Synthesis and Reactions of Alkyne Complexes $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}RC_2R)]$ (R = Me or Ph) containing Six Different Monodentate Ligands

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The complex $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ reacts with RC_2R (R = Me or Ph) in CH_2Cl_2 to give alkyne complexes $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**) containing six different monodentate ligands. Reaction of **1** with an equimolar quantity of L [L = PPh_3, $PPh_2(C_6H_{11})$, PMe_2Ph, imidazole or 2-methylimidazole] afforded complexes $[MoCl(GeCl_3)(CO)L(PPh_3)(\eta^2\text{-}MeC_2Me)]$ in high yield. Equimolar quantities of **1** and L–L {L–L = $Ph_2P(CH_2)_nPPh_2$ (n = 1–6), $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$, $(C_6H_{11})N{=}CHCH{=}N(C_6H_{11})$, 2,2′-bipyridine, 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, $S_2CP(C_6H_{11})_3$ or $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$} gave $[MoCl(GeCl_3)(CO)(PPh_3)\{\sigma\text{-}Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ and the cationic complexes $[Mo(GeCl_3)(CO)(PPh_3)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]Cl$ in good yield. The cationic nature of several of these complexes was confirmed by exchange with $Na[BPh_4]$ to afford complexes with tetraphenylborate as the counter anion. The fluxionality of some of the complexes was determined by variable-temperature ^1H NMR spectroscopy. Solution and solid-state ^{13}C NMR spectroscopy was used to confirm that the alkyne ligand in several of these complexes is donating four electrons to the molybdenum.

The importance of alkyne complexes of molybdenum(II) and tungsten(II) has been highlighted in the review by Templeton[1] published in 1989. Since the reports in 1982 of $[WBr_2(CO)(\eta^2\text{-}CF_3C_2CF_3)_2]$ by Davidson *et al.*[2] and $[WI_2(CO)_2L(\eta^2\text{-}HC_2H)]$ (L = PMe_3 or $AsMe_3$) and $[WI_2(CO)_2L(\eta^2\text{-}PhC_2H)]$ (L = PMe_3, $AsMe_3$ or $CNBu^t$) by Umland and Vahrenkamp[3] halogenocarbonyl–alkyne complexes of molybdenum(II) and tungsten(II) have received considerable attention. In 1983, Templeton and co-workers[4] described the reactions of $[MX_2(CO)_nL_2]$ [X = Cl or Br; n = 2 or 3; L = PPh_3, PEt_3 or pyridine (py), L_2 = $Ph_2P(CH_2)_2PPh_2$] with RC_2R' (R = R′ = Me, Et or Ph; R = H, R′ = Bu^n or Ph) to give $[MX_2(CO)L_2(\eta^2\text{-}RC_2R')]$. Davidson and Vasapollo[5] described the reactions of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ with RC_2R' (R = R′ = Me or Ph; R = Me, R′ = Ph) to give $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R')_2\}_2]$. In 1985, Bennett and Boyd[6] described the reactions of $[MBr_2(CO)_3(PEt_3)_2]$ (M = Mo or W) with cyclooctyne to afford $[MBr_2(CO)(PEt_3)_2(\eta^2\text{-}C_8H_{12})]$. More recently, in 1988 we described the synthesis of $[\{M(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}RC_2R')\}_2]$ (M = Mo or W; R = R′ = Me, Ph or CH_2Cl; R = Ph, R′ = Me or CH_2OH; R = Me, R′ = PhS or $p\text{-}MeC_6H_4S$) and their reactions with donor ligands.[7] In the same year[8] we described the preparation of the bis(alkyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (M = Mo or W, R = R′ = Ph, R = Me, R′ = Ph; M = W, R = R′ = Me, CH_2Cl or $p\text{-}MeC_6H_4$; R = Ph, R′ = CH_2OH) and $[\{Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2\}_2]$. The reaction chemistry of the two tungsten bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) has been studied in detail.[9] Apart from our mixed-halide complexes $[\{W(\mu\text{-}I)Br(CO)(NCMe)(\eta^2\text{-}RC_2R')\}_2]$ (R = R′ = Me, Ph or CH_2Cl; R = Me, R′ = Ph) and $[WBrI(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (R = R′ = Me, Ph or CH_2Cl; R = Me, R′ = Ph)[10] no other reports of mixed-halide alkyne complexes have been made. In this paper we describe the synthesis of the alkyne complexes $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}RC_2R)]$ (R = Me or Ph), containing six different monodentate ligands, and the reactions of the but-2-yne derivatives with a series of mono- and bi-dentate neutral-donor ligands. A preliminary communication on this work has been published.[11]

