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The synthesis and substitution reactions of $CpM(CO)_2(\mu\text{-}RC\equiv CR)Co(CO)_3$ (M = Mo, W; R = COOEt, COOMe)

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Abstract

The synthesis of $[CpM(CO)_2(\mu\text{-}RC\equiv CR)Co(CO)_3]$ (M = Mo, W; R = COOMe, COOEt) from $[CpM(CO)_3Co(CO)_4]$ and $RC\equiv CR$ is reported. The dimers react in refluxing benzene with phosphorus donor ligands, L, to give the Co substituted complexes $[CpMo(CO)_2(\mu\text{-}RC\equiv CR)Co(CO)_2L]$ in 15–87% yield. The PdO catalysed reaction (room temperature) between $[CpMo(CO)_2(\mu\text{-}RC\equiv CR)Co(CO)_3]$ and R'NC (R' = ^tBu, 2,6-$Me_2C_6H_3$) readily gave the products $[CpMo(CO)_2(\mu\text{-}RC\equiv CR)Co(CO)_{3-x}(R'NC)_x]$ ($x = 1, 2$). The new complexes have been characterised by IR and NMR (^{31}P, ^1H, ^{13}C) spectroscopy and mass spectrometry.

Introduction

The presence of two or more different metals in a dimer or cluster compound adds new and interesting possibilities to the compound's reactivity patterns. In addition to co-operative effects between adjacent metal centres [1], the steric and electronic environments of metal sites may be influenced by neighbouring metal-ligand fragments. Also, the presence of different metals in proximity to a ligand may result in varying patterns of ligand stabilisation and reactivity. Moreover, and most importantly, substitution may occur at various sites in heteronuclear compounds, and metallo-selective substitution reactions are therefore possible [2]. Some of the observations made to date on metal dimer and cluster carbonyl complexes include: (i) the kinetic and thermodynamic products of a substitution reaction are not necessarily the same [2a]; (ii) ligand addition and loss may occur at the same or different metal atoms [2a,3]; (iii) reaction methodology may influence the product distribution, *e.g.*, photolysis, catalysis, type of ligand, *etc.* [2a,4]; (iv) a variable stereochemistry of the products resulting from CO replacement by various

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ligands may be possible; *i.e.* the ligand may be co-ordinated in an axial or equatorial site [5].

To date, work in our laboratory on the CO substitution reactions of mixed metal dimer complexes has concentrated on an investigation of non-bridged dimers *i.e.* dimers held together *only* by the metal–metal bond [2a,3,4,6,7]. To extend these studies an investigation has now commenced on mixed metal dimers containing bridging ligands. Here we report our investigation of the CO substitution reactions of alkyne-bridged Mo–Co and W–Co complexes $[CpM(CO)_3(\mu\text{-}RC{\equiv}CR)Co(CO)_4]$ (M = Mo, W; R = COOMe, COOEt) by Group 15 donor ligands and isonitriles.

Reports on heterobimetallic μ-alkyne compounds of the type $[L_nM(\mu\text{-}RC{\equiv}CR)CoL'_m]$ are relatively rare in the literature. Examples of complexes that have been described are $[CpMo(CO)_2(\mu\text{-}CF_3C{\equiv}CCF_3)Co(CO)_3]$ [8], $[CpM(CO)_2(\mu\text{-}RC{\equiv}CR')Co(CO)_3]$, M = Mo, W [9], $[(L)W(CO)_2(\mu\text{-}RC{\equiv}CR')Co(CO)_3]$, L = Cp, $(\eta^5\text{-}C_5Me_5)$ [10], $[CpNi(\mu\text{-}RC{\equiv}CR')Co(CO)_3]$ [11], $[(CO)_4Mn(\mu\text{-}RC{\equiv}CR')Co(CO)_3]$ [12] and $[(CO)_3Rh(\mu\text{-}RC{\equiv}CR')Co(CO)_3]$ [13]. In only two instances have carbonyl substitution reactions of the complexes been investigated. In the first, the site of PPh_3 substitution at Co in $[CpW(CO)_2(\mu\text{-}RC{\equiv}CR')Co(CO)_2(PPh_3)]$ [10] was determined by $^{31}P\{^1H\}$ NMR spectroscopy. In the second, Jensen *et al.* [8] reported the synthesis and characterisation of the Co-substituted dimer $[CpMo(CO)_2(\mu\text{-}CF_3C{\equiv}CCF_3)Co(CO)_2(PPh_3)]$. Co-ordination of the PPh_3 to the Co centre was shown by the absence of ^{31}P coupling to the $^1H(Cp)$ resonance [8]. This observation may be contrasted with that reported by Davidson [14] for a bis-alkyne complex, $[CpMo(PEt_3)(\mu\text{-}CF_3C{\equiv}CCF_3)_2Co(CO)_2]$, in which the phosphine is co-ordinated to the Mo centre and shows a coupling constant, $J(PH) = 1.6$ Hz.

