

Synthesis and structure of the diyanyl complexes [Mo(C≡CC≡CR)L₂(η-C₇H₇)], L₂ = chelate N- or P-donor ligand, R = SiMe₃ or H: X-ray crystal structures of [Mo(C≡CC≡CSiMe₃)(2,2'-bipyridine)(η-C₇H₇)] and [Mo(C≡CC≡CH)(Ph₂PCH₂CH₂PPh₂)(η-C₇H₇)]

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Abstract

The reaction of LiC≡CC≡CSiMe₃ with [MoBr(*N-N*)(η-C₇H₇)] in thf affords the diyanyl complexes [Mo(C≡CC≡CSiMe₃)(*N-N*)(η-C₇H₇)], **1**, *N-N* = 2,2'-bipyridine (bipy); **2**, *N-N* = 1,4-Bu₂-1,3-diazabutadiene (Bu^t-dab); an analogous procedure yields [Mo(C≡CC≡CSiMe₃)(CO)(PPh₃)(η-C₇H₇)], **3** starting from [MoBr(CO)(PPh₃)(η-C₇H₇)]. Replacement of bipy in complex **1** with Ph₂PCH₂CH₂PPh₂ (dppe) in refluxing toluene gives [Mo(C≡CC≡CSiMe₃)(dppe)(η-C₇H₇)], **4**. Proto-desilylation of **2** and **4** leads to formation of the unsubstituted diyanyl [Mo(C≡CC≡CH)L₂(η-C₇H₇)] (**5**, L₂ = Bu^t-dab; **6**, L₂ = dppe). Cyclic-voltammetric studies in CH₂Cl₂ reveal that each of complexes **1**, **2** and **4-6** undergo reversible one-electron oxidation processes on the electrochemical time-scale. The X-ray crystal structures of complexes **1** and **6** are reported; the bipyridine complex **1**, exhibits a π-π stacking interaction between the bipy ligands of adjacent molecules leading to a head-to-head interaction between diyanyl ligands and a resultant substantial bending of the diyanyl chain.

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1. Introduction

Investigations into metal diyanyl complexes constitute an area of intense current activity in organometallic chemistry [1,2]. These studies are driven by potential applications as precursors to one-dimensional molecular wires and metal containing polymers. An important feature of many recent advances has been the incorporation of redox-active, electron-rich metal centres into metal diyanyl complexes and subsequent use as precursors to all-carbon bridged, diyandiyl

complexes M-C≡CC≡C-M; leading metal end-caps M for this purpose are the d⁶ centres Fe(dppe)Cp* [3,4], Ru(dppe)Cp* [5-7] and Re(NO)(PPh₃)Cp* [8,9] (dppe = Ph₂PCH₂CH₂PPh₂, Cp* = C₅Me₅). It is well established that the identity of the metal end-cap group, M, plays a key role in the properties and electronic structure of all-carbon bridged systems [M-C≡CC≡C-M]^{z+}, but this notwithstanding, the range of electron-rich metal end-cap groups is still relatively limited with none to rival the strongly electron donating capacity of the Fe(dppe)Cp* system.

The isoelectronic character of MCp/MCp* (M = Fe, Ru) and the d⁶, cycloheptatrienyl molybdenum system Mo(η-C₇H₇) is well recognised [10,11] as a factor in promoting analogies in structure and reactivity – the large

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steric requirements of the C_7H_7 ligand (cone angle 154°) [12] make comparison with the Cp^* system particularly appropriate. We have demonstrated that complexes of the $Mo(dppe)(\eta-C_7H_7)$ auxiliary not only exhibit reactivity patterns analogous to those of $M(dppe)Cp^*$ ($M = Fe$ or Ru) [13,14] systems but also possess very electron-rich metal centres and, as 17-electron radicals, highly resolved epr spectra [15]. These properties render the $MoL_2(\eta-C_7H_7)$ auxiliary as a potential novel end-cap group in investigations into all-carbon bridged organometallics, delivering the unique combination of a second row metal with the electron-donor capacity of the $Fe(dppe)Cp^*$ auxiliary and the application of a highly resolved epr probe previously only possible with the $Re(NO)(PPh_3)Cp^*$ end-cap.