Results and Discussion

Treatment of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$[12] with 4 equivalents of MeC_2Me in CH_2Cl_2 at 0 °C or 1 equivalent of PhC_2Ph in CH_2Cl_2 at room temperature afforded the novel alkyne complexes $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**) in good yield. Complexes **1** and **2** were characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^1H and ^{13}C NMR spectroscopy (Tables 3 and 4). The but-2-yne complex **1** is soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ and acetonitrile, but insoluble in hydrocarbon solvents and diethyl ether. The diphenylacetylene analogue is only slightly soluble in chlorinated solvents and acetonitrile and totally insoluble in hydrocarbon solvents and diethyl ether. Both the alkyne complexes **1** and **2** are air sensitive in solution and the solid state, however, they can be stored under nitrogen in the dark for several days. It is interesting that reaction of the seven-co-ordinate mono(acetonitrile) complex $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ with an excess of but-2-yne in CH_2Cl_2 did not afford the complex $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}MeC_2Me)]$ whereas reaction of $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ with 2 equivalents of PhC_2Ph in CH_2Cl_2 gave only very low yields of $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}PhC_2Ph)]$ and several other products which were difficult to separate. While most of our previous work on alkyne complexes has been carried out with tungsten as the metal,[7–9] the tungsten complex $[WCl(GeCl_3)(CO)_3(NCMe)_2]$ {synthesised by treating *fac*-$[W(CO)_3(NCMe)_3]$ (prepared *in situ*) with an equimolar amount of $GeCl_4$} is very unstable and hence no alkyne-donor ligand chemistry with tungsten was attempted.

The IR spectra of **1** and **2** both show an asymmetric doublet in the region of ν(C≡N) at 2300 cm^{-1} which is consistent with an acetonitrile attached to a transition-metal centre. As expected both complexes show single carbonyl bands at ν(C≡O) 1975 and 1984 cm^{-1} for **1** and **2** respectively. The weak alkyne stretching bands ν(C≡C) at 1684 and 1637 cm^{-1} respectively are at considerably lower wavenumber compared to the unco-ordinated alkynes. This is due to back donation of electron density from filled metal d orbitals into empty π* orbitals on the alkyne ligand. The room-temperature ^1H NMR spectrum of **1** shows a

Table 1 Physical and analytical data * for the complexes [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-RC$_2$R)] (R = Me or Ph) and derivatives

Complex	Colour	Yield (%)	Analysis (%) C	H	N
1 [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)]	Grey-green	73	43.2 (43.2)	3.5 (3.5)	1.4 (2.0)
2 [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-PhC$_2$Ph)]	Green	58	51.0 (51.3)	3.2 (3.4)	1.8 (1.7)
3 [MoCl(GeCl$_3$)(CO)(PPh$_3$)$_2$(η^2-MeC$_2$Me)]	Green	77	54.2 (53.7)	3.8 (4.0)	—
4 [MoCl(GeCl$_3$)(CO)(PPh$_3$){PPh$_2$(C$_6$H$_{11}$)}(η^2-MeC$_2$Me)]	Green	54	53.6 (53.3)	5.1 (4.6)	—
5 [MoCl(GeCl$_3$)(CO)(PPh$_3$)(PMe$_2$Ph)(η^2-MeC$_2$Me)]	Brown	51	47.5 (47.0)	4.5 (4.1)	—
6 [MoCl(GeCl$_3$)(CO)(PPh$_3$)(Him)(η^2-MeC$_2$Me)]	Green	69	43.6 (43.2)	3.7 (3.5)	4.3 (3.9)
7 [MoCl(GeCl$_3$)(CO)(PPh$_3$)(2-mim)(η^2-MeC$_2$Me)]	Green	66	43.5 (44.0)	3.9 (3.7)	3.2 (3.8)
8 [MoCl(GeCl$_3$)(CO)(PPh$_3$){σ-Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)]	Brown	78	55.1 (55.5)	4.3 (4.0)	—
9 [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_2$PPh$_2$}(η^2-MeC$_2$Me)]Cl	Green	57	56.2 (55.9)	4.3 (4.3)	—
10 [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_2$PPh$_2$}(η^2-MeC$_2$Me)][BPh$_4$]	Brown	58	65.0 (65.5)	4.9 (4.9)	—
11 [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_3$PPh$_2$}(η^2-MeC$_2$Me)]Cl	Green	47	56.2 (56.3)	4.7 (4.4)	—
12 [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_4$PPh$_2$}(η^2-MeC$_2$Me)]Cl·CH$_2$Cl$_2$	Green	55	53.8 (53.6)	4.4 (4.6)	—
13 [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_5$PPh$_2$}(η^2-MeC$_2$Me)]Cl	Green	48	57.2 (57.0)	5.1 (4.7)	—
14 [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_6$PPh$_2$}{(η^2-MeC$_2$Me)]Cl	Green	40	58.0 (57.4)	5.1 (4.8)	—
15 [Mo(GeCl$_3$)(CO)(PPh$_3$){Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$}(η^2-MeC$_2$Me)]Cl	Brown	67	56.7 (56.6)	4.4 (4.1)	—
16 [Mo(GeCl$_3$)(CO)(PPh$_3$){(C$_6$H$_{11}$)NCHCHN(C$_6$H$_{11}$)}(η^2-MeC$_2$Me)]Cl	Purple	70	50.3 (50.8)	5.4 (5.2)	3.0 (3.2)
17 [Mo(GeCl$_3$)(CO)(PPh$_3$)(bipy)(η^2-MeC$_2$Me)]Cl	Green	74	49.2 (48.8)	4.0 (3.9)	3.2 (3.4)
18 [Mo(GeCl$_3$)(CO)(PPh$_3$)(bipy)(η^2-MeC$_2$Me)][BPh$_4$]	Brown	65	62.2 (62.5)	4.8 (4.5)	2.6 (2.6)
19 [Mo(GeCl$_3$)(CO)(PPh$_3$)(phen)(η^2-MeC$_2$Me)]Cl	Blue	40	50.4 (50.4)	3.8 (3.5)	3.1 (3.4)
20 [Mo(GeCl$_3$)(CO)(PPh$_3$)(phen)(η^2-MeC$_2$Me)][BPh$_4$]	Dark green	77	62.9 (63.3)	4.5 (4.4)	2.5 (2.5)
21 [Mo(GeCl$_3$)(CO)(PPh$_3$)(4,7-dmphen)(η^2-MeC$_2$Me)]Cl	Red	58	54.8 (54.2)	4.4 (3.8)	2.5 (3.2)
22 [Mo(GeCl$_3$)(CO)(PPh$_3$)(5,6-dmphen)(η^2-MeC$_2$Me)]Cl	Brown	60	53.8 (54.2)	4.1 (3.8)	2.9 (3.2)
23 [Mo(GeCl$_3$)(CO)(PPh$_3$){S$_2$CP(C$_6$H$_{11}$)$_3$}(η^2-MeC$_2$Me)]Cl·0.5CH$_2$Cl$_2$	Blue	74	47.8 (47.9)	5.4 (5.3)	—
24 [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_2$PPh(CH$_2$)$_2$PPh$_2$}(η^2-MeC$_2$Me)]Cl	Green	80	57.4 (57.6)	4.8 (4.6)	—