While this programme was being completed, Yanez *et al.* [15] reported the synthesis of a range of $CpW(CO)_3(\mu\text{-}RC{\equiv}CR)Co(CO)_4$ and $CpW(CO)_2(\mu\text{-}RC{\equiv}CR)_2Co(CO)_3$ complexes, in work similar to some of that described here.

Experimental

$[CpMo(CO)_3]_2$ and $[Co_2(CO)_8]$ were purchased from Strem Chemicals and $[W(CO)_6]$ from Climax Molybdenum Company. Me_3NO (Aldrich) was dried using a Dean-Stark apparatus (toluene as solvent). The group 15 donor ligands were purchased from Strem, with the exception of PPh_3 (Merck). ^tBuNC, XylNC (Xyl = $2,6\text{-}Me_2C_6H_3$) and acetylene ligands were obtained from Fluka and PdO from Engelhard. Column chromatography was performed on silica gel (Merck 60F, 70–230 mesh or SAARCHEM Unilab 60, 63–200 microns). Infrared spectra were recorded on a JASCO IRA-1 or Pye-Unicam SP300 and NMR (^1H, ^{13}C, ^{31}P) spectra on a Bruker AC 200 NMR spectrometer. Melting point data were recorded on a Kofler micro hot plate apparatus and are uncorrected. Analytical data were determined by the Division of Energy Technology, CSIR, Pretoria. The calculated data were generally 1–3% removed from the observed values (in ±50% C) and hence purity was ascertained from the NMR (^1H, ^{31}P) spectra. High resolution MS data, recorded on a Bruker CMS47X FT mass spectrometer were used to provide further confirmation of the composition of the new complexes. Reactions were routinely carried out under nitrogen in degassed and distilled solvents.

$[CpW(CO)_3]_2$ [16], $[CpMo(CO)_3Co(CO)_4]$ and $[CpW(CO)_3Co(CO)_4]$ [17] were prepared by literature procedures.

(a) Synthesis of $[CpM(CO)_2(\mu\text{-}RCO_2C{\equiv}CCO_2R)_xCo(CO)_{4-x}]$ *(M = Mo, W; x = 1, 2; R = Me, Et)*

Reaction of $[CpMo(CO)_3Co(CO)_4]$ *and* $EtCO_2C{\equiv}CCO_2Et$. A mixture of $[CpMo(CO)_3Co(CO)_4]$ (1.000 g; 2.404 mmol) and $EtCO_2C{\equiv}CCO_2Et$ (0.42 ml, 2.624 mmol) in benzene (50 ml) was stirred overnight. The solution was pumped to dryness to yield a mixture of $[CpMo(CO)_3]_2$ and mono- and di-substituted products. Column chromatography yielded $[CpMo(CO)_3]_2$ (1:1 CH_2Cl_2 : hexane), followed by pure $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$ (CH_2Cl_2), (20% yield, mp. ~ 25°C) and $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)_2Co(CO)_2]$ (1 : 1 CH_2Cl_2 : acetone) as a red oil (28% yield).

Reaction of $[CpMo(CO)_3Co(CO)_4]$ *and* $MeCO_2C{\equiv}CCO_2Me$ *[15].* A mixture of $[CpMo(CO)_3Co(CO)_4]$ (1.186 g; 2.851 mmol) and $MeCO_2C{\equiv}CCO_2Me$ (0.35 ml; 2.821 mmol) in benzene (80 ml) was stirred overnight. The solution was pumped to dryness to yield a mixture of $[CpMo(CO)_3]_2$ and mono- and di-substituted products. Column chromatography gave $[CpMo(CO)_3]_2$ (3:2 hexane : CH_2Cl_2), followed by pure $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (CH_2Cl_2), (33% yield, as an orange-red solid, mp. = 75°C) and $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2)_2Co(CO)_2]$ (1:1 CH_2Cl_2 : acetone) as a red oil (2% yield).

Reaction of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ *and* $MeCO_2C{\equiv}CCO_2Me$. A mixture of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.833 g; 1.659 mmol) and $MeCO_2C{\equiv}CCO_2Me$ (224 μl; 1.824 mmol) in benzene (30 ml) was heated under reflux for *ca.* 2 h. The reaction was monitored by IR spectroscopy and TLC, and when no further change in the IR spectra was observed, the solution was pumped to dryness. Column chromatography yielded $[CpMo(CO)_3]_2$ (3:1 CH_2Cl_2 : hexane), $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (CH_2Cl_2) and $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)_2Co(CO)_2]$ (1:1 CH_2Cl_2 : acetone) as a red oil (48% yield).

