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Alkynyl and butadiynyl complexes of the cycloheptatrienylmolybdenum auxiliary $Mo(CO)_2(\eta\text{-}C_7H_7)$

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Abstract

The new alkynyl complexes $[Mo(C{\equiv}CR)(CO)_2(\eta\text{-}C_7H_7)]$ (**1**, $R = Bu^t$; **2**, $R = SiMe_3$; **3**, $R = CO_2Et$) have been prepared by reaction of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with alkynyl lithium (**1**, **2**) or alkynyl copper (**3**) reagents. The σ-butadienyl complex $[Mo\{C(=C(CN)_2)C(Ph)=C(CN)_2\}(CO)_2(\eta\text{-}C_7H_7)]$ **6**, is formed by reaction of $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ with tetracyanoethene. Treatment of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with $LiC{\equiv}CC{\equiv}CSiMe_3$ affords $[Mo(C{\equiv}CC{\equiv}CSiMe_3)(CO)_2(\eta\text{-}C_7H_7)]$ **7** which is a precursor to $[Mo(C{\equiv}CC{\equiv}CH)(CO)_2(\eta\text{-}C_7H_7)]$ **8** by desilylation with KF in methanol/THF. The butadiynyl complexes $[Mo(C{\equiv}CC{\equiv}CH)(CO)L(\eta\text{-}C_7H_7)]$ (**8**, L = CO; **9**, $L = PMe_3$) are also formed directly by reaction of $[MoBr(CO)L(\eta\text{-}C_7H_7)]$ with $Li_2C{\equiv}CC{\equiv}C$ in THF. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cycloheptatrienyl; Molybdenum; Alkynyl; Butadiynyl

1. Introduction

In a series of papers we have developed synthetic routes to, and the reaction chemistry of, alkynyl complexes of the cycloheptatrienylmolybdenum auxiliary [1–4]. Although a synthesis of the dicarbonyl complex $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ was developed at an early stage [1], our investigations have, so far, focused on phosphine substituted derivatives, principally $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]$ ($dppe = Ph_2PCH_2CH_2PPh_2$). In this paper we re-examine the synthesis and reactivity of the dicarbonyl systems and use this work as a foundation for the construction of the first examples of butadiynyl complexes of the cycloheptatrienylmolybdenum system.

2. Results and discussion

2.1. Alkynyl complexes $[Mo(C{\equiv}CR)L_2(\eta\text{-}C_7H_7)]$ ($L = CO$ or $L_2 = dppe$)

We have previously described the preparation of $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ in moderate yield by reaction of $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ with $LiC{\equiv}CPh$ in THF [1]. The objectives of the current work were (i) to develop a superior synthetic route in terms of yield and (ii) to extend the range of alkynyl derivatives of this system. Three modifications were made to the original synthesis. Firstly, the more labile bromide derivative $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ was employed as starting material, secondly the alkynyl lithium reagent was used in a substantial excess and finally the chromatographic work up of the reaction mixture was carried out at low temperature. The outcome of these modifications was to improve the yield of $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ from 37 to 71%. Application of the revised procedure to the syntheses of the new complexes [Mo(C≡

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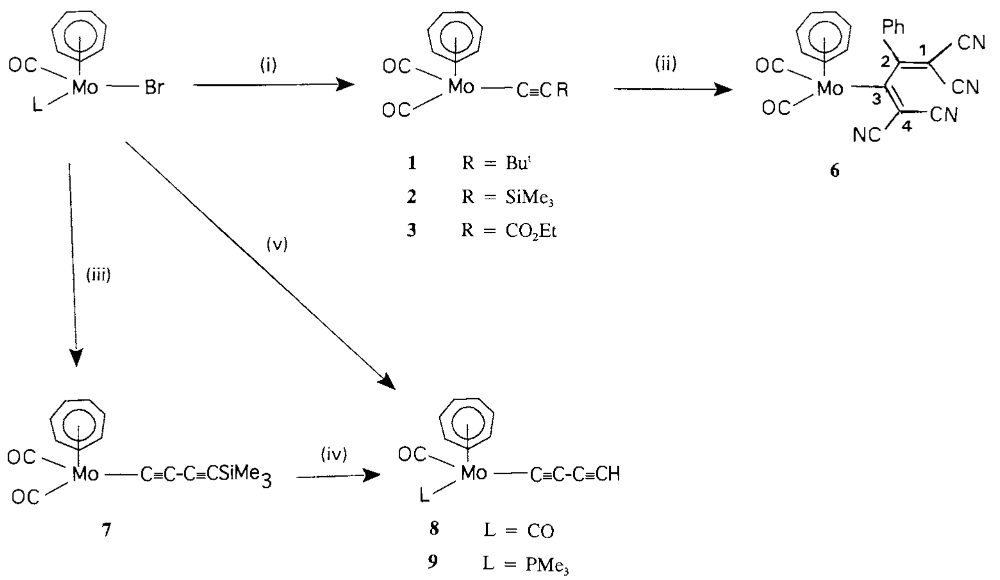

Scheme 1. Reagents and conditions: (i) L = CO, R = Bu^t or SiMe$_3$: LiC≡CR in THF, −78°C then slow warming to 0°C. L = CO, R = CO$_2$Et: HC≡CCO$_2$Et + CuI in NEt$_3$, 0°C, 5 min; (ii) R = Ph: tcne in CH$_2$Cl$_2$, 45 min; (iii) L = CO: LiC≡CC≡CSiMe$_3$ in THF, −78°C then slow warming to r.t.; (iv) KF in refluxing methanol/THF (1:1), 5 h; (v) L = CO or PMe$_3$: Li$_2$C≡CC≡C in THF, −78°C then slowly warmed to r.t.