* Calculated values in parentheses.

Table 2 Infrared data[a] for the complexes [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-RC$_2$R)] (R = Me or Ph) and derivatives

Complex	ν(C≡O)[b]/cm^{-1}	ν(C≡C)/cm^{-1}	Complex	ν(C≡O)[b]/cm^{-1}	ν(C≡C)/cm^{-1}
1[c]	1975	1684w	**13**	1951	—
2[d]	1984	1637w	**14**	1951	1649vw
3	1973	1682vw	**15**	1960	—
4	1964	1687vw	**16**[e]	1953	—
5	1949	1649vw	**17**	1948	1687vw
6	1954	—	**18**	1956	—
7	1951	1670vw	**19**	1953	1672vw
8	1949	1658vw	**20**	1957	1665vw
9	1974	1652vw	**21**	1949	—
10	1982	1651vw	**22**	1972	—
11	1952	1667vw	**23**	1955	1641vw
12	1951	—	**24**	1975	1672vw

s = Strong, m = medium, vw = very weak.

[a] Spectra recorded as thin films between NaCl plates in CHCl$_3$. [b] Strong. [c] ν(N≡C) 2313w and 2286w cm^{-1}. [d] ν(N≡C) 2311w and 2285w cm^{-1}. [e] ν(C=N) 1465m cm^{-1}.

very broad but-2-yne resonance at δ 3.00, which suggests the but-2-yne ligand is undergoing rapid propeller-like rotation at room temperature. It was very difficult to obtain satisfactory ^{13}C NMR spectra of **1** and **2** in solution since the complexes decomposed fairly rapidly, even in the absence of air. However, the solid-state ^{13}C NMR spectra were obtained for **1** and **2** using the TOSS program[13a] to eliminate side-bands. The broad alkyne contact carbon shifts for **1** and **2** were centred at δ 228.98 and 231.41 respectively. These values suggest[13b] that the alkyne ligand in **1** and **2** is donating a total of four electrons to the molybdenum in these complexes. Many attempts were made to grow single crystals suitable for X-ray crystallography without success. The ^{31}P NMR spectrum (CDCl$_3$, +25 °C) for **1** indicates there are several isomers present in solution. There are at least 30 different isomers (15 diastereoisomers, each one with an enantiomer) for **1**. This explains the broad resonance for the but-2-yne methyl groups in the ^{1}H NMR spectrum, not alkyne rotation.

The reaction chemistry of the but-2-yne complex [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] **1** with both neutral mono- and bi-dentate donor ligands is shown in Scheme 1. Equimolar quantities of [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] **1** and L [L = PPh$_3$, PPh$_2$(C$_6$H$_{11}$), PMe$_2$Ph, imidazole (Him) or 2-methylimidazole(2-mim)] in CH$_2$Cl$_2$ at room temperature gave the acetonitrile–exchanged products [MoCl(GeCl$_3$)(CO)L(PPh$_3$)(η^2-MeC$_2$Me)] **3**–**7** generally in high yield. Complexes **3**–**7** were characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^{1}H NMR spectroscopy (Table 3) and for L = PPh$_3$ by ^{13}C NMR spectroscopy (Table 4). Complexes **3**–**7** are generally more soluble and more stable relative to the analogous acetonitrile complex **1**.