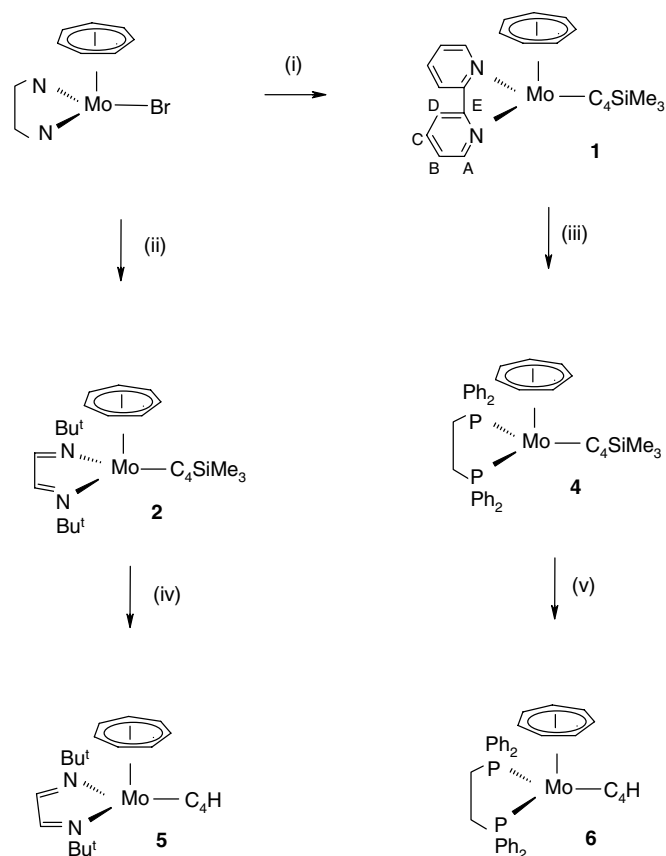
Investigations into metal-diyne and all-carbon-bridged diyndiyl complexes of the group VI metals are well developed for d^4 systems based upon $Mo(CO)(dppe)Cp$ [16,17] and $W(CO)_3(\eta-C_5R_5)$ ($R = H, Me$) [18,19] as supporting fragments whilst we have previously reported the syntheses of butadiynyl derivatives of dicarbonyl cycloheptatrienyl molybdenum complexes $[Mo(C\equiv CC\equiv CR)(CO)_2(\eta-C_7H_7)]$ ($R = SiMe_3$ or H) [20]. However, where the redox chemistry of these examples has been investigated [19] it is clear that the presence of carbonyl acceptor groups results in poor accessibility of higher oxidation states and therefore limited application as end-caps in all-carbon bridged organometallics. This paper describes the advance of our studies to syntheses of the vital electron-rich systems $[Mo(C\equiv CC\equiv CR)L_2(\eta-C_7H_7)]$ ($R = SiMe_3$ or H) [$L_2 = 2,2'$ -bipyridine (bipy), 1,4- Bu^t -1,3-diazabutadiene (Bu^t -dab) and $dppe$].

2. Results and discussion

2.1. Synthetic studies

The substance of the synthetic work is summarised in Scheme 1 and characterisation details for the six new butadiynyl complexes described are presented in Table 1 (microanalytical, infrared, mass spectroscopic and electrochemical data) and Table 2 (1H and $^{13}C\{^1H\}$ NMR data). The synthetic studies focused on three objectives as follows: (i) development of electron-rich diyne complexes with N-donor supporting ligands, an approach not so far adopted for examples based upon MCp^* ($M = Fe$ or Ru) systems; (ii) syntheses of phosphine derivatives including the $dppe$ complex, $[Mo(C\equiv CC\equiv CSiMe_3)(dppe)(\eta-C_7H_7)]$, the benchmark for comparisons with the analogous chemistry of Fe and Ru ; and (iii) proto-desilylation reactions to afford $[Mo(C\equiv CC\equiv CH)L_2(\eta-C_7H_7)]$, the key precursors to diyndiyl- and tetrayndiyl- [21,22] bridged complexes.

We have previously described the synthesis and redox chemistry of the complexes $[MoBr(N-N)(\eta-C_7H_7)]$ ($N-N = bipy$ or Bu^t -dab) and the halide substitution reactions of these complexes with $LiMe$ to yield the corresponding methyl derivatives [23]. Similarly, solutions of $[MoBr(N-$



Scheme 1. Reagents and conditions (i) $N-N = bipy$, LiC_4SiMe_3 , thf, 2 h; (ii) $N-N = Bu^t$ -dab, LiC_4SiMe_3 , thf, 2 h; (iii) $dppe$, toluene reflux, 3 h; (iv) KF , $MeOH/thf$ reflux, 15 h; and (v) Bu_4NF , thf, 90 min.

