å) is slightly longer than in (η^6-arene)tricarbonylchromium compounds incorporating propargyl amine units (average 1.70 Å).[5] Furthermore, it can be noticed that the aromatic carbons remain in the mean plane of the arene. The CrC–O bond distances (average 1.169 Å) are slightly longer than those observed in **1b** (1.144 Å average)[5] as a result of the electron-withdrawing capacity of the "$Mo_2Cp_2(CO)_4$" as already indicated by the ^{1}H and ^{13}C NMR results. As a general trend, the cluster core $Mo_2(C{\equiv}C)$ shows the common tetrahedron geometry where the alkyne unit is almost perpendicular to the Mo–Mo bond. The coordination of the alkyne ligand to the Mo$_2$ unit is not symmetrical. Owing to the asymmetric nature of the alkyne it is slightly closer to Mo(1) [Mo(1)–C(1) 2.187(7), Mo(1)–C(2) 2.177(7) Å] than to Mo(2) [Mo(2)–C(1) 2.195(7), Mo(2)–C(2) 2.211(7) Å] resulting in a build up of electron density on Mo(1) released by CO(16), which interacts with Mo(2) in a semi-bridging fashion (Mo(2)–C(16) 2.837(8) Å). The smallish Mo(2)–Mo(1)–C(16) angle, slightly bent Mo(1)–C(16)–O(16) angle, away from Mo(2), and close non-bonding Mo(2)···C(16) distance are characteristic of a weakly interacting type II semi-bridging carbonyl.[15] The angle between the Mo(1)–Mo(2) and C(1)–C(2) vectors is 90.8°. The cyclopentadienyl rings, which have an average C–C bond distance of 1.415 Å, are in the *trans* position with respect to each other (pseudo torsion angle Ct(1)–Mo(1)–Mo(2)–Ct(2) 169.3(3)° (Ct = Cp ring centroid)). The Mo(2)–Ct(2) distance is slightly shorter than the Mo(1)–Ct(1) distance. This could be due to a donation of electron density from Mo(2) to the semi-bridging carbonyl of Mo(1). Neither ring shows slippage and both distances are in agreement with values observed for similar compounds.[16]

In the alkyne–dimolybdenum cluster the RC≡CR moiety is no longer linear (C(31)–C(1)–C(2) 139.5(7), and C(3)–C(2)–C(1) 130.7(6)°) and the substituents are bent back by *ca.* 45°. In addition, the presence of substituents leads to a twisting of the C(1)–C(31) bond relative to the C(2)–C(3) vector to give a dihedral angle of 5.2(1.5)°. As expected, the coordinated triple bond C(1)–C(2) (1.381(10) Å) is significantly longer than the uncoordinated triple bond (1.187(3) Å)[5] indicating the reduction of the C≡C bond to a C=C bond upon coordination to the two atoms due to a release of steric strain within the ring upon formally changing the hybridisation of the two ring C atoms from sp^3 to sp^2.

Comparing the molecular structures of **2a** and **3** it was observed that the C≡C bond distance (1.345(4) Å) in **2a** is shorter than that found in **3** (1.381(10) Å). Furthermore, the bond distance of C–O in the C_2Co_2 core (**2a**) is shorter than in the C_2Mo_2 core (**3**), indicating that the C_2Mo_2 core possesses a stronger ability to delocalise electron density. The orientation of the carbonyl groups coordinated to the chromium atom with respect to the arene ligand is dependent on the bimetallic fragment bonded to the C≡C bond as observed in Fig. 3. For instance, the $Cr(CO)_3$ unit adopts a nearly staggered conformation in **2a** (average torsion angle 30.2°) and eclipsed in **3** (average torsion angle 4.4°). Taking into account that both bimetallic fragments "$Co_2(CO)_6$" and "$Mo_2Cp_2(CO)_4$" withdraw some electron density from the arene unit, the different conformations adopted for $Cr(CO)_3$ in **2a** and **3** can be rationalised in terms of steric and/or packing effects that override the electronic effects.[13]

Conclusion

We have shown that the novel heterotrimetallic complexes are readily prepared by the reaction of (η^6-arene)tricarbonylchromium bearing propargyl units with binuclear species such as $[Co_2(CO)_8]$ and $[Mo_2Cp_2(CO)_4]$. Structural data revealed that the $Cr(CO)_3$ unit adopts a nearly staggered conformation in **2a** and eclipsed in **3**. These results strongly suggest that the steric and/or packing effects are preponderant on the electronic features.