CBu^t)(CO)$_2$(η-C$_7$H$_7$)], **1** and [Mo(C≡CSiMe$_3$)(CO)$_2$(η-C$_7$H$_7$)], **2** (Scheme 1) met with mixed success; both complexes were obtained as green solids but the yields [**1**, (12%); **2**, (40%)] were poor or moderate only. In addition to the use of lithium reagents, copper(I) alkynyls may also be employed in the synthesis of [Mo(C≡CR)(CO)$_2$(η-C$_7$H$_7$)]. Although copper(I) alkynyl reagents have been used to particularly good effect in the syntheses of [W(C≡CPh)(CO)$_3$(η-C$_5$H$_5$)] and [Fe(C≡CPh)(CO)$_2$(η-C$_5$H$_5$)] [5], application to the cycloheptatrienylmolybdenum system is more restricted [1]. However a copper assisted synthesis does provide a reliable route to [Mo(C≡CCO$_2$Et)(CO)$_2$(η-C$_7$H$_7$)] **3**, starting from [MoBr(CO)$_2$(η-C$_7$H$_7$)] and HC≡CCO$_2$Et in triethylamine in the presence of a catalytic quantity of copper(I) iodide.

Details of the characterisation of **1**, **2** and **3** and subsequently described complexes are presented in Table 1 (microanalytical, IR and mass spectroscopic data) and Table 2 (^{1}H- and ^{13}C{^{1}H}-NMR spectroscopic data). We have previously reported NMR data for [Mo(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)] [1] and the phosphine substituted derivatives [Mo(C≡CR)(CO)L(η-C$_7$H$_7$)] (L = PMe$_3$, R = Bu^t or Ph; L = PPh$_3$, R = Ph) [2] but satisfactory NMR data for [Mo(C≡CR)(dppe)(η-C$_7$H$_7$)] (R = Bu^t or Ph) was not obtained [1], an observation which may be attributed to the presence of trace quantities of the paramagnetic 17-electron radicals [Mo(C≡CR)(dppe)(η-C$_7$H$_7$)]$^+$ in the NMR samples. Recently however we have demonstrated that good NMR spectra for the related complex [MoBr(bipy)(η-C$_7$H$_7$)] (bipy = 2,2′-bipyridine) are obtained by the addition of a trace quantity of the one-electron reducing agent cobaltocene to the NMR sample [6]. This observation prompted a successful extension of the technique to complexes of the Mo(dppe)(η-C$_7$H$_7$) auxiliary and the hitherto unreported ^{1}H- and ^{13}C{^{1}H}-NMR data for [Mo(C≡CR)(dppe)(η-C$_7$H$_7$)] (**4**, R = Bu^t; **5**, R = Ph), recorded in solution in CD$_2$Cl$_2$ with cobaltocene as a trace additive, are now presented in Table 2.

The principal interest in these new results lies in the ^{13}C-NMR data for the alkynyl carbons C$_\alpha$ and C$_\beta$. The unequivocal assignment of ^{13}C-NMR data for alkynyl carbons presents some difficulty but the availability of data for the series of complexes [Mo(C≡CR)L$_2$(η-C$_7$H$_7$)] (R = Bu^t or Ph, L$_2$ = (CO)$_2$, (CO)(PMe$_3$), [2] or dppe) now provides the opportunity for judicious comment. Considering first the Bu^t derivatives, in the cases of [Mo(C≡CBu^t)(CO)(PMe$_3$)(η-C$_7$H$_7$)] and **4**, the assignment of C$_\alpha$ is clear from ^2J(P–C$_\alpha$) data; a shift of C$_\alpha$ to low field with increase in the degree of phosphine substitution is also apparent (see Table 3). It is therefore probable that the assignments for **1** are (δ (ppm): C$_\alpha$, 88.7; C$_\beta$ 121.4). The identification of C$_\alpha$ and C$_\beta$ in the phenylalkynyl complexes [Mo(C≡CPh)(CO)L(η-C$_7$H$_7$)] (L = CO or PMe$_3$) and **5** is further complicated by resonances due to the phenyl substituent of the alkynyl ligand. In the cases of [Mo(C≡CPh)(CO)L(η-C$_7$H$_7$)] (L = CO or PMe$_3$) all resonances for C$_\alpha$ and C$_\beta$ were situated to high field of the phenyl region with the exception of C$_\alpha$ for [Mo(C≡CPh)(CO)(PMe$_3$)(η-C$_7$H$_7$)] which was located with the aid of ^2J(P–C$_\alpha$) data [2]. For the dppe complex **5**, the low intensity of the resonance at δ 121.6 ppm and chemical shift just out-