Reaction of $[CpW(CO)_3Co(CO)_4]$ *and* $EtCO_2C{\equiv}CCO_2Et$. A mixture of $[CpW(CO)_3Co(CO)_4]$ (0.102 g; 0.202 mmol) and $EtCO_2C{\equiv}CCO_2Et$ (32.1 μl; 0.200 mmol) in benzene (10 ml) was stirred at room temperature. The reaction was monitored by IR spectroscopy and TLC and after 24 h the solvent was evaporated. Column chromatography, with 3 : 2 hexane : acetone as eluant, yielded $[CpW(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$ (30% yield) and $[CpW(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)_2Co(CO)_2]$ (10% yield), both as orange oils. Decomposition products were present at the top of the column.

Reaction of $[CpW(CO)_3Co(CO)_4]$ *and* $MeCO_2C{\equiv}CCO_2Me$ *[15].* A mixture of $[CpW(CO)_3Co(CO)_4]$ (0.098 g; 0.194 mmol) and $MeCO_2C{\equiv}CCO_2Me$ (26.2 μl; 0.214 mmol) in benzene (10 ml) was stirred for 2 h at room temperature. After filtration through cellulose (to remove dark brown decomposition products) and evaporation of the solvent the residue was crystallised from CH_2Cl_2/hexane to give $[CpW(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.021 g, 18% yield) as an orange wax. (Traces of starting material and di-substituted product were present in the product mixture before purification.)

(b) Group 15 donor ligand substitution reactions of $[CpM(CO)_2(\mu\text{-}RCO_2C{\equiv}CCO_2R)Co(CO)_3]$ *(M = Mo, W; R = Me, Et)*

Synthesis of $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PPh_2Me)]$. A solution of $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$ (0.144 g; 0.272 mmol) and PPh_2Me (55.6 μl; 0.299 mmol) in benzene (11 ml) was stirred for 5 days. The reaction was monitored by IR spectroscopy and the crude product purified by column chromatography (1 : 1 hexane : acetone) to yield $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PPh_2Me)]$ as an orange-red oil (15% yield). Decomposition products were noted at the top of the column.

Synthesis of $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PMe_2Ph)]$. A solution of $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$ (0.310 g; 0.585 mmol) and PMe_2Ph (91.5 μl; 0.643 mmol) in benzene (20 ml) was heated under reflux overnight. The reaction was monitored by IR spectroscopy and TLC. After filtration through cellulose, to remove dark decomposition products, the solvent was removed and the product passed through a cellulose column (with benzene as eluant). This gave $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PMe_2Ph)]$ as a dark orange oil (60% yield). The purity was established by NMR spectroscopy.

Synthesis of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(O\text{-}o\text{-}C_6H_4\text{-}CH_3)_3\}]$. A solution of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.100 g; 0.202 mmol) and $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ (65.2 μl; 0.222 mmol) in benzene (20 ml) was heated under reflux for 3 h. The solution was then pumped to dryness and the residue was dissolved in ether. Crystallisation from ether/hexane yielded $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(O\text{-}o\text{-}C_6H_4CH_3)_3\}]$ as a dark red solid, mp. = 97–98°C (68% yield).

Synthesis of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(CH_2Ph)_3\}]$. A solution of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.100 g; 0.202 mmol) and $P(CH_2Ph)_3$ (0.068 g; 0.222 mmol) (15 ml) was stirred in benzene at *ca.* 85°C for 10 h. The reaction was monitored by IR spectroscopy and TLC and did not reach completion until additional $P(CH_2Ph)_3$ (0.031 g; 0.101 mmol) was added. The solvent was evaporated and the residue dissolved in CH_2Cl_2. Crystallisation from CH_2Cl_2/ hexane gave $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(CH_2Ph)_3\}]$ as an orange-red solid, mp. = 151–153°C (54% yield).

Synthesis of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_2Me)]$. A solution of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.143 g; 0.285 mmol) and PPh_2Me (58.3 μl; 0.313 mmol) (15 ml) was stirred in benzene for 7 days. The reaction was monitored by IR spectroscopy. The solution was pumped to dryness to yield crude $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_2Me)]$. Purification by column chromatography (CH_2Cl_2) yielded the pure product as a red oil, in 87% yield.

Synthesis of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PMe_2Ph)]$. A solution of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.215 g; 0.428 mmol) and PMe_2Ph (67.0 μl; 0.471 mmol) (15 ml) was heated under reflux in benzene for 1 h, after which the reaction was complete (as indicated by IR spectroscopy). The solution was pumped to dryness and crystallisation of the residue from CH_2Cl_2/ hexane yielded orange-red $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PMe_2Ph)]$ (53% yield).

Synthesis of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_3)]$. A solution of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.206 g; 0.410 mmol) and PPh_3

(0.118 g; 0.451 mmol) in benzene (15 ml) was heated under reflux for 1 h during which the reaction was monitored by IR spectroscopy. Solvent evaporation gave [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_2$(PPh$_3$)] and a small amount of starting material. The pure product was obtained as an orange solid in 79% yield by recrystallisation from toluene/hexane.