Experimental

All manipulations were performed using vacuum-line or Schlenk techniques under a purified argon atmosphere. Solvents were stored under argon or vacuum prior to use. Hexane and di-*n*-butyl ether were distilled from Na–benzophenone and CH_2Cl_2 was distilled from P_2O_5. $[Co_2(CO)_8]$ (Strem) and $[Mo_2Cp_2(CO)_6]$ (Aldrich) were purchased and used as received. Complexes $[Cr\{C_6H_5C{\equiv}CCH(R)Y\}(CO)_3]$ (**1a**, R = Me and Y = NMe_2; **1b**, R = H and Y = NMe_2; **1c**, R = H and Y = OH) were prepared following described procedures.[5,10] NMR spectra were recorded on a Varian-300 spectrometer in Teflon-valved NMR tubes at ambient probe temperature. ^1H and ^{13}C-$\{^1H\}$ chemical shifts are reported *versus* Me_4Si and were determined by reference to the residual ^1H and ^{13}C-$\{^1H\}$ solvent peaks. Coupling constants are reported in hertz. Elemental analyses were performed by the Central Analítica IQ/UFRGS (Porto Alegre, Brazil).

Preparation

Complex 2a. A solution of **1a** (1.02 g, 3.30 mmol) in CH_2Cl_2 (50 mL) was cannula-transferred at 0 °C to $[Co_2(CO)_8]$ (1.13 g, 3.30 mmol), allowed to warm to 25 °C and stirred for 12 h. The solvent was removed under vacuum, the crude oily residue redissolved in CH_2Cl_2 and the solution mixed with silica gel. The solvent was removed under vacuum and the resulting coated silica gel loaded on the top of a silica gel column packed in dry hexane. The mixture was chromatographed using hexane–diethyl ether (85 : 15) affording **2a** as a dark red solid (1.21 g, 62%). ^1H NMR ($CDCl_3$): δ 6.35 (d, 1H, ^3J(HH) = 6.6, H_o Ph), 5.83 (d, 1H, ^3J(HH) = 6.6, H_o Ph), 5.54 (t, 1H, ^3J(HH) = 6.6, H_p Ph), 5.29 (t, 1H, ^3J(HH) = 6.6, H_m Ph), 5.22 (t, 1H, ^3J(HH) = 6.6, H_m Ph), 4.17 (q, 1H, ^3J(HH) = 6.6, C*H*Me), 2.39 (s, 6H, N*Me*$_2$), 1.39 (d, 3H, ^3J(HH) = 6.6, CH*Me*). ^{13}C-$\{^1H\}$ ($CDCl_3$): δ 232.6 (CO), 199.1 (s, br, CO, Co), 106.8 (*C*=C), (C=*C*) not observed, 98.0, 97.0, 94.6, 89.6, 89.0 (aromatic, CH, Ph), 60.5 (*CH*Me), 41.6 (N*Me*$_2$), 13.2 (CH*Me*). IR (KBr, cm^{-1}): ν(CO) 2091s, 2055s, 2038s, 2021s, 2000m, 1961s, 1906s, 1874m. Found: C, 42.26; H, 2.48; N, 2.32. $C_{21}H_{15}Co_2CrNO_9$ requires: C, 42.35; H, 2.52; N, 2.35%.