Table 1
Microanalytical, IR and mass spectroscopic data

Complex	Analysis (%)[a]		IR[b]		Mass spectral data[c]
	C	H	ν(CO) (cm^{-1})	ν(C≡C) (cm^{-1})	
$[Mo(C{\equiv}CBu^t)(CO)_2(\eta\text{-}C_7H_7)]$ **1**	55.4 (55.6)	4.6 (4.9)	2008, 1954	2054	326 (M^+), 298 ($[M\text{–}CO]^+$), 268 ($[M\text{–}2CO]^+$)
$[Mo(C{\equiv}CSiMe_3)(CO)_2(\eta\text{-}C_7H_7)]$ **2**	48.8 (49.4)	4.9 (4.7)	2021, 1961	2001	342 (M^+), 314 ($[M\text{–}CO]^+$), 286 ($[M\text{–}2CO]^+$)
$[Mo(C{\equiv}CCO_2Et)(CO)_2(\eta\text{-}C_7H_7)]$ **3**	49.3 (49.4)	3.6 (3.5)	2017, 1972	2073[d]	342 (M^+), 286 ($[M\text{–}2CO]^+$), 214 ($[M\text{–}2CO\text{–}CO_2Et]^+$)
$[Mo\{C({=}C(CN)_2)C(Ph){=}C(CN)_2\}\text{-}(CO)_2(\eta\text{-}C_7H_7)]$ **6**	58.6 (58.5)	2.5 (2.5)[e]	2026, 1983	[f]	475 (M^+), 418 ($[M\text{–}2CO]^+$), 392 ($[M\text{–}2CO\text{–}CN]^+$)[h]
$[Mo(C{\equiv}CC{\equiv}CSiMe_3)(CO)_2\text{-}(\eta\text{-}C_7H_7)]$ **7**	52.5 (52.7)	4.4 (4.4)	2020, 2003(sh), 1969	2117, 2161	366 (M^+), 338 ($[M\text{–}CO]^+$), 310 ($[M\text{–}2CO]^+$)
$[Mo(C{\equiv}CC{\equiv}CH)(CO)_2(\eta\text{-}C_7H_7)]$ **8**	53.4 (53.4)	3.0 (2.7)	2018, 1969	2127, 3301[g]	294 (M^+), 266 ($[M\text{–}CO]^+$), 238 ($[M\text{–}2CO]^+$)
$[Mo(C{\equiv}CC{\equiv}CH)(CO)(PMe_3)\text{-}(\eta\text{-}C_7H_7)]$ **9**	53.0 (52.9)	4.9 (5.0)	1923	2114, 3301[g]	342 (M^+), 314 ($[M\text{–}CO]^+$), 238 ($[M\text{–}CO\text{–}PMe_3]^+$)[h]

[a] Calculated values in parentheses.

[b] Solution spectra in CH_2Cl_2, sh = shoulder.

[c] By EI mass spectroscopy unless stated otherwise, m/z values based on ^{98}Mo.

[d] ν(C=O) CO_2Et 1673 cm^{-1}.

[e] N, 12.3 (11.9)%.

[f] ν(CN) 2218 cm^{-1}.

[g] ν(≡CH).

[h] By FAB mass spectroscopy.

side the phenyl carbon region permitted assignment to C_β. A triplet signal centred at δ 141.4 ppm, partially overlapping with the dppe phenyl resonances, was assigned to C_α of **5** based upon (i) the estimated coupling constant of 26.3 Hz, typical of $^2J(P\text{–}C_\alpha)$ in these systems, (ii) a shift of C_α to high field by approximately 10 ppm by comparison with $[Mo(C{\equiv}CPh)(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ and (iii) the absence of a corresponding triplet signal in this region of the ^{13}C-NMR spectrum of the analogous Bu^t derivative **4**. Some interesting points also arise from comparison of the data for **4** and **5** with the related complexes $[Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)]$ (R = Bu^t or Ph) and $[Ru(C{\equiv}CBu^t)(dppe)(\eta\text{-}L')]$ [$L' = C_5Me_5$ or C_9H_7 (indenyl)] (see Table 3). Firstly, it is clear that even allowing for differences in solvent, the chemical shift of C_α is markedly dependent on the metal centre to which it is attached, with the $Mo(dppe)(\eta\text{-}C_7H_7)$ auxiliary promoting the shift to lowest field. Secondly the typical value for $^2J(P\text{–}C_\alpha)$ in complexes of both the $Mo(CO)(PMe_3)(\eta\text{-}C_7H_7)$ and $Mo(dppe)(\eta\text{-}C_7H_7)$ auxiliaries is of the order of 27 Hz. This is very similar to $^2J(P\text{–}C_\alpha)$ values observed for alkynyl phosphine complexes of $Ru(\eta\text{-}L')$ auxiliaries but smaller than typical values for the corresponding iron analogues.