(c) Reactions of [CpMo(CO)$_2$(μ-RCO$_2$C≡CCO$_2$R)$_x$Co(CO)$_{4-x}$] (R = Me, Et; x = 1, 2) and R′NC (R′ = ^{t}Bu, 2,6-Me$_2$C$_6$H$_3$)

Uncatalysed reaction of [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_3$] and ^{t}BuNC. A solution of [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_3$] ((0.050 g; 0.096 mmol) and ^{t}BuNC (12.3 μl; 0.110 mmol) in benzene (10 ml) was stirred at room temperature for 3 days. IR spectroscopy indicated that no reaction had occurred. Heating to 65°C for 3 h also caused no change, but heating under reflux (0.5 h) resulted in consumption of the reactants. The solution was filtered through cellulose and the solvent evaporated to give a red oil (36% yield), which was identified as [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)(^{t}BuNC)$_2$] (see Discussion).

PdO-catalysed reaction of [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_3$] and ^{t}BuNC. A mixture of [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_3$] (0.050 g; 0.096 mmol), ^{t}BuNC (12.3 μl; 0.110 mmol) and PdO (5 mg) (10 ml) was stirred in benzene at room temperature for 5 h, after which IR spectroscopy indicated that the reaction was complete. The solution was filtered through cellulose and the solvent removed to yield [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_2$(^{t}BuNC)] (90% yield) as a red oil, which contained a small amount of the di-substituted product (< 5%). Repeated attempts at crystallisation were unsuccessful. The purity of the product was established by ^{1}H NMR spectroscopy.

PdO-catalysed reaction of [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_2$ (^{t}BuNC)] and ^{t}BuNC. A solution of [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co (CO)$_2$(^{t}BuNC)] ((0.048 g; 0.086 mmol), ^{t}BuNC (9.6 μl; 0.086 mmol) and PdO (5 mg) in benzene (10 ml) was stirred at room temperature overnight. Filtration through cellulose and solvent evaporation gave [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$-Me)Co(CO)(^{t}BuNC)$_2$] in 36% yield as a red oil. A small amount of [CpMo(CO)$_2$(μ-MeCO$_2$C≡CCO$_2$Me)Co(CO)$_2$(^{t}BuNC)] (< 5% as indicated by ^{1}H NMR spectroscopy) was present as an impurity.

Reaction of [CpMo(CO)$_2$(μ-EtCO$_2$C≡CCO$_2$Et)Co(CO)$_3$] and XylNC. A solution of [CpMo(CO)$_2$(μ-EtCO$_2$C≡CCO$_2$Et)Co(CO)$_3$] (0.101 g; 0.191 mmol) and XylNC (0.027 g; 0.210 mmol) in benzene (15 ml) was stirred at room temperature overnight. IR spectroscopy revealed that no reaction had taken place. PdO (10 mg) was added and the mixture stirred for a further 7 h at room temperature during which the reaction went to completion. Filtration through cellulose and solvent evaporation gave a mixture containing [CpMo(CO)$_2$(μ-EtCO$_2$C≡CCO$_2$Et)Co-(CO)$_2$(XylNC)] (> 90%) and [CpMo(CO)$_2$(μ-EtCO$_2$C≡CCO$_2$Et)Co(CO)(XylNC)$_2$] (< 10%), which were identified by IR and NMR spectroscopy. The product mixture was re-dissolved in benzene (15 ml) and a further equivalent of XylNC (0.025 g; 0.191 mmol) was added. After 1 h of stirring at room temperature no reaction had taken place, and so PdO (10 mg) was added and the mixture was stirred at room temperature overnight. This resulted in the disappearance of [CpMo(CO)$_2$(μ-EtCO$_2$C≡CCO$_2$Et)Co(CO)$_2$(XylNC)] and an increase in the extent of formation of $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)(XylNC)_2]$ (> 90%) as indicated by ^1H NMR spectroscopy. Unfortunately a third complex, believed to be $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(XylNC)_3]$, was also detected. After filtration of the solution through cellulose and solvent removal, the impure di-substituted product was isolated as a red oil (43% yield).

PdO-catalysed reaction of [CpMo(CO)₂(μ-MeCO₂C≡CCO₂Me)Co(CO)₃] and XylNC A solution of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ (0.050 g; 0.096 mmol), XylNC (0.014 g; 0.110 mmol) and PdO (10 mg) in benzene (10 ml) was stirred at room temperature for 0.5 h. The solution was filtered through cellulose and the solvent evaporated to yield a dark red oil, which was a mixture of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(XylNC)]$ (> 90%) and $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)(XylNC)_2]$ (< 10%) (0.064 g in total); the products were identified by a combination of IR and NMR spectroscopy.

Results and discussion

The new compounds $[CpM(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)_xCo(CO)_{4-x}]$ (M = Mo, W; $x = 1, 2$) were formed in the sluggish reaction when $[CpM(CO)_3Co(CO)_4]$ (M = Mo, W) and $EtCO_2C{\equiv}CCO_2Et$ were allowed to react in benzene. The analogous $MeCO_2C{\equiv}CCO_2Me$-substituted compounds, recently reported by Yanez *et al.* [15], were also synthesised by this procedure.