Table 3 Summary of crystallographic data for **2a** and **3**

	2a	**3**
Formula	$C_{21}H_{15}Co_2CrNO_9$	$C_{28}H_{23}CrMo_2NO_7$
M	595.20	729.35
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a/Å	8.2527(1)	8.8575(6)
b/Å	16.0306(1)	17.2298(10)
c/Å	18.2571(3)	17.6676(11)
β/°	99.807(1)	
V/Å^3	2380.04(5)	2696.3(3)
Z	4	4
T/K	173(2)	150(2)
μ/mm^{-1}	1.876	1.359
Unique reflections collected	11706	35384
Observed data [$I > 2\sigma(I)$]	4181 (R_{int} = 0.0285)	4953 (R_{int} = 0.057)
Data/parameters	4181/310	4953/355
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0338, 0.0640	0.0481, 0.1113

Refinement method: full-matrix least squares on F^2. Graphite-monochromatised Mo-Kα radiation, λ = 0.71073 Å.

Complex 2b. This compound was prepared according to the method described for **2a** using $[Co_2(CO)_8]$ (0.84 g, 2.46 mmol) and **1b** (0.73 g, 2.46 mmol), as a dark red solid (1.14 g, 80%). ^1H NMR ($CDCl_3$): δ 5.93 (d, 2H, ^3J(HH) = 6.3, H_o Ph), 5.50 (t, 1H, ^3J(HH) = 6.3, H_p Ph), 5.28 (d, 2H, ^3J(HH) = 5.6, H_m Ph), 3.86 (s, 2H, C*H*$_2$NMe$_2$), 2.48 (s, 6H, CH$_2$N*Me*$_2$). ^{13}C-$\{^1H\}$ ($CDCl_3$): δ 232.6 (CO, Cr), 199.0 (s, br, CO, Co), 106.7 (*C*=C), (C=*C*) not observed, 96.6, 94.0, 92.7, 89.7 (aromatic, CH, Ph), 61.6 (*CH*$_2$Me), 46.6 (N*Me*$_2$). IR (KBr, cm^{-1}): ν(CO) 2089s, 2052s, 2038s, 2021s, 2000m, 1961s, 1906s, 1873s. Found: C, 41.21; H, 2.21; N, 2.39. $C_{20}H_{13}Co_2CrNO_9$ requires: C, 41.33; H, 2.26; N, 2.41%.

Complex 2c. This compound was prepared according to the method described for **2a** using $[Co_2(CO)_8]$ (0.34 g, 1.00 mmol) and **1c** (0.27 g, 1.00 mmol), as a dark red solid (0.40 g, 72%). ^1H NMR ($CDCl_3$): δ 5.80 (d, 2H, ^3J(HH) = 5.8, H_o Ph), 5.50 (t, 1H, ^3J(HH) = 6.3, H_p Ph), 5.28 (d, 2H, ^3J(HH) = 5.8, H_m Ph), 5.12 (d, 2H, C*H*$_2$OH), 2.27 (s, br, 1H, OH). ^{13}C-$\{^1H\}$ ($CDCl_3$): δ 232.6 (CO, Cr), 199.2 (s, br, CO, Co), 106.1 (*C*=C), (C=*C*) not observed, 96.6, 93.7, 91.8, 90.1 (aromatic, CH, Ph), 61.6 (*CH*$_2$OH). IR (KBr, cm^{-1}): ν(CO) 2097m, 2057s, 2045s, 2029s, 2015s, 1956s, 1901s, 1877s. Found: C, 38.98; H, 1.44. $C_{18}H_8Co_2CrO_{10}$ requires: C, 39.02; H, 1.46%.