The improved synthesis of $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ together with the extended range of derivatives made available by the current work now provide a basis with which to explore the chemistry of the dicarbonyl systems. To confirm the feasibility of this project, the reaction of $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ with tetracyanoethene (tcne) was investigated; the addition of tcne to transition-metal alkynyl complexes is a well established reaction and proceeds via a σ-cyclobutenyl intermediate to a ring-opened σ-butadienyl product [10,11]. Treatment of a green solution of $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ with tcne in CH_2Cl_2 resulted in a gradual colour change to brown–red accompanied by the disappearance of ν(C≡C) in the IR spectrum and an increase in $\nu(CO)_{average}$ by approximately 18 cm^{-1}. The σ-butadienyl product, $[Mo\{C({=}C(CN)_2)C(Ph){=}C(CN)_2\}(CO)_2(\eta\text{-}C_7H_7)]$ **6** was isolated as a maroon solid and characterised as detailed in Table 1 and Table 2. The assignment of **6** as a σ-butadienyl complex is based principally upon the $^{13}C\{^1H\}$-NMR data from which it is clear that resonances assigned to C_{1-4} (numbering as in Scheme 1) correspond very closely with those reported for $[M'\{C({=}C(CN)_2)C(Ph){=}C(CN)_2\}]$ [$\delta(^{13}C)$, (ppm): $M' = Fe(CO)_2(\eta\text{-}C_5H_5)$, 215.1, C_3; 181.2, C_2; 98.0, C_4; 74.9, C_1; $M' = Ru(CNBu^t)_2(\eta\text{-}C_5H_5)$, 226.2, C_3; 179.7, C_2; 90.8, C_4; 69.3, C_1] [11]. As with the alkynyl complexes the main difference is in the chemical shift of the metal-bound carbon, C_3, and again the cycloheptatrienylmolybdenum system promotes a shift to low field.

Table 2

^{1}H- and ^{13}C-NMR data for $[Mo(C\equiv C\mathit{R})L_2(\eta\text{-}C_7H_7)]$[a]

Complex	^{1}H-NMR data			^{13}C-NMR			
	C_7H_7	L	$C\equiv C\mathit{R}$	C_7H_7	L	C_α, C_β	$C\equiv C\mathit{R}$
1	5.32		1.11, Bu^t	94.4	216.8	121.4, 88.7	32.3, C*Me*$_3$; 29.1, *C*Me$_3$
2[b]	5.39		0.11, Si*Me*$_3$	94.5	215.3	135.0, 120.6	1.5, Si*Me*$_3$
3[b]	5.45		4.16, q, (7.1), *CH*$_2$Me; 1.29, t, (7.1), CH$_2$*Me*	94.8	213.7	127.1, 105.9	152.6, *C*O$_2$Et; 60.9, 14.3 CO$_2$*Et*
4[c]	4.66	7.82, m, 7.37, m, 7.25, m, Ph (dppe); 2.60, m, 2.20, m, C*H*$_2$ (dppe)	0.40, Bu^t	86.6	141.9–127.3, Ph (dppe); 26.7, m, *C*H$_2$ (dppe)	113.1, t, {26.8}, C_α[d]	31.4, C*Me*$_3$; 28.6, *C*Me$_3$
5[c]	4.82, t, {2.1}	7.85, m, 7.48, m, 7.40, m, 7.33, m, Ph (dppe); 2.49, m, 2.11, m, C*H*$_2$ (dppe)	6.84 (2H), m, 6.74 (1H), m, 6.03 (2H), m, Ph	86.8	141.7–127.1, Ph (dppe); 26.3, m, *C*H$_2$ (dppe)	141.4, t, {26.3}, C_α;[e] 121.6, C_β	122.6 [f]
6[g]	5.65		7.77, m, $C_4(CN)_4$*Ph*	98.5	215.9, 213.4		236.0, C_3; 182.5, C_2; 89.9, C_4; 72.9, C_1; 133.9, 132.5, 130.6, 129.4, Ph; 118.0, 114.0, 113.7, 112.9, *C*N
7[b,h]	5.40		0.15 Si*Me*$_3$	94.7	214.0	114.2, C_α; 95.9, C_β	90.8, C_γ; 74.8, C_δ; 0.2 Si*Me*$_3$
8[h,j]	5.42		1.66, C_δ*H*	94.9	214.9	111.6, C_α; 94.4, C_β	71.1, C_γ; 57.1, C_δ
9[h]	5.09, d, {2.6}	1.42, d, {8.5}, P*Me*$_3$	1.64, d, {1.8}, C_δ*H*	90.8, d, {0.8}	232.3, d, {19.3}, CO; 18.8, d, {26.9}, P*Me*$_3$	125.6, d, {26.2}, C_α; 93.7, C_β	71.7, d, {4.4}, C_γ; 56.2, d, {2.5}, C_δ

[a] 300 MHz ^{1}H-NMR spectra, 75 MHz ^{13}C-NMR spectra; all signals singlets unless stated otherwise, d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants in Hz indicated in parentheses: ( ) indicates J(H–H), { } indicates J(P–H) or J(P–C). Chemical shifts downfield from $SiMe_4$, spectra recorded in CD_2Cl_2 unless stated otherwise.