At room temperature, a period of at least 12 h was generally required for the reaction to reach completion. In addition, poor yields (< 50%) were obtained, and $[CpMo(CO)_3]_2$ was always present as a by-product. This is to be expected if homolytic Mo–Co bond cleavage occurs, since the $[CpMo(CO)_3]_2$ dimer acts as the thermodynamic "sink" for the system [17]. Addition of Me_3NO to the reaction [18] did not increase the yield. Under reflux conditions, and in the presence of an excess of acetylene, the reaction time is reduced and higher yields (60–70%) are obtained [15].

The reaction of a 1:1 stoichiometric ratio of $[CpM(CO)_3Co(CO)_4]$ (M = Mo, W) and $RCO_2C{\equiv}CCO_2R$ (R = Et, Me) yielded both mono- and di-substituted acetylene dimers. The highest yield of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)_2Co(CO)_2]$, 48%, was, however, achieved from the reaction of $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ and $MeCO_2C{\equiv}CCO_2Me$. The crystal structure of $[CpMo(CO)_2(PhC{\equiv}CPh)_2Co(CO)_2]$ indicates the presence of a molybdacyclopentadiene ring in the diacetylene complexes [15].

The new acetylene-bridged starting materials and substituted products were characterised by IR, MS and NMR (^1H, ^{13}C) spectroscopy (see Tables 1–5). The IR spectroscopic data for the unsubstituted acetylene dimers correlate well with the data reported by Yanez and co-authors [15] (see Table 1). Upon co-ordination to the dimer, the ^1H resonances of the acetylene moieties are shifted downfield, as expected. However, upon disubstitution, there is no further shift in the acetylene alkyl resonances, although the Cp resonances do shift upfield.

The methyl substituents of the acetylene ligands show only one ^1H NMR resonance. Rotation of the acetylene moiety with respect to the metal–metal bond is not expected. This implies that both sides of the acetylene are in equivalent environments, *i.e.*, the acetylene is coordinated in a $\mu\text{-}\eta^2,\eta^2$ or $\perp$ manner [19,20].

Table 1

IR data of acetylene complexes and their derivatives

Complex	IR (cm^{-1}) [a]	
	(C≡CCO)	(CO)
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$	1697m	1973m 2003sh 2011s 2031s 2057w,sh 2072s
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$ [b]	1702m	1975m 2004sh 2012s 2032s 2055w,sh 2073s
$[CpW(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$	1715s	1970s 1998s 1990s 2030m 2060w,sh 2075m
$[CpW(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$	1705m	1973m 2000sh 2009s 2025s 2060w 2079s
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)_2Co(CO)_2]$	1737vs	1966m 2006s 2031w 2056s 2068sh 2096w
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)_2Co(CO)_2]$ [c]	1737m,br	1969w 2008s 2030w,sh 2058s 2071sh 2098w
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PPh_2Me)]$	1686m,br 1722sh	1946sh 1965s 1995s 2026m 2055sh 2070mw
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PMe_2Ph)]$	1687s 1729m	1861w,br 1944s 1965s 1993s 2025m 2037m 2055sh
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(O\text{-}o\text{-}C_6H_4CH_3)_3\}]$	1697m 1736sh	1884w,br 1961sh 1979s 2005s [g] 2037m 2052sh
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(CH_2Ph)_3\}]$	1691m 1742m	1883w,br 1948sh 1966s 1998s [g] 2026m 2055w
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_2Me)]$	1694m 1742m	1878vw,br 1947sh 1966s 1997s 2030s 2054sh 2078mw
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PMe_2Ph)]$	1689m 1735w	1864w 1944ms 1963s 1993s 2026m 2037m 2053sh
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_3)]$	1692m 1733w	1946sh 1966s 1996s 2026m 2055m
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(^tBuNC)]$ [d]	1690m 1738m	1860w 1950m 1969s 1993s 2022m 2038m 2058sh 2079m
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)(^tBuNC)_2]$ [e]	1690m 1738w	1840w 1945m 1989m 2040w
$[CpMo(CO)_2(\mu\text{-}CF_3C{\equiv}CCF_3)Co(CO)_2(PPh_3)$ [f]		1962sh 1979vs 2004s 2018ms 2035m 2052w

[a] Recorded in CH_2Cl_2 unless otherwise stated. [b] Reference [15]: (recorded in hexane) 1970w 1995s 2005sh 2028s 2065m. [c] Reference [15]: (recorded in hexane) 1950w 1998m 2048s. [d] ν(NC): 2158m. [e] ν(NC): 2140s. [f] Reference [8]. [g] Possible shoulder at 1980 cm^{-1}.