The ^{1}H NMR spectra of **3**–**7** all showed broad single resonances for the but-2-yne methyl groups. A variable-temperature ^{1}H NMR study was carried out on [MoCl(GeCl$_3$)(CO)(PPh$_3$)$_2$(η^2-MeC$_2$Me)] **3**. The barrier to but-2-yne rotation for **3** was calculated using the equation $\Delta G^{\ddagger} = -RT_c \ln \pi\Delta\nu h/2^{\frac{1}{2}}k_BT_c$ (T_c/K = coalescence temperature, $\Delta\nu$/s^{-1} = the separation of signals undergoing collapse).[14] The barrier to but-2-yne rotation ($\Delta\nu$ = 23.22 Hz, T_c = 239 K) for **3** was calculated to be 50.3 ± 1 kJ mol^{-1}. It is interesting that the barrier to but-2-yne rotation for the dichloro complexes [MCl$_2$(CO)(PPh$_3$)$_2$(η^2-MeC$_2$Me)] (M = Mo or W)[4b] was calculated to be 40.2 kJ mol^{-1}, *i.e.* considerably lower than for **3**. The reason for the higher barrier to but-2-yne rotation for **3** is likely to be due to the larger size of the GeCl$_3$ group compared to the chloride ligand. The ^{13}C NMR spectrum for **3** showed a broad alkyne contact carbon resonance at δ 235.24, which from the observations of Templeton and Ward [13b] indicates the but-2-yne donates four electrons to the molybdenum in **3**. This allows complex **3** to obey the effective atomic number rule. It is likely that the reactions of **1** with an equimolar quantity of L proceed *via* an associative mechanism. The alkyne in the proposed seven-co-ordinate intermediate [MoCl(GeCl$_3$)(CO)(NCMe)L(PPh$_3$)(η^2-MeC$_2$Me)] acts as a two-electron donor, which can revert back to four-electron donation in **3**–**7** with loss of acetonitrile. Other workers [15] have proposed that reactions of alkyne complexes of molybdenum(II) or tungsten(II) with neutral-donor ligands occur *via* an associative mechanism.

Table 3 Proton NMR data* for the complexes [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-RC$_2$R)] (R = Me or Ph) and derivatives

Complex	^{1}H NMR (δ)
1	7.4 (m, 15 H, Ph), 3.0 (vbr s, 6 H, $\equiv$CMe), 2.35 (s, 3 H, NCMe)
2	7.5 (m, 25 H, Ph), 2.45 (s, 3 H, NCMe)
3	7.4 (m, 30 H, Ph), 2.45 (br s, 6 H, $\equiv$CMe)
4	7.6, 7.4 (m, 25 H, Ph), 2.42 (br s, 6 H, $\equiv$CMe), 1.7, 1.3 (m, 11 H, C$_6$H$_{11}$)
5	7.35 (m, 20 H, Ph), 2.55 (br s, 6 H, $\equiv$CMe), 1.9–1.6 (m, 6 H, Me)
6	11.7 (s, 1 H, NH), 9.05 (br s, 3 H, =CH), 7.55, 7.4, 7.3 (m, 15 H, Ph), 3.1 (br s, 6 H, $\equiv$CMe)
7	11.7 (s, 1 H, NH), 9.0 (br s, 2 H, =CH), 7.5 (m, 15 H, Ph), 3.0 (br s, 6 H, $\equiv$CMe)
8	7.6 (br s, 20 H, PPh), 7.3 (m, 15 H, Ph), 3.90 (br s, 2 H, PCH$_2$), 2.3 (s, 6 H, $\equiv$CMe)
9	7.35 (m, 35 H, Ph), 3.4 (m, 4 H, PCH$_2$), 2.4 (br s, 6 H, $\equiv$CMe)
10	7.4 (m, 55 H, Ph), 3.4 (m, 4 H, PCH$_2$), 2.35 (br s, 6 H, $\equiv$CMe)
11	7.4, 7.3 (m, 35 H, Ph), 3.0 (m, 4 H, PCH$_2$), 2.4 (br s, 6 H, $\equiv$CMe), 2.3 (m, 2 H, PCH$_2$C*H*$_2$)
12	7.6, 7.4, 7.3 (m, 35 H, Ph), 5.6 (s, 2 H, CH$_2$), 2.95 (m, 4 H, PCH$_2$), 2.4 (br s, 6 H, $\equiv$CMe), 2.3 (m, 4 H, PCH$_2$C*H*$_2$)
13	7.6, 7.35, 7.3 (m, 35 H, Ph), 3.2 (m, 4 H, PCH$_2$), 2.4 (br s, 6 H, $\equiv$CMe), 2.3 (m, 4 H, PCH$_2$C*H*$_2$), 1.45 (m, 2 H, PCH$_2$CH$_2$C*H*$_2$)
14	7.6, 7.35, 7.25 (m, 35 H, Ph), 3.2 (m, 4 H, PCH$_2$), 2.4 (br s, 6 H, $\equiv$CMe), 2.3 (m, 4 H, PCH$_2$C*H*$_2$), 1.34 (m, 4 H, PCH$_2$CH$_2$C*H*$_2$)
15	7.6, 7.35 (m, 35 H, Ph), 4.5 (m, 4 H, C$_5$H$_4$), 4.15 (m, 4 H, C$_5$H$_4$), 2.45 (br s, 6 H, $\equiv$CMe)
16	7.7 (s, 2 H, =CH), 7.35 (s, 15 H, Ph), 3.05, 3.0 (d, 6 H, $\equiv$CMe), 1.9, 1.5 (m, 22 H, C$_6$H$_{11}$)
17	9.55 (d, 2 H, bipy), 8.5 (m, 4 H, bipy), 7.8 (d, 2 H, bipy), 7.35 (s, 15 H, Ph), 3.05, 3.0 (d, 6 H, $\equiv$CMe)
18	9.7 (d, 2 H, bipy), 8.4 (m, 4 H, bipy), 7.9 (d, 2 H, bipy), 7.5 (m, 35 H, Ph), 3.10, 3.05 (d, 6 H, $\equiv$CMe)
19	8.8 (d, 2 H, phen), 8.25 (m, 2 H, phen), 7.9 (m, 4 H, phen), 7.4 (m, 15 H, Ph), 3.15, 3.10 (d, 6 H, $\equiv$CMe)
20	8.95 (d, 2 H, phen), 8.35 (m, 2 H, phen), 8.0 (m, 4 H, phen), 7.4 (m, 35 H, Ph), 3.10, 3.05 (d, 6 H, $\equiv$CMe)
21	8.9 (d, 2 H, phen), 8.5 (m, 2 H, phen), 8.0 (m, 2 H, phen), 7.45, 7.35 (m, 15 H, Ph), 3.15, 3.10 (d, 6 H, $\equiv$CMe), 2.9 (s, 6 H, Me)
22	9.15 (d, 2 H, phen), 8.9 (d, 2 H, phen), 8.2 (m, 2 H, phen), 7.4, 7.3 (m, 15 H, Ph), 3.15, 3.10 (d, 6 H, $\equiv$CMe), 2.8 (s, 6 H, Me)
23	7.4 (s, 15 H, Ph), 5.6 (s, 1 H, CH$_2$), 2.45 (s, 6 H, $\equiv$CMe), 1.9, 1.8, 1.5 (m, 33 H, C$_6$H$_{11}$)
24	7.4, 7.3 (m, 40 H, Ph), 3.4 (m, 8 H, PCH$_2$), 2.2 (s, 6 H, $\equiv$CMe)