[b] In $CDCl_3$.

[c] Trace quantity of $CoCp_2$ added to NMR sample.

[d] C_β overlapping with dppe Ph resonances.

[e] C_α resonance partially overlapping with dppe Ph resonances.

[f] Other $C\equiv C\mathit{Ph}$ resonances overlapping with dppe Ph.

[g] In acetone-d-6, numbering scheme in **6**: see Scheme 1.

[h] Assignment of C_4 chain in complexes **7**, **8** and **9**: $C_\alpha\equiv C_\beta-C_\gamma\equiv C_\delta-R$.

[j] H-coupled ^{13}C-NMR data for **8**, J(C–H) in parentheses: 111.6 (1), 94.4 (7), 71.1 (51), 57.1 (253)

Table 3
^{13}C-NMR data for the alkynyl carbons C$_\alpha$ and C$_\beta$ in selected alkynyl complexes[a]

Complex	C$_\alpha$	^2J(P–C$_\alpha$)	C$_\beta$	Solvent	Reference
[Mo(C≡CBu^t)(CO)(PMe$_3$)(η-C$_7$H$_7$)]	102.1	28.2	119.0	C$_6$D$_6$	[2]
[Mo(C≡CBu^t)(dppe)(η-C$_7$H$_7$)]	113.1	26.8	[b]	CD$_2$Cl$_2$	This work
[Fe(C≡CBu^t)(dppe)(η-C$_5$Me$_5$)]	107.0	40	125.3	C$_6$D$_6$	[7]
[Ru(C≡CBu^t)(dppe)(η-C$_5$Me$_5$)]	102.2	25	116.4	C$_6$D$_6$	[8]
[Ru(C≡CBu^t)(dppe)(η-C$_9$H$_7$)]	89.0	25.4	118.0	CD$_2$Cl$_2$	[9]
[Mo(C≡CPh)(CO)(PMe$_3$)(η-C$_7$H$_7$)]	126.3	27.2	112.7	C$_6$D$_6$	[2]
[Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)]	141.4	26.3	121.6	CD$_2$Cl$_2$	This work
[Fe(C≡CPh)(dppe)(η-C$_5$Me$_5$)]	137.4	40	120.5	CDCl$_3$	[7]

[a] Chemical shifts in ppm, ^2J(P–C$_\alpha$) in Hz.

[b] C$_\beta$ overlapping with dppe phenyl resonances.

2.2. Butadiynyl complexes [Mo(C≡CC≡CR)(CO)L(η-C$_7$H$_7$)] (L = CO or PMe$_3$)

The synthesis and reactions of metal butadiynyl complexes, M–C≡CC≡CH, have received much recent attention [12–17]. In particular the application of butadiynyl systems to the synthesis of butadiyndiyl complexes in which a C$_4$ chain links two metal centres is the focus of a growing area of research. We are seeking to extend such investigations to the cycloheptatrienylmolybdenum system which offers the advantages of a well behaved redox chemistry and highly resolved esr spectral data [4]. As the first step in our investigations we now report syntheses of the butadiynyl complexes [Mo(C≡CC≡CR)(CO)L(η-C$_7$H$_7$)] (L = CO, R = SiMe$_3$ or H; L = PMe$_3$, R = H).

A number of routes have been developed to butadiynyl systems but that reported for [Fe(C≡CC≡CH)(CO)$_2$(η-L′)] (L′ = C$_5$H$_5$ [12] or C$_5$Me$_5$ [14,15]) involving [Fe(C≡CC≡CSiMe$_3$)(CO)$_2$(η-L′)] as an intermediate is the most appropriate for extension to the cycloheptatrienylmolybdenum system. Thus, in a synthesis analogous to that developed for the alkynyl complexes [Mo(C≡CR)(CO)$_2$(η-C$_7$H$_7$)] (R = Ph, Bu^t or SiMe$_3$), the C≡CC≡CSiMe$_3$ ligand can be introduced at the Mo(CO)$_2$(η-C$_7$H$_7$) centre by reaction of [MoBr(CO)$_2$(η-C$_7$H$_7$)] with LiC≡CC≡CSiMe$_3$. Treatment of a cooled solution of [MoBr(CO)$_2$(η-C$_7$H$_7$)] in THF with a THF solution of LiC≡CC≡CSiMe$_3$ followed by low temperature chromatographic work up of the reaction mixture resulted in the isolation of [Mo(C≡CC≡CSiMe$_3$)(CO)$_2$(η-C$_7$H$_7$)], **7** as a green solid in a 60% yield. The IR spectrum of this complex exhibits two bands in the ν(C≡C) stretching region (ν(C≡C), (CH$_2$Cl$_2$) 2161, 2117 cm^{-1}) closely similar to the corresponding data for [Fe(C≡CC≡CSiMe$_3$)(CO)$_2$(η-C$_5$Me$_5$)], (ν(C≡C), (KBr/CH$_2$Cl$_2$) 2171, 2119 cm^{-1}] [15]. An additional IR feature common to **7** and [Fe(C≡CC≡CSiMe$_3$)(CO)$_2$(η-C$_5$Me$_5$)] is the unexpected observation of a third band in the ν(CO) stretching region—in the case of **7** this additional band is a shoulder at 2003 cm^{-1}. An explanation based on coupling of normal modes has been suggested [15].