Table 2

^1H NMR data of acetylene complexes and their derivatives

Complex	δ (ppm)[a]						J (Hz)[b]	
	Cp	CH_2	CH_3	$P-CH_n$[c]	Ph	Me[d]	(H-H)	(P-H)
$EtCO_2C{\equiv}CCO_2Et$		3.72q	0.74t				7.15	
$MeCO_2C{\equiv}CCO_2Me$			3.02s					
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$	4.60s	4.08q	1.01t				6.88	
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$	4.57s		3.45s					
$[CpW(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$	4.27s	4.07q	1.02t				6.60	
$[CpW(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$	4.51s		3.45s					
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)_2Co(CO)_2]$	4.32s	4.10q	1.00t				7.14	
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)_2Co(CO)_2]$	4.53s		3.45s					
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PPh_2Me)]$	4.83s	3.96m	0.97t	2.08d	7.56m 7.02m		7.11	9.04
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PMe_2Ph)]$	4.86s	4.09q	1.06t	1.61d	7.49m 7.06m		7.11	9.35
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(O\text{-}o\text{-}C_6H_4CH_3)_3\}]$	4.68s		3.47s	2.26s	7.57m 6.92m			
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(CH_2Ph)_3\}]$	4.69s		3.56s	3.31d	7.19m 7.06m			8.59
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_2Me)]$	4.81s		3.33s	2.01d	7.52m 7.01m			9.27
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PMe_2Ph)]$	4.80s		3.46s	1.54d	7.44m 7.04m			8.95
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_3)]$	4.53s		2.90s		7.43m 6.77m			
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2({}^tBuNC)]$	4.88s		3.56s			1.00s		
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)({}^tBuNC)_2]$	5.17s		3.39s			1.07s		
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(XylNC)]$[e]	4.91	–	3.43s			2.22		
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)(XylNC)_2]$	5.08	–	3.47s			2.26		
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(XylNC)]$	4.90	4.13q	1.04t			2.24		
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)(XylNC)_2]$	5.17	4.17	1.06t			2.35		

[a] Recorded in C_6D_6 unless otherwise stated, relative to TMS. [b] $^1H-^1H$ and $^{31}P-^1H$ coupling constants. [c] $n = 2, 3$. [d] isonitrile resonance. [e] ^{13}C data Cp: 91.3; CO_2*Me*: 52.8; RNC(*Me*) 19.3 ppm.

Table 3

^{13}C NMR data of acetylene complexes and their derivatives [a,b]

Complex	δ (ppm)								
	Cp	Mo(CO)	Co(CO)	CH_3	CH_2	CO_2	C≡C	P–CH*n* [c]	P–Ph
$EtCO_2C{\equiv}CCO_2Et$				13.60	62.81	151.76	74.89		
$MeCO_2C{\equiv}CCO_2Me$				52.80		151.86	74.86		
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$	90.76	221.34	204.30	14.29	61.59	171.65	79.30		
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$	90.74	221.18	199.30	52.54		172.30	79.30		
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)_2Co(CO)_2]$	90.78			13.82	62.37	165.05			
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)_2Co(CO)_2]$	90.71	229.48	197.98	52.60		165.29			
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PPh_2Me)]$	90.00	224.71	203.89	14.31	60.64	172.88	71.30	16.10 15.65	128.30–138.85
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PMe_2Ph)]$	90.67	226.39	205.42	14.46	60.74	173.65	71.79	17.08 16.58	128.30–132.98
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(O\text{-}o\text{-}C_6H_4CH_3)_3\}]$	90.72	223.61	205.30	52.00		172.80	73.60	16.75	120.04–151.04
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(CH_2Ph)_3\}]$	89.54	224.15	205.29	52.05		174.81	70.58	34.21 33.95	126.90–135.38
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_2Me)]$	90.15	224.80	207.80	51.70		172.80		16.00 15.54	128.68–138.80
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PMe_2Ph)]$	90.70			51.87		174.30		16.98 16.48	128.29–129.70
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_3)]$	90.22			51.50					128.34–133.91

[a] Recorded in C_6D_6 unless otherwise stated, referenced to C_6D_6. [b] Absent entries imply that the resonances could not be observed in dilute solution. [c] $n = 2, 3$.

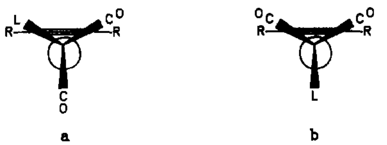

Fig. 1. Newman projection of $CpMo(CO)_2(\mu\text{-}RC{\equiv}CR)Co(CO)_2L$ viewed down the Mo–Co bond axis. Two expected conformers are shown: (a) with L close to and (b) L removed from the alkyne ligand.

The substitution reactions of the $[CpMo(CO)_2(\mu\text{-}RCO_2C{\equiv}CCO_2R)Co(CO)_3]$ (R = Me, Et) dimers with the ligands, L, where L = PPh_2Me, PMe_2Ph, $P(O\text{-}o\text{-}C_6H_4CH_3)_3$, $P(CH_2Ph)_3$ and PPh_3, were investigated. The reactions were sluggish and either refluxing or a long reaction time was required for isolation of the mono-substituted products in high yields (60–87%).