* Spectra recorded in CD$_3$COCD$_3$ (+25 °C) and referenced to SiMe$_4$; s = singlet, d = doublet, m = multiplet, br = broad singlet.

Table 4 Selected ^{13}C NMR data for the complexes [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-RC$_2$R)] (R = Me or Ph) and derivatives

Complex	^{13}C NMR (δ)
1[a]	228.98 (C$\equiv$C), 200.86 (CO), 131.18 (Ph), 23.18 (*Me*C$_2$*Me*), 4.53 (NC*Me*)
2[a]	231.41 (C$\equiv$C), 195.74 (CO), 140.33, 134.95, 132.05, 128.72, 123.68 (Ph and $\equiv$C*Ph*), 4.36 (NC*Me*)
3[b]	235.24 (C$\equiv$C), 213.98 (CO), 133.26, 131.83, 131.29, 131.14, 128.65, 128.46 (Ph), 17.52, 17.05 (C$\equiv$C*Me*)
15[b]	228.43 (C$\equiv$C), 205.99 (CO), 131.76, 131.42, 131.18, 131.04, 130.38, 130.24, 128.57, 128.38, 128.31, 128.13 (Ph), 73.08, 72.64, 72.45 (C$_5$H$_4$), 16.57, 16.23 (C$\equiv$C*Me*)
20[a]	225.40 (C$\equiv$C), 204.14 (CO), 147.93 (phen), 135.72, 130.80, 127.15 (Ph), 16.42, 16.1 (C$\equiv$C*Me*)
21[b]	235.88 (C$\equiv$C), 203.74 (CO), 151.38, 151.19, 149.79, 149.10 (phen), 131.78, 131.56, 131.2, 131.0, 128.72, 128.57, 128.38 (Ph), 19.09, 18.99 (4,7-Me$_2$), 16.53, 16.19 (C$\equiv$C*Me*)

[a] Spectrum recorded as a solid sample (+25 °C) on a Bruker AC 250 CP/MAS spectrometer. [b] Spectrum recorded in Me$_2$SO (+32 °C) on a Bruker WH 400 spectrometer and referenced to SiMe$_4$.

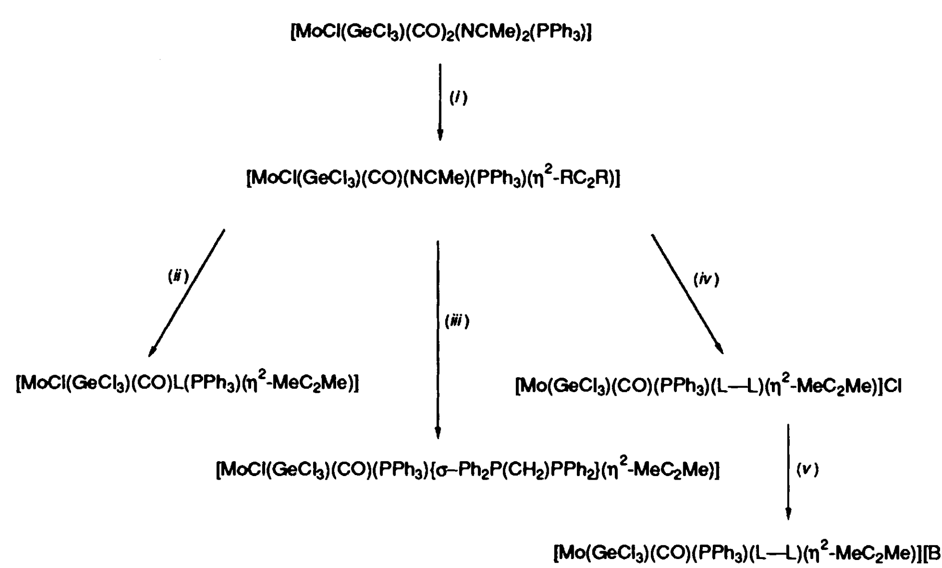
Table 5 Phosphorus-31 NMR data* for selected complexes