The standard method for conversion of M–C≡CC≡CSiMe$_3$ to M–C≡CC≡CH involves reaction with a source of the fluoride ion [12,15] and treatment of **7** with potassium fluoride in a refluxing methanol/THF mixture (1:1) afforded the desired butadiynyl product [Mo(C≡CC≡CH)(CO)$_2$(η-C$_7$H$_7$)], **8** which was isolated as a green solid in a 55% yield. An alternative, more direct synthesis of **8** was also explored. The reaction of the dilithiated butadiyndiyl anion Li$_2$C≡CC≡C with [FeCl(CO)$_2$(η-C$_5$H$_5$)] is reported to give either [{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-C≡CC≡C)] or [Fe(C≡CC≡CH)(CO)$_2$(η-C$_5$H$_5$)] dependent upon reaction conditions [12] and therefore an identical approach starting from [MoBr(CO)$_2$(η-C$_7$H$_7$)] was investigated. However, despite numerous attempts, the reaction of [MoBr(CO)$_2$(η-C$_7$H$_7$)] with Li$_2$C≡CC≡C (prepared from hexachloro-1,3-butadiene and Bu^{n}Li [18]) led to the isolation of [Mo(C≡CC≡CH)(CO)$_2$(η-C$_7$H$_7$)] **8** in low yield only. An analogous reaction between Li$_2$C≡CC≡C and [MoBr(CO)(PMe$_3$)(η-C$_7$H$_7$)] similarly produced the phosphine substituted derivative [Mo(C≡CC≡CH)(CO)(PMe$_3$)(η-C$_7$H$_7$)], **9**, also in low yields.

The ^{13}C-NMR spectroscopic data for **7**, **8** and **9** are of immediate interest for comparison with existing butadiynyl complexes [14–16]. For complexes **8** and **9**, the assignment of ^{13}C-NMR resonances in the C$_\alpha$≡C$_\beta$C$_\gamma$≡C$_\delta$H chain is based upon signal intensity (to identify C$_\delta$H) and the magnitudes of J(C–H) (**8**, proton coupled spectrum) or J(C–P) (**9**, proton decoupled spectrum) (see Table 2). The chemical shifts of C$_\beta$, C$_\gamma$ and C$_\delta$ are self-consistent and compare well with other butadiynyl complexes [16]. Chemical shifts for C$_\alpha$ reveal the expected trends of (i) a shift to low field with an increased degree of phosphine substitution and (ii) a shift to low field by comparison with the analogous iron complexes [Fe(C≡CC≡CH)(CO)L(η-C$_5$H$_5$)], (δ, (ppm), C$_\alpha$: L = CO, 96.8; L = PPh$_3$, 109.4), [12,14]. In the phosphine derivative **9**, the magnitude of $^2J(P-C_\alpha)$ (26.2 Hz) is typical of $^2J(P-C_\alpha)$ observed for the alkynyl complexes [Mo(C≡CR)(CO)(PMe$_3$)(η-C$_7$H$_7$)] [2], and assignments for C_β and C_γ are based upon the generally accepted trend $^4J(P-C_\gamma) > {}^3J(P-C_\beta)$ [16]. A full attribution of the ^{13}C-NMR data for the C$_4$ chain of the trimethylsilylbutadiynyl complex **7** cannot be made with the aid of J(C–P) or J(C–H) data but the assignments in Table 2 are based upon the expected low field shift of C_α in the cycloheptatrienylmolybdenum system and the general observation for δ_C values in the C$_4$R ligand that $C_\alpha > C_\beta > C_\gamma > C_\delta$ [14]. Moreover the ^{13}C-NMR chemical shifts for C_β, C_γ and C_δ in **7** compare well with those reported for [Fe(C≡CC≡CSiMe$_3$)(CO)$_2$(η-C$_5$Me$_5$)] (δ_C, (ppm), (C$_6$D$_6$): 96.5, C_β; 94.7, C_γ; 69.5, C_δ) [15].