The IR spectra containing the phosphorus of the complexes ligands (see Table 1) show carbonyl stretching frequencies due to both the acetylene moiety and the carbonyl groups attached to the metals. The shifts in the carbonyl stretching frequencies are consistent with the trend of the donor ligand's basicity and not with ligand steric effects [21].

IR data for the new mono-substituted dimers were recorded in CH_2Cl_2, and more than the expected four $\nu(CO)$ absorptions were observed. Similar spectral results (in hexane) were reported by Jensen *et al.* [8] for $CpMo(CO)_2(\mu\text{-}CF_3C{\equiv}CF_3)Co(CO)_2(PPh_3)$. One significant difference between the two sets of data (Table 1) relates to our observation of a weak band at ~ 1850 cm^{-1}, which increases in intensity with increase in the size of L. An extra absorption was observed, at ~ 2078 cm^{-1}, for L = PMe_2Ph (a small ligand).

It is possible that these extra absorptions arise from the presence of different ratios of conformers in solution. Thus, for L = PMe_2Ph, access to conformers in which the ligand is close to the alkyne ligand (Fig. 1a) is easier than when L is bulkier. The most probable conformer for all the complexes is that shown in Fig. 1b. The presence of the weak absorption at ~ 1850 cm^{-1} could thus arise from a semi-bridging interaction of the carbonyl ligands in a favourable conformer.

Another notable feature of the IR spectra is the presence of two absorptions in the region associated with the $\nu(CO)$ vibrations of the acetylene COOR group. The approximate ratio of the bands is 1:6 (1740:1690 cm^{-1} bands). It would be expected that the COOR groups lie in a plane which will reduce steric interactions with the rest of the dimer. Since the C–C alkyne bond is at right angles to the metal–metal bond, the COOR groups will also be near to perpendicular to the M–M bond. The two COOR groups can thus be *cis* or *trans* (Fig. 2) to each other

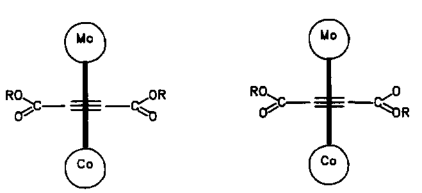

Fig. 2. Two possible arrangements of the alkyne ligand in $CpMo(CO)_2(\mu\text{-}RC{\equiv}CR)Co(CO)_2L$ as viewed from above the Mo–Co bond axis. Ligands attached to the Co and Mo atoms are not shown.

Table 4

^{31}P NMR data of phosphine-substituted acetylene complexes [a]

Complex	δ (ppm)
$[\mathrm{CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PPh_2Me)}]$	37.5
$[\mathrm{CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PMe_2Ph)}]$	18.2
$[\mathrm{CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(O\text{-}\mathit{o}\text{-}C_6H_4CH_3)_3\}}]$	154.0
$[\mathrm{CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2\{P(CH_2Ph)_3\}}]$	51.4
$[\mathrm{CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_2Me)}]$	37.0
$[\mathrm{CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PMe_2Ph)}]$	18.4
$[\mathrm{CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PPh_3)}]$	52.5

[a] Recorded in C_6D_6, relative to external H_3PO_4.

with respect to the alkyne C–C bond axis. Whether this effect is responsible for the two COOR absorptions as well as the extra features in the vibrational spectrum associated with the carbonyl ligands must await further studies.

Only mono-substitution of the heterometallic dimers by the phosphorus donor ligands was observed. The integrated intensities of the acetylene Et/Me group ^{1}H NMR resonances may be compared to those of the Me groups in the phosphorus ligands: a 1 : 1 acetylene to phosphine ratio is obtained for all the substituted products.

The ^{31}P NMR data for the phosphorus ligand-substituted compounds are tabulated in Table 4. From the data it is possible to conclude that the phosphorus ligand is on the Co atom. A broad signal is seen, owing to the ^{59}Co quadrupolar effect. This conclusion is in agreement with the results reported by Jensen *et al.* for related compounds [8].

Table 5 contains mass spectral data for selected compounds. In most cases, especially for the $\mathrm{EtCO_2C{\equiv}CCO_2Et}$-substituted complexes, the parent ions are not detected. The highest mass fragments seen are those corresponding to the loss of the carbonyl groups from the compound. The Mo isotope pattern may be clearly seen in the spectra, and accurate mass determinations confirm the composition of the ions. The accurate mass data are found in Table 5, and the error margins are less than 10 ppm in each case.

A consideration of the various techniques used to characterise the substituted dimer complexes indicates that, at present, only the ^{31}P NMR spectra can unequivocally confirm that the site of the CO substitution is at Co. The IR spectra tend to be complex, and no ^{1}H NMR data are available for reference. It should be noted that small amounts of the Mo (or W) substituted derivatives may possibly have been formed in the reaction, but if they were of low stability then decomposition could have occurred during work up. However, the major product is the Co substituted derivative.