$N)(\eta-C_7H_7)]$ in thf react with $LiC\equiv CC\equiv CSiMe_3$ [24,25] to give the diyne products $[Mo(C\equiv CC\equiv CSiMe_3)(N-N)(\eta-C_7H_7)]$ (**1**, $N-N = bipy$; **2**, $N-N = Bu^t$ -dab) which were isolated in moderate to good yields as purple–red solids, following purification by column chromatography on alumina. An analogous procedure starting from the mono-phosphine complex $[MoBr(CO)(PPh_3)(\eta-C_7H_7)]$ gave green–brown $[Mo(C\equiv CC\equiv CSiMe_3)(CO)(PPh_3)(\eta-C_7H_7)]$, **3**. However, attempts to extend the synthetic method to formation of the $dppe$ derivative, $[Mo(C\equiv CC\equiv CSiMe_3)(dppe)(\eta-C_7H_7)]$, **4**, were unsuccessful; an observation which concurs with the result of the analogous reaction in the chemistry of the $Fe(dppe)Cp^*$ system [26]. Several synthetic routes to **4** were explored including photolysis of the previously reported dicarbonyl $[Mo(C\equiv CC\equiv CSiMe_3)(CO)_2(\eta-C_7H_7)]$ with $dppe$ in toluene which did afford **4** in low yield and purity (identified by $\nu(C\equiv C)$ infra-red data and mass spectroscopy). However, a novel, high yield route to **4** was effected by a simple, thermally driven, ligand substitution in complex **1** via replacement of $bipy$ by $dppe$. Thus, reflux of a purple, toluene solution of **1** with a small excess of $dppe$ rapidly resulted in a colour change to a green–brown solution from which **4** was isolated as a deep green solid following purification by column chromatography on celite (the complex

Table 1
Microanalytical, infrared, mass spectroscopic and electrochemical data

| Complex | Analysis(%) ^a | | | Infrared ^b $\nu(\text{C}\equiv\text{C})$ (cm ⁻¹) | Mass spectral data ^c | Electrochemical data ^d |
|--|--------------------------|-----------|-----------|---|--|-----------------------------------|
| | C | H | N | | | |
| 1 [Mo(C≡CC≡CSiMe ₃)(bipy)(η-C ₇ H ₇)] | 61.9 (62.1) | 5.5 (5.2) | 5.9 (6.0) | 2151 (m), 2111 (m), 1991 (w) | 466 (M ⁺), 345 ([M-C ₄ SiMe ₃] ⁺) ^e | -0.12 (1.0) |
| 2 [Mo(C≡CC≡CSiMe ₃)(Bu ^t -dab)(η-C ₇ H ₇)] | 60.6 (60.3) | 7.6 (7.5) | 5.9 (5.9) | 2154 (m), 2113 (m) | 478 (M ⁺), 421, ([M-Bu ^t] ⁺) 357 ([M-C ₄ SiMe ₃] ⁺) | 0.30 (1.0) |
| 3 [Mo(C≡CC≡CSiMe ₃)(CO)(PPh ₃)(η-C ₇ H ₇)] | 66.2 (66.2) | 5.2 (5.2) | | 2156 (m), 2114 (m), 1937 (s, CO) | 572 ([M-CO] ⁺), 450 ([M-CO-C ₄ SiMe ₃] ⁺) | 0.49 (0.85) |
| 4 [Mo(C≡CC≡CSiMe ₃)(dppe)(η-C ₇ H ₇)] | 67.8 (68.0) | 6.0 (5.7) | | 2153 (w), 2105 (sh), 2090 (m), 2063 (sh), 1976 (w) | 708 (M ⁺), 587 ([M-C ₄ SiMe ₃] ⁺) | -0.04 (1.0) |
| 5 [Mo(C≡CC≡CH)(Bu ^t -dab)(η-C ₇ H ₇)] | 61.9 (62.1) | 7.1 (6.9) | 6.5 (6.9) | 3301 (m) ≡CH, 2120 (m) | 406 (M ⁺), 357 ([M-C ₄ H] ⁺) | 0.30 (1.0) |
| 6 [Mo(C≡CC≡CH)(dppe)(η-C ₇ H ₇)] | 69.7 (70.0) | 5.3 (5.0) | | 3300 (m) ≡CH, 2098 (m), 1956 (w) | 636 (M ⁺), 587 ([M-C ₄ H] ⁺) ^f | -0.04 (1.0) |

^a Calculated values in parentheses.