3. Experimental

3.1. General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The compounds [MoBr(CO)L(η-C$_7$H$_7$)] (L = CO, [19]; L = PMe$_3$ [2]) and [Mo(C≡CR)(dppe)(η-C$_7$H$_7$)] (R = Bu^t or Ph) [1], were prepared by published procedures. Lancaster Synthesis supplied the alkynes HC≡CBu^t, HC≡CSiMe$_3$, HC≡CCO$_2$Et and Me$_3$SiC≡CC≡CSiMe$_3$. Hexachloro-1,3-butadiene and Bu^{n}Li (1.6 M solution in hexane) were purchased from Fluka and tetracyanoethene and the MeLi–LiBr complex (1.5 M solution in diethyl ether) from Aldrich; column chromatography was carried out on alumina (Brockmann activity II) supplied by Merck. The 300 MHz ^{1}H- and 75 MHz ^{13}C{^{1}H}-NMR spectra were recorded on Bruker AC 300 E, Varian Associates XL 300 or Varian Unity Inova 300 spectrometers. IR spectra were obtained on a Perkin Elmer FT 1710 spectrometer and mass spectra were recorded using Kratos Concept 1S (FAB spectra) or Micromass Trio 2000 (EI spectra) instruments. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

3.2. Preparations

3.2.1. [Mo(C≡CBu^t)(CO)$_2$(η-C$_7$H$_7$)] **1**

A solution of LiC≡CBu^t [prepared from HC≡CBu^t (0.48 g, 5.85 mmol) and Bu^{n}Li (2.9 cm^3 of a 1.6 M solution in hexane) in THF (10 cm^3)] was added dropwise to a stirred, cooled (−78°C) solution of [MoBr(CO)$_2$(η-C$_7$H$_7$)] (1.00 g, 3.10 mmol) in THF (15 cm^3). The reaction mixture was allowed to warm slowly to 0°C resulting in a colour change from green to yellow–brown. After 10 min at 0°C the entire reaction mixture was transferred to an n-hexane–alumina chromatography column maintained at −30°C. Elution with n-hexane–CH$_2$Cl$_2$ (1:1) gave a green band which was collected and evaporated to dryness. The residue was dissolved in diethyl ether, filtered then n-hexane added and the volume of the solution reduced to ca. 5 cm^3. Subsequent cooling to −78°C gave the product, **1**, as a green, crystalline solid; yield 0.12 g (12%). The preparation of [Mo(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)] in a 71% yield from [MoBr(CO)$_2$(η-C$_7$H$_7$)] (2.00 g, 6.19 mmol) in THF (120 cm^3) and LiC≡CPh [prepared from HC≡CPh (1.07 g, 10.48 mmol) and Bu^{n}Li (6.2 cm^3 of a 1.6 M solution in hexane) in THF (20 cm^3)] was effected by an identical procedure except that reaction proceeded over a period of 30 min at −30°C and the temperature of the reaction mixture was not allowed to exceed −30°C.

3.2.2. [Mo(C≡CSiMe$_3$)(CO)$_2$(η-C$_7$H$_7$)] **2**

A solution of LiC≡CSiMe$_3$ [prepared from HC≡CSiMe$_3$ (0.29 g, 2.95 mmol) and Bu^{n}Li (1.45 cm^3 of a 1.6 M solution in hexane) in THF (10 cm^3)] was added dropwise to a stirred, cooled (−78°C) solution of [MoBr(CO)$_2$(η-C$_7$H$_7$)] (0.50 g, 1.55 mmol) in THF (10 cm^3). The reaction mixture was allowed to warm slowly to −10°C resulting in a colour change from green to yellow–brown. After 10 min the entire reaction mixture was transferred to an n-hexane–alumina chromatography column maintained at −30°C. Elution with n-hexane–CH$_2$Cl$_2$ (1:1) then neat CH$_2$Cl$_2$ gave a green band which was collected and evaporated to dryness. The residue was recrystallised from CH$_2$Cl$_2$-n-hexane then diethyl ether-n-hexane to give **2** as a green solid; yield 0.21 g (40%).

3.2.3. [Mo(C≡CCO$_2$Et)(CO)$_2$(η-C$_7$H$_7$)] **3**

A stirred suspension of [MoBr(CO)$_2$(η-C$_7$H$_7$)] (1.00 g, 3.10 mmol) in triethylamine (35 cm^3) maintained at 0°C in a foil protected flask was treated with HC≡CCO$_2$Et (0.30 g, 3.10 mmol) and CuI (0.01 g). The [MoBr(CO)$_2$(η-C$_7$H$_7$)] rapidly dissolved to give a yellow brown solution and after 5 min the reaction mixture was evaporated to dryness. The residue, dissolved in CH$_2$Cl$_2$ (5 cm^3), was transferred to an alumina-n-hexane column and elution with CH$_2$Cl$_2$-n-hexane (1:1) gave a green band which was collected and evaporated to dryness. Recrystallisation of the residue from CH$_2$Cl$_2$-n-hexane gave **3** as a green–brown solid; yield 0.33 g (31%).

3.2.4. [Mo{C(=(CN)$_2$)C(Ph)=C(CN)$_2$}(CO)$_2$(η-C$_7$H$_7$)] **6**

A solution of [Mo(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)] (0.195 g, 0.57 mmol) and tcne (0.080 g, 0.62 mmol) in CH$_2$Cl$_2$ (30 cm^3) was stirred for 45 min resulting in a colour change from green to red–brown. The reaction mixture was filtered, reduced in volume and *n*-hexane added to precipitate **6** as a maroon solid; yield 0.08 g (30%).