The reactions between $[\mathrm{CpMo(CO)_2(\mu\text{-}RCO_2C{\equiv}CCO_2R)}_x\mathrm{Co(CO)}_{4-x}]$ (R = Me, Et; $x = 1, 2$) and isonitriles were also investigated. No reaction occurred when the mixtures were stirred at room temperature (24 h) or at *ca.* 60°C (0.5 h). For example, treatment of $[\mathrm{CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3}]$ with ^{t}BuNC at 65°C (3 h) caused no reaction, but treatment of the related $[\mathrm{CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3}]$ dimer with XylNC in refluxing benzene produced a mixture of $[\mathrm{CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(XylNC)}]$ and [CpMo-

Table 5

Mass spectral data of acetylene complexes and their derivatives

Complex	Ion	Accurate Mass/ amu [a]	Composition of ion						Mass difference/ ppm	I (%) [a]
			C	H	O	Co	Mo	P		
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_3]$	$M^+ - 5(CO)$	391.9332206	13	15	4	1	1		4.77	
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_3]$	M^+	508.8825606	16	11	9	1	1		8.33	26
	$M^+ - (CO)$	475.8877215	15	11	8	1	1		8.98	68
	$M^+ - 2(CO)$	447.8914798	14	11	7	1	1		6.58	71
	$M^+ - 3(CO)$	419.8976014	13	11	6	1	1		9.49	58
	$M^+ - 4(CO)$	391.9023051	12	11	5	1	1		9.19	24
	$M^+ - 5(CO)$	363.9069097	11	11	4	1	1		8.58	100
$[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)_2(PPh_2Me)]$	$M^+ - 4(CO)$	592.0081647	26	28	4	1	1	1	4.08	
$[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)Co(CO)_2(PMe_2Ph)]$	$M^+ - (CO)$	585.9538676	22	22	7	1	1	1	9.38	65
	$M^+ - 2(CO)$	557.9572963	21	22	6	1	1	1	6.88	74
	$M^+ - 3(CO)$	529.9628760	20	22	5	1	1	1	8.18	91
	$M^+ - 4(CO)$	501.9608512	19	22	4	1	1	1	5.53	100

[a] Relative to ^{98}Mo.

$(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)(XylNC)_2]$. Addition of further XylNC resulted in a change in the mono/di product ratio, but mixtures of products were always formed.

Transition metal oxides are known to catalyse isonitrile substitution reactions [22]. Catalysed reaction of the Mo–Co dimers with ${}^tBuNC$ or XylNC resulted in rapid reactions even at room temperature, to give the required products in high yield. In all cases, the di-substituted derivatives were present as impurities, and pure mono-isonitrile substituted derivatives could not be isolated. The product mixture was treated with another equivalent of XylNC in an attempt to produce pure $[CpMo(CO)_2(\mu\text{-}EtCO_2C{\equiv}CCO_2Et)Co(CO)(XylNC)_2]$, but this led to further difficulties. The PdO-catalysed reaction yielded a third complex, possibly the tri-substituted derivative, and attempted separation of the mixture was again unsuccessful.

The isonitrile derivatives were characterised by IR and ${}^1H$ NMR spectroscopy, and the data are tabulated in Tables 1 and 2, respectively. The IR spectra show both carbonyl and isonitrile stretching frequencies. Resonances corresponding to the Cp, Me and ${}^tBuNC$ moieties are present in the ${}^1H$ NMR spectra. The NMR spectra obtained on the complexes produced by the thermal and PdO catalysed routes were identical.

The spectroscopic data do not conclusively establish that the site of substitution is at the Co atom. However, from the known correlated reactivity patterns of Group 15 donor ligands and isonitriles, substitution at Co is expected. A crystallographic investigation will be needed to confirm that this is the case. Cleavage reactions with halogens, which have proved useful in establishing the site of reactivity in other dimer systems, could not be used in these studies.

No reaction took place between the di-acetylene compound, $[CpMo(CO)_2(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)_2Co(CO)_2]$ and various isonitrile ligands (${}^tBuNC$, XylNC, ${}^iPrNC$) (room temperature, benzene), even in the presence of PdO. In refluxing benzene only decomposition of the carbonyl reagents took place.

The above results add to the growing collection of data on the site of carbonyl substitution of metal carbonyl dimers containing commonly used metal carbonyl fragments [3]. The preferred product, with substitution at Co, is consistent with predictions from earlier studies on other related Fe–Co complexes [23]. Attempts to confirm these conclusions were made, *e.g.*, reactions of the *non-bridged* Mo–Co and W–Co complexes, $CpM(CO)_3Co(CO)_4$ (M = Mo, W), with isonitriles and Group 15 donor ligands were attempted. However, in all instances M–Co bond cleavage occurred, and no new substituted heterobimetallic complexes were isolated.

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