Complex	^{31}P (δ)
8	34.1 (d, J_{pp} 60.8, dppm), 30.4 (d, J_{pp} 59.7, dppm), 21.73 (m, PPh$_3$), −23.53 (d, J_{PP} 59.7, dppm), −25.4 (d, J_{PP} 61.0 Hz, dppm)
12	36.19 [m, Ph$_2$P(CH$_2$)$_4$PPh$_2$], 21.24 (m, PPh$_3$)
13	36.04 [m, Ph$_2$P(CH$_2$)$_5$PPh$_2$], 21.46 (m, PPh$_3$)
14	36.8 [m, Ph$_2$P(CH$_2$)$_6$PPh$_2$], 21.73 (m, PPh$_3$)
15	42.8 [m, Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$], 28.71 (m, PPh$_3$)

* Spectra recorded in CD$_3$COCD$_3$ (+25 °C).

The reaction of [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] **1** with an equimolar quantity of L–L {L–L = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1–6), [Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$], (C$_6$H$_{11}$)N=CHCH=N(C$_6$H$_{11}$), 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen), 5,6-dimethyl-1,10-phenanthroline (5,6-dmphen), S$_2$CP(C$_6$H$_{11}$)$_3$ or Ph$_2$P(CH$_2$)$_2$PPh(CH$_2$)$_2$PPh$_2$} in CH$_2$Cl$_2$ at room temperature affords the neutral complex [MoCl(GeCl$_3$)(CO)(PPh$_3$){σ-Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)] **8** or the monocationic complexes [Mo(GeCl$_3$)(CO)(PPh$_3$)(L–L)(η^2-MeC$_2$Me)]Cl **9**, **11–17**, **19**, **21–24**. The cationic nature of these complexes was confirmed by treatment of [Mo(GeCl$_3$)(CO)(PPh$_3$)(L–L)(η^2-MeC$_2$Me)]Cl with Na[BPh$_4$] in acetonitrile at room temperature to give the anion-exchanged products [Mo(GeCl$_3$)(CO)(PPh$_3$)(L–L)(η^2-MeC$_2$Me)][BPh$_4$] [L–L = Ph$_2$P(CH$_2$)$_2$PPh$_2$ **10**, bipy **18** or phen **20**] in good yield. The complexes **8–24** were all characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^{1}H NMR spectroscopy (Table 3) and in selected cases ^{13}C and ^{31}P NMR spectroscopy (Tables 4 and 5). Complexes **12** and **23** were confirmed as CH$_2$Cl$_2$ and 0.5CH$_2$Cl$_2$ solvates respectively by repeated elemental analyses and ^{1}H NMR spectroscopy. The cationic complexes **9–24** were soluble in chlorinated solvents, but insoluble in hydrocarbon solvents and diethyl ether. These complexes were the most stable and least air sensitive and could be stored in the solid state for several months under a nitrogen atmosphere.

The complex [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] **1** reacts with 1 equivalent of Ph$_2$P(CH$_2$)PPh$_2$ (dppm) in CH$_2$Cl$_2$ at room temperature to give the brown neutral monodentate co-ordinated complex [MoCl(GeCl$_3$)(CO)(PPh$_3$)(σ-dppm)(η^2-MeC$_2$Me)] **8**. The monodentate co-ordination mode of dppm was shown by the lack of chloride exchange when the complex was treated with Na[BPh$_4$] and also by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **8** is complex and suggests the presence of two isomers in solution. However, the high-field resonances which are both doublets at δ −25.4 (J_{PP} 61.0 Hz) and −23.53 (J_{PP} 59.7 Hz) are very likely to be due to the unco-ordinated phosphorus on the dppm ligand. The ^{31}P NMR spectra (Table 5) of [Mo(GeCl$_3$)(CO)(PPh$_3$)(L–L)(η^2-MeC$_2$Me)]Cl {L–L = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 4–6) or [Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$]} all show no high-field resonances, which suggests that both phosphorus atoms in Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 4–6) and [Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$] are attached to the metal. The cationic nature of the dppe complex is confirmed by preparation of the tetraphenylborate complex **10**. The ligand Ph$_2$P(CH$_2$)PPh$_2$ co-ordinates in a monodentate manner in this type of complex due to its much smaller bite angle by comparison to Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2–6) and [Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$], where the strain upon co-ordination is smaller than for dppm. It should be noted that there are many



Scheme 1 All reactions [(*i*)–(*iv*)] were carried out in CH_2Cl_2 at room temperature. For (*v*) the reactions were carried out in NCMe at room temperature. Reagents: (*i*) RC_2R (R = Me or Ph), 72 h; (*ii*) L = PPh_3, $PPh_2(C_6H_{11})$, PMe_2Ph, Him or 2-mim, 18 h; (*iii*) $Ph_2P(CH_2)PPh_2$, 18 h; (*iv*) L–L = $Ph_2P(CH_2)_nPPh_2$ (*n* = 2–6), $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$, $(C_6H_{11})N{=}CHCH{=}N(C_6H_{11})$, bipy, phen, 4,7-dmphen, 5,6-dmphen, $S_2CP(C_6H_{11})_3$ or $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, 18 h; (*v*) $Na[BPh_4]$ [for L–L = $Ph_2P(CH_2)_2PPh_2$, bipy or phen], 24 h