^b Solution spectra in CH₂Cl₂.

^c FAB mass spectra unless stated otherwise, *m/z* values based on ⁹⁸Mo.

^d By cyclic voltammetry. *E*^o values in V vs. Ag/AgCl electrode. Conditions: CH₂Cl₂ solvent, 0.1 M [Bu₄ⁿN][PF₆] supporting electrolyte, 20 °C, Pt working electrode, sweep rate 0.100 Vs⁻¹. The ferrocene-ferrocenium couple (0.54 V vs. Ag/AgCl) was used as internal reference, values in parentheses are *i*_p^c/*i*_p^A at scan rate 0.100 V s⁻¹.

^e Electrospray spectrum.

^f MALDI spectrum.

Table 2
¹H and ¹³C{¹H} NMR data^a for complexes [Mo(C≡CC≡CR)L₂(η-C₇H₇)]

| | ¹ H NMR | | | ¹³ C{ ¹ H} NMR | | | | | | |
|----------------------|--------------------|-------------------------------|--|--------------------------------------|----------------|----------------|----------------|------|-------------------------------|---|
| | R | C ₇ H ₇ | L ₂ | C _α | C _β | C _γ | C _δ | R | C ₇ H ₇ | L ₂ |
| 1 | 0.01 | 4.89 | 9.13, d (5.7), H _A ; 8.08, d, (8.2), H _D ; 7.46, m, H _C ; 7.11, m, H _B | 142.1 | 95.1 | 91.6 | 76.7 | -0.4 | 90.0 | 149.1, C _A , 147.6, C _E , 130.8, C _C 121.3, 120.5, C _B , C _D |
| 2 | 0.12 | 5.07 | 7.32, NCH, 1.50, NBu ^t | 134.6 | 92.0 | 91.6 | 74.5 | -0.2 | 89.9 | 140.0, NCH, 62.7, CMe ₃ , 31.4, CMe ₃ |
| 3 | 0.08 | 4.88, d, {2.3} | 7.54–7.37, Ph | 129.1, d, {23.8} | 99.4 | 92.4 | 74.2 | 0.4 | 92.8 | 230.4, d {17.6}, CO 136.1–128.3, PPh ₃ |
| 4^b | 0.05 | 4.77, t, {1.8} | 2.43, 2H, m, 2.05, 2H, m, PCH ₂ ; 7.75–7.29, m, PPh ₂ | 142.8, t, {25.0} | 105.1 {2} | 93.0, t, {4} | 75.7 | 0.6 | 87.8 | 26.9, m, PCH ₂ ; 140.5–128.1, PPh ₂ |
| 5 | 1.78 | 5.07 | 7.32, NCH, 1.50, NBu ^t | 131.2 | 90.4 | 71.8 | 58.2 | – | 89.8 | 140.0, NCH, 62.7, CMe ₃ , 31.4, CMe ₃ |
| 6^b | 1.65, t, {1.6} | 4.78, t, {2.2} | 2.46, 2H, m, 2.01, 2H, m, PCH ₂ ; 7.76–7.28, m, PPh ₂ | 138.7, t {25.1} | 103.6 | 72.7, t, {3.8} | 59.5 | – | 87.7 | 26.8, m, PCH ₂ ; 140.5–128.0, PPh ₂ |

^a 300 MHz ¹H, 75 MHz ¹³C{¹H} NMR spectra unless stated otherwise; d, doublet; t, triplet; m, multiplet; chemical shifts downfield from SiMe₄, coupling constants in Hz, *J*(H–H) as (), *J*(H–P) or *J*(C–P) as { }; in CD₂Cl₂ at ambient temperature, numbering/lettering as in Scheme 1.

^b 400 MHz ¹H, 100 MHz ¹³C{¹H} NMR spectra.

could not be eluted from other common chromatographic materials such as silica or alumina). An analogous reaction of the Bu^t-dab complex **2** with dppe did not proceed to give **4**; presumably the enhanced π-acceptor capacity of the Bu^t-dab ligand stabilises complex **2** with respect to substitution.