Complex 3. To a solution of $[Mo_2Cp_2(CO)_6]$ (0.49 g, 1.00 mmol) in di-*n*-butyl ether (50 ml) previously refluxed for 7 h was added dropwise over a period of 10 min at 0 °C to a solution of **1b** (0.30 g, 1.00 mmol) in CH_2Cl_2 (30 ml). The mixture was allowed to warm to 25 °C and stirred for 12 h. The solvent was removed under vacuum and the residue subjected to chromatography on silica gel. Elution with diethyl ether–hexane (8 : 1) gave the desired compound as a dark red solid. Recrystallisation from hexane yielded dark red crystals of **3** (0.37 g, 51%). ^1H NMR ($CDCl_3$): δ 5.77 (d, 2H, ^3J(HH) = 6.0, H_o Ph), 5.45 (t, 1H, ^3J(HH) = 6.0, H_p Ph), 5.29 (s, 10H, Cp), 5.19 (t, 2H, ^3J(HH) = 5.5, H_m Ph), 3.81 (s, 2H, C*H*$_2$NMe$_2$), 2.37 (s, 6H, CH$_2$N*Me*$_2$). ^{13}C-$\{^1H\}$ ($CDCl_3$): δ 234.1 (CO, Cr), 229.9 and 229.1 (CO, Mo), 119.3 (*C*=C), (C=*C*) not observed, 97.5, 94.1, 92.0, 89.6 (aromatic, CH, Ph), 65.1 (*CH*$_2$Me), 46.7 (N*Me*$_2$). IR (KBr, cm^{-1}): ν(CO) 1990s, 1960s, 1930s, 1915s, 1877s, 1868s, 1852m. Found: C, 46.03; H, 3.11; N, 1.89. $C_{28}H_{23}CrMo_2NO_7$ requires: C, 46.11; H, 3.18; N, 1.92%.

X-Ray crystallography

The structure of **2a** was determined by V. G. Young, Jr. (University of Minnesota), that of **3** by Robert Burrow

(Universidade de Santa Maria, RS) using data collected by Drs David H. Farrer and Alan J. Lough (University of Toronto). Crystal data, data collection details, and solution and refinement procedures are provided in Table 3.

Crystals were grown from a saturated hexane solution at −20 °C. All non-H atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.[17]

CCDC reference numbers 154135 and 154136.

See http://www.rsc.org/suppdata/dt/b0/b009591p/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the CNPq and FAPERGS for financial support. E. L. S. G. is a Ph.D. student from CPGQUI-UNESP-Araraquara-SP (Brazil) and acknowledges CNPq (Brazil) for a fellowship. The X-ray structural analysis of **2a** was performed by Dr V. G. Young, Jr. (University of Minnesota), that of **3** by Drs David H. Farrar and Alan J. Lough (University of Toronto). The Nonius Kappa CCD at the University of Toronto was purchased with funds from NSERC (Canada).

References

1 L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, CA, 1994, ch. 10; J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, vol. 20, p. 921; T. J. J. Müller and A. Netz, *Organometallics*, 2000, **19**, 1452; T. J. J. Müller, M. Ansorge and K. Polborn, *Organometallics*, 1999, **18**, 3690; C. A. Merlic and J. C. Walsh, *Tetrahedron Lett.*, 1998, **39**, 2083.

2 J. P. Djukic, A. Maisse and M. Pfeffer, *Organometallics*, 1997, **16**, 657; A. D. Hunter, D. Ristic-Petrovic and J. L. McLernon, *Organometallics*, 1992, **11**, 864; J. Li, A. D. Hunter, R. McDonald, B. D. Santarsiero, S. G. Bott and J. L. Atwood, *Organometallics*, 1992, **11**, 3050; J. P. Djukic, A. Maisse and M. Pfeffer, *J. Organomet. Chem.*, 1998, **567**, 65; T. Kuhnen, M. Stradiotto, R. Ruffollo, D. Ulbrich, M. J. McGlinchey and M. A. Brook, *Organometallics*, 1997, **16**, 5048; G. R. Clark, M. R. Metzler, G. Whitaker and P. D. Woodgate, *J. Organomet. Chem.*, 1996, **513**, 109.

3 J. P. Djukic, C. Michon, A. Maisse, R. Allagapen, M. Pfeffer, K. H. Dotz, A. De Cian and J. Fischer, *Chem. Eur. J.*, 2000, **6**, 1064; J. P. Djukic, A. Maisse, M. Pfeffer, K. H. Dötz and M. Nieger, *Organometallics*, 1999, **18**, 2786; J. P. Djukic, A. Maisse, M. Pfeffer, K. H. Dötz and M. Nieger, *Eur. J. Inorg. Chem.*, 1998, 1781.