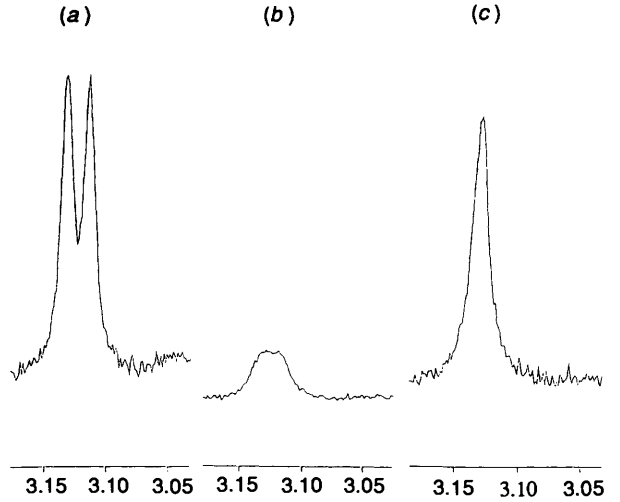


Fig. 1 The but-2-yne methyl resonances for $[Mo(GeCl_3)(CO)(PPh_3)(phen)(\eta^2\text{-}MeC_2Me)]Cl$ **19** at 293 (*a*), 317 (*b*) and 330 K (*c*)

examples[16] where dppm bridges two transition-metal centres and forms bimetallic complexes.

It is interesting that the bidentate phosphorus-donor ligand complexes **9**–**15** all show a broad single resonance in their room-temperature ^1H NMR spectra, whereas the bidentate nitrogen-donor compounds all show doublets for the but-2-yne methyl group resonances. The ^1H NMR spectra of $[Mo(GeCl_3)(CO)(PPh_3)(bipy)(\eta^2\text{-}MeC_2Me)]Cl$ **17** and $[Mo(GeCl_3)(CO)(PPh_3)(5,6\text{-}dmphen)(\eta^2\text{-}MeC_2Me)]Cl$ **22** at 323 K showed two resonances for the but-2-yne methyl groups, with no indication that the methyl resonances would collapse to a single resonance at this temperature. Using the Gutowsky–Holm equations,[14] it was calculated that the barriers to but-2-yne rotation ($\Delta G^{\ddagger}_{T_c}$ for **17** and **22** are greater than 71.6 and 72.6 kJ mol^{-1} respectively. However, the ^1H NMR spectrum for $[Mo(GeCl_3)(CO)(PPh_3)(phen)(\eta^2\text{-}MeC_2Me)]Cl$ **19** shows a doublet at δ 3.1 for the but-2-yne resonances at room temperature, which upon warming collapsed and coalescence was observed at 317 K. Upon further warming of the solution, a sharp singlet was observed at 330 K which corresponds to the but-2-yne undergoing a rapid propeller-like rotation. The but-2-yne methyl resonances in the ^1H NMR spectra at different temperatures for **19** are shown in Fig. 1. The barrier for but-2-yne rotation for **19** was calculated, $\Delta G^{\ddagger}_{T_c}$ = 71.68 kJ mol^{-1}, which is higher than most previously reported barriers to but-2-yne rotation for molybdenum(II) and tungsten(II) but-2-yne complexes.[1] Since the crystal structures[1] of most of the halogenocarbonyl alkyne complexes have the alkyne ligand *trans* to the halide or related ligand, a possible structure of **9**–**24** is shown in Fig. 2. Unfortunately, no suitable single crystals could be grown for X-ray crystallography to support this suggestion.

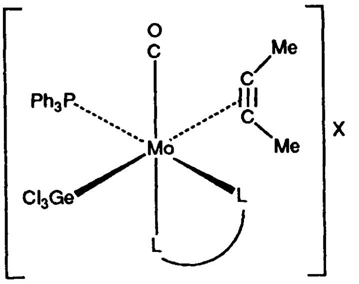


Fig. 2 Proposed structure of $[Mo(GeCl_3)(CO)(PPh_3)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]X$ **9**–**24** (X = Cl or BPh_4)

The ^{13}C NMR spectra for **15**, **20** and **21** showed broad but-2-yne resonances at δ 228.43, 225.40 and 235.88 respectively which, from Templeton and Wards' correlation,[13b] indicates that the alkyne ligand is donating four electrons to the molybdenum in these complexes.

In summary, the novel mixed $Cl/GeCl_3$ alkyne complexes $[MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**) are the first examples of complexes of molybdenum(II) containing six different monodentate ligands to be reported. This co-ordination arrangement is obviously not possible with the previously reported dihalogenoalkyne complexes of molybdenum(II) and tungsten(II). The reaction chemistry of **1** with neutral donor ligands (see Scheme 1) is similar to that of the related dihalogenoalkyne complexes; however, the barrier to but-2-yne rotation of several mono(but-2-yne) complexes derived from **1** is considerably higher owing to the bulky $GeCl_3$ group replacing Cl in the dihalogenoalkyne complexes.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk-line techniques. The complex [MoCl(GeCl$_3$)(CO)$_2$(NCMe)$_2$(PPh$_3$)] was prepared by the literature method.[12] All chemicals used were purchased from commercial sources. Proton, ^{31}P and solid-state ^{13}C NMR spectra were recorded on a Bruker AC/250 CP/MAS spectrometer. Solution ^{13}C NMR spectra were recorded on a Bruker WH 400 MHz spectrometer. Proton and ^{13}C NMR spectra were referenced to tetramethylsilane, ^{31}P NMR spectra to H_3PO_4. Infrared spectra were recorded on a Perkin Elmer 197 spectrometer. Elemental analyses (C, H and N) were determined by using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas).