3.2.5. [Mo(C≡CC≡CSiMe$_3$)(CO)$_2$(η-C$_7$H$_7$)] **7**

A stirred solution of Me$_3$SiC≡CC≡CSiMe$_3$ (0.750 g, 3.87 mmol) in THF (25 cm^3) at −78°C was treated with MeLi–LiBr (2.6 cm^3 of a 1.5 M solution in diethyl ether) and the reaction mixture was then allowed to warm to room temperature (r.t.) over a period of 3 h. The solution of LiC≡CC≡CSiMe$_3$, thus prepared, was added to a stirred, cooled (−78°C) solution of [MoBr(CO)$_2$(η-C$_7$H$_7$)] (1.00 g, 3.10 mmol) in THF (20 cm^3). The reaction mixture was allowed to warm slowly to r.t. over a period of 1 h and retained at r.t. for a further 20 min. The entire reaction mixture was then transferred to an *n*-hexane–alumina chromatography column maintained at −30°C and elution with *n*-hexane–CH$_2$Cl$_2$ (1:1) gave a green band which was collected and evaporated to dryness. The residue was extracted with toluene, filtered and evaporated to dryness. Subsequent recrystallisation from CH$_2$Cl$_2$-*n*-hexane gave **7** as a green solid; yield 0.680 g (60%).

3.2.6. [Mo(C≡CC≡CH)(CO)$_2$(η-C$_7$H$_7$)] **8**

3.2.6.1. Method a. Potassium fluoride (0.090 g, 1.55 mmol) was added to a solution of [Mo(C≡CC≡CSiMe$_3$)(CO)$_2$(η-C$_7$H$_7$)] **7**, (0.450 g, 1.24 mmol) in 40 cm^3 of a methanol/THF mixture (1:1). The reaction mixture was refluxed for 5 h to give a green–brown solution which was evaporated to dryness. The residue, dissolved in CH$_2$Cl$_2$ (10 cm^3) was transferred to an *n*-hexane–alumina chromatography column and elution with *n*-hexane–CH$_2$Cl$_2$ (1:1) then neat CH$_2$Cl$_2$ gave a green band which was collected and evaporated to dryness. Subsequent recrystallisation from CH$_2$Cl$_2$-*n*-hexane gave **8** as a green solid; yield 0.200 g (55%).

3.2.6.2. Method b. Hexachloro-1,3-butadiene (0.44 g, 1.69 mmol) in THF (2 cm^3) was added dropwise over a period of 10 min to a stirred, cooled (−78°C) solution of Bu^{n}Li (4.50 cm^3 of a 1.6 M solution in hexane) in THF (5 cm^3). After the addition was complete, the reaction mixture was maintained at −78°C for 10 min and then allowed to stir at r.t. for 1.5 h. The solution of Li$_2$C≡CC≡C, thus prepared, was re-cooled to −78°C and [MoBr(CO)$_2$(η-C$_7$H$_7$)] (0.50 g, 1.55 mmol) added as a solid. The brown reaction solution was allowed to warm to 0°C and was then retained at this temperature for 10 min. The entire reaction mixture was then transferred to an *n*-hexane–alumina chromatography column maintained at −30°C and elution with *n*-hexane–CH$_2$Cl$_2$ (1:1) then neat CH$_2$Cl$_2$ gave a green band which was collected and evaporated to dryness. The product was recrystallised from CH$_2$Cl$_2$-*n*-hexane to give **8** as a green solid; yield 0.056 g (12%).

3.2.7. [Mo(C≡CC≡CH)(CO)(PMe$_3$)(η-C$_7$H$_7$)] **9**

Hexachloro-1,3-butadiene (0.39 g, 1.49 mmol) in THF (2 cm^3) was added dropwise over a period of 10 min to a stirred, cooled (−78°C) solution of Bu^{n}Li (4.0 cm^3 of a 1.6 M solution in hexane) in THF (5 cm^3). After addition was complete, the reaction mixture was maintained at −78°C for 10 min and then allowed to stir at r.t. for 1.5 h. The solution of Li$_2$C≡CC≡C, thus prepared, was then transferred to a stirred, cooled (−78°C) solution [MoBr(CO)(PMe$_3$)(η-C$_7$H$_7$)] (1.00 g, 2.69 mmol) in THF (5 cm^3). The reaction mixture was allowed to warm to r.t. and the resulting brown solution was then transferred to an *n*-hexane–alumina chromatography column maintained at −30°C. Elution with *n*-hexane–CH$_2$Cl$_2$ (1:1) gave a green–brown band which was collected and evaporated to dryness. The residue was recolumned at r.t. on an *n*-hexane–alumina column using *n*-hexane–CH$_2$Cl$_2$ (2:1) as eluant. The first green band from the column was collected, evaporated to dryness and the residue recrystallised from diethyl ether-*n*-hexane to give **9** as a light green solid; yield 0.030 g (3%).

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