4 J. Dupont, O. L. Casagrande, Jr., A. C. Aiub, J. Beck, M. Hörner and A. Bortoluzzi, *Polyhedron*, 1994, **13**, 2583; J. Dupont, N. R. Basso and M. R. Meneghetti, *Polyhedron*, 1996, **15**, 2299; J. Dupont, O. L. Casagrande, Jr., A. C. Aiub, N. R. Basso, C. M. Mössmer, M. Hörner and A. Bortoluzzi, *J. Coord. Chem.*, 1996, **40**, 35; J. Dupont, N. R. Basso, M. R. Meneghetti, R. Konrath, R. Burrow and M. Hörner, *Organometallics*, 1997, **16**, 2386; M. P. Gil, J. Dupont and O. L. Casagrande, Jr., *J. Coord. Chem.*, 2000, **51**, 1.

5 E. L. S. Gomes, V. Caliman, M. Horner, V. G. Young, Jr., J. Dupont and O. L. Casagrande, Jr., *Organometallics*, 1999, **18**, 3898; E. L. S. Gomes and O. L. Casagrande, Jr., *Thermochim. Acta*, 1999, **331**, 87.

6 M. J. Went, *Adv. Organomet. Chem.*, 1997, **41**, 69; M. J. Winter, *Adv. Organomet. Chem.*, 1989, **29**, 128.

7 S. P. Tunik, A. V. Vlasov, A. B. Nikol'skii, G. L. Starova, S. Ooi, H. Nakai and T. Sato, *J. Organomet. Chem.*, 1994, **464**, 71.

8 R. D. Fisher, *Chem. Ber.*, 1960, **93**, 165; D. A. Brown and J. R. Raju, *J. Chem. Soc. A*, 1966, 1617.

9 R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, 1974, **12**, 323; D. Seyferth, T. Kugita, A. Rheingold and G. P. A. Yap, *Organometallics*, 1995, **14**, 5632.

10 T. J. J. Muller and M. Ansorge, *Chem. Ber.*, 1997, **130**, 1135.

11 Determination of $\Delta\nu$ was done with average values of ν_E. $\Delta\nu_M$ = (ν_E of heterotrimetallic complex − ν_E of the corresponding starting (η^6-arene)tricarbonylchromium complex).

12 A. D. Hunter, V. Mozol and S. D. Tsai, *Organometallics*, 1992, **11**, 2251; A. D. Hunter, L. Shilliday, W. S. Furey and M. J. Zaworotko, *Organometallics*, 1992, **11**, 1550.

13 E. L. Muetterties, J. R. Bleeke, E. J. Wucherer and T. A. Albright, *Chem. Rev.*, 1982, **82**, 499.

14 X. Verdaguer, A. Moyano, M. A. Pericàs, A. Riera, A. Alvarez-Larena and J.-F. Piniella, *Organometallics*, 1999, **18**, 4275; J. Lewis, B. Lin, M. S. Khan, M. R. A. Al-Mandhury and P. R. Raithby, *J. Organomet. Chem.*, 1994, **484**, 161; M. I. Bruce, P. J. Low, A. Werth, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 1551; B. F. G. Johnson, J. Lewis, P. R. Raithby and D. A. Wilkinson, *J. Organomet. Chem.*, 1991, **408**, C9.

15 R. H. Crabtree and M. Lavin, *Inorg. Chem.*, 1996, **25**, 805.

16 N. A. Ustynyuk, V. N. Vinogradova, V. N. Korneva, D. N. Kravtsov, V. G. Andrianov and Yu. T. Struchkov, *J. Organomet. Chem.*, 1984, **277**, 285.

17 SHELXTL Plus V 5.0, Siemens Industrial Automation, Inc., Madison, WI, 1996; G. M. Sheldrick, SHELXS 97, University of Göttingen, 1997; Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.