The final synthetic goal was to effect proto-desilylation of the SiMe₃ protected complexes **1–4** to yield products of the type [Mo(C≡CC≡CH)L₂(η-C₇H₇)], suitable as precursors for the construction of diyndiyl- and tetrayndiyl-bridged systems. Two reagents are commonly employed

for this purpose, KF and $\text{Bu}_4^{\text{n}}\text{NF}$; the appropriateness of each reagent is partly dependent upon the metal centre. Thus the $\text{Bu}^{\text{t}}\text{-dab}$ complex **2**, reacts with KF in refluxing thf/methanol to give $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{Bu}^{\text{t}}\text{-dab})(\eta\text{-C}_7\text{H}_7)]$, **5**, but the more electron-rich complexes **1** and **4** did not yield the required products under these conditions. However, treatment of the dppe derivative **4** in thf with 0.2 mole equivalents of a solution of $\text{Bu}_4^{\text{n}}\text{NF}$ in thf led to formation of $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$, **6**, which was isolated in good yield as a deep-brown solid following purification by chromatography on celite. The reaction of the bipy complex **1** with $\text{Bu}_4^{\text{n}}\text{NF}$ in thf also resulted in desilylation to give $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{bipy})(\eta\text{-C}_7\text{H}_7)]$ as a brown solid, identified by infrared (3301 m, ($\equiv\text{CH}$), 2113 m, 1967 w) and mass spectroscopic data ($m/z = 394$). However, attempted purification of this complex resulted in decomposition and further characterisation was therefore not achieved.

2.2. Spectroscopic and electrochemical data

The spectroscopic data for the new complexes **1–6** described here (Tables 1 and 2) augment an increasing body of data for electron-rich diyne systems. Key comparisons of infrared, $^{13}\text{C}\{^1\text{H}\}$ NMR, and electrochemical data for **4** and **6**, with closely related complexes $\text{M}-\text{C}\equiv\text{CC}\equiv\text{CR}$ [$\text{M} = \text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)$, $\text{Fe}(\text{dppe})\text{Cp}^*$, $\text{Ru}(\text{dppe})\text{Cp}^*$ and $\text{Mo}(\text{CO})(\text{dppe})\text{Cp}$; $\text{R} = \text{SiMe}_3$ or H], are presented in Table 3.

Infrared data for the SiMe_3 derivatives **1–4** reveal $\nu(\text{C}\equiv\text{C})$ stretching bands in the range 2156–1956 cm^{-1} . Complexes **2** and **3** each exhibit two bands in the region

2156–2113 cm^{-1} but the bipy and dppe derivatives are less straightforward with an additional third band below 2000 cm^{-1} . This phenomenon has been reported previously for $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)\text{L}_2(\eta\text{-C}_5\text{R}_5)]$ ($\text{L}_2 = \text{dppe}$, $\text{R} = \text{Me}$, $\text{M} = \text{Fe}$ or Ru ; $\text{L}_2 = 2\text{PPh}_3$, $\text{R} = \text{H}$, $\text{M} = \text{Ru}$) and is ascribed to Fermi coupling of one of the $\nu(\text{C}\equiv\text{C})$ modes with another oscillator [3,27]. An additional feature of **4**, not previously reported in infra red data for metal diyne complexes, is the observation of two shoulders (2105, 2063 cm^{-1}) on the main band at 2090 cm^{-1} ; these features were also present in a sample of **4** prepared by photolysis of $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ with dppe. Along the series $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$, **3** and **4** there is a steady decrease in wavenumber of the two main $\nu(\text{C}\equiv\text{C})(\text{CH}_2\text{Cl}_2)$ stretching bands as the extent of phosfine substitution increases (from 2161, 2117 cm^{-1} in $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ to 2153, 2090 cm^{-1} in **4**) and a similar pattern is observed for $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ and **6**. It is not prudent to attribute these trends to an increase in retrodonation to the butadiynyl ligand since the major interaction with the metal centre is thought to be principally as a σ -donor, π -donor ligand [1,28]. Nevertheless it is notable that the infra red data for the electron-rich pairs **4** with $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*]$ and **6** with $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*]$ are almost identical (see Table 3) yet clearly distinct from the Ru analogues $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*]$ ($\text{R} = \text{SiMe}_3$ or H). The desilylated complexes **5** and **6** are characterised by a high wavenumber $\nu(\equiv\text{CH})$ stretch at around 3300 cm^{-1} and only one main $\nu(\text{C}\equiv\text{C})$ band, moved to high wavenumber by approximately 10 cm^{-1} by comparison with the SiMe_3 precursor. The dppe derivative **6** again