Syntheses.—[MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] **1**. To [MoCl(GeCl$_3$)(CO)$_2$(NCMe)$_2$(PPh$_3$)] (4.0 g, 5.63 mmol) dissolved in CH_2Cl_2 (100 cm^3) with continuous stirring under a stream of dry nitrogen in an ice-bath was added MeC$_2$Me (1.218 g, 22.52 mmol) in a four-fold excess. The mixture was stirred for 72 h, after which the product was filtered off and the solvent removed *in vacuo* to give the grey-green complex [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] **1** (yield: 2.86 g, 73%), which was recrystallised from CH_2Cl_2–Et_2O.

[MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-PhC$_2$Ph)] **2**. To [MoCl(GeCl$_3$)(CO)$_2$(NCMe)$_2$(PPh$_3$)] (4.15 g, 5.84 mmol) dissolved in CH_2Cl_2 (100 cm^3) with continuous stirring under a stream of dry nitrogen was added PhC$_2$Ph (1.04 g, 5.84 mmol). The mixture was stirred for 72 h, after which the product was filtered off and the solvent removed *in vacuo* to give the green complex [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-PhC$_2$Ph)] **2** (yield: 2.78 g, 58%), which was washed several times with Et_2O, and recrystallised from CH_2Cl_2–Et_2O.

[MoCl(GeCl$_3$)(CO)(PPh$_3$)$_2$(η^2-MeC$_2$Me)] **3**. To [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] (0.500 g, 0.719 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh$_3$ (0.188 g, 0.719 mmol). After the mixture was stirred for 18 h, the product was filtered off and the solvent removed *in vacuo* to afford the green compound [MoCl(GeCl$_3$)(CO)(PPh$_3$)$_2$(η^2-MeC$_2$Me)] **3** (yield: 0.51 g, 77%), which was recrystallised from CH_2Cl_2–Et_2O.

Similar reactions of [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] with 1 equivalent of L [L = PPh$_2$(C$_6$H$_{11}$), PMe$_2$Ph, Him and 2-mim] gave the complexes [MoCl(GeCl$_3$)(CO)(PPh$_3$)L(η^2-MeC$_2$Me)] [L = PPh$_2$(C$_6$H$_{11}$) **4**, PMe$_2$Ph **5**, Him **6** or 2-mim **7**].

[MoCl(GeCl$_3$)(CO)(PPh$_3$)(σ-dppm)(η^2-MeC$_2$Me)] **8**. To [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] (0.500 g, 0.719 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added dppm (0.276 g, 0.719 mmol). The mixture was stirred for 18 h, after which the product was filtered off and the solvent removed *in vacuo* to afford the brown complex [MoCl(GeCl$_3$)(CO)(PPh$_3$)(σ-dppm)(η^2-MeC$_2$Me)] **8** (yield: 0.58 g, 78%), which was recrystallised from CH_2Cl_2–Et_2O.

Similar reactions of [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] with L–L gave the cationic complexes [Mo(GeCl$_3$)(CO)(PPh$_3$)(L–L)(η^2-MeC$_2$Me)]Cl {L–L = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2–6) **9**, **11–14**, [Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$] **15**, (C$_6$H$_{11}$)NCHCHN(C$_6$H$_{11}$) **16**, bipy **17**, phen **19**, 4,7-dmphen **21**, 5,6-dmphen **22**, S$_2$CP(C$_6$H$_{11}$)$_3$ **23** or Ph$_2$P(CH$_2$)$_2$PPh(CH$_2$)$_2$PPh$_2$ **24**}.

[Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_2$PPh$_2$}(η^2-MeC$_2$Me)][BPh$_4$] **10**. To [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_2$PPh$_2$}(η^2-MeC$_2$Me)]Cl (0.5 g, 0.48 mmol) dissolved in acetonitrile (20 cm^3) with continuous stirring under a stream of dry nitrogen was added Na[BPh$_4$] (0.16 g, 0.48 mmol). After stirring the solution for 24 h, the solvent was removed *in vacuo*. The mixture was redissolved in CH_2Cl_2, followed by filtration to remove NaI, and removal of the solvent gave the brown complex [Mo(GeCl$_3$)(CO)(PPh$_3$){Ph$_2$P(CH$_2$)$_2$PPh$_2$}(η^2-MeC$_2$Me)][BPh$_4$] **10** (yield: 0.37 g, 58%), which was recrystallised from CH_2Cl_2–Et_2O.

Similar reactions of [Mo(GeCl$_3$)(CO)(PPh$_3$)(L–L)(η^2-MeC$_2$Me)]Cl (L–L = bipy **17** or phen **19**) with Na[BPh$_4$] in NCMe afforded the complexes [Mo(GeCl$_3$)(CO)(PPh$_3$)(L–L)(η^2-MeC$_2$Me)][BPh$_4$] **18** or **20** respectively.

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