Table 3
Key $^{13}\text{C}\{^1\text{H}\}$ NMR, IR and electrochemical data for diyne complexes $\text{M}-\text{C}\equiv\text{CC}\equiv\text{CR}$

| Complex | $^{13}\text{C}\{^1\text{H}\}$ NMR data ^a | | | | Infrared $\nu(\text{C}\equiv\text{C})$ ^b | CV Data ^c | Reference |
|---|---|------------------|-------------------|-------------------|--|----------------------|-----------|
| | C_α | C_β | C_γ | C_δ | | | |
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$, 4 | 142.8 (25.0) | 105.1 (2) | 93.0 (4) | 75.7 | 2153 w, 2105 sh, 2090 m, 2063sh, 1976 w ^d | -0.04 (1.0) | This work |
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ | 114.2 | 95.9 | 90.8 | 74.8 | 2161 m, 2117 m | | [20] |
| $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ | 142.2 (38) | 102.3 (2) | 96.2 (3) | 69.7 | 2162 w, 2081 s, 1977 m | 0.08 (1.0) | [3] |
| $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ | 120.1 | 115.8 | 96.6 | 66.9 | 2171 w, 2095 m, 1990 w ^e | 0.51 (irr) | [5] |
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})(\text{dppe})(\eta\text{-C}_5\text{H}_5)]$ | 137.0 (32) | 100.2 | 87.9 | 70.5 | 2185 w, 2065 w | | [16] |
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$, 6 | 138.7 (25.1) | 103.6 | 72.7 (3.8) | 59.5 | 2098 m, 1956 w | -0.04 (1.0) | This work |
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ | 111.6 | 94.4 | 71.1 | 57.1 | 2127 m | | [20] |
| $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ | 136.6 (38) | 100.7 | 75.1 (3) | 50.5 | 2095 s, 1955 w | 0.08 (0.48) | [3] |
| $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ | 124.9 | 91.7 | 75.3 | 52.5 | 2109 w, 1971 w ^e | 0.52 (irr) | [5] |
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})(\text{dppe})(\eta\text{-C}_5\text{H}_5)]$ | 136.7 (21) | 94.5 | 71.9 | 59.9 | 1981 w, 1968 w | | [16] |

^a Data for $\text{C}\equiv\text{CC}\equiv\text{CR}$ chain only, data in parentheses indicate $J(\text{C}-\text{P})$.

^b In CH_2Cl_2 unless stated otherwise.

^c Cyclic voltammetric data, E° values vs. Ag/AgCl in CH_2Cl_2 ($E^\circ[\text{FeCp}_2]/[\text{FeCp}_2]^+ = 0.54$ V), electrochemical data for $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ ($\text{M} = \text{Fe}$, Ru ; $\text{R} = \text{H}$, SiMe_3) adjusted via E° value for $[\text{FeCp}_2]/[\text{FeCp}_2]^+$, figures in parentheses indicate $i_p^{\text{C}}/i_p^{\text{A}}$ at 100 mV s^{-1} , irr = irreversible.

^d ir (Nujol, cm^{-1}) for **4**: 2150 w, 2107 w, 2085 m, 2062 m, 1975 w.

^e Medium not stated – probably KBr/Nujol .

exhibits one additional weak band below 2000 cm^{-1} in common with $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*]$ ($\text{M} = \text{Fe}$ or Ru).

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complexes **1–6**, four resonances for each compound can be assigned to the carbons of the C_4 chain, C_α , C_β , C_γ and C_δ (C_α is attached directly to the metal centre). The chemical shift of C_α is strongly dependent on electron density at the metal centre with electron-rich metal centres inducing a low field shift. Thus the bipy and dppe derivatives **1** and **4** both exhibit δC_α around 142 ppm, almost identical to the values observed for $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*]$ and the alkynyl complex $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ [3,20]. A high field shift in C_α is observed for the less electron-rich centres of **2**, **3**, the dicarbonyl $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]$ and the ruthenium analogue $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*]$. As is evident from Tables 2 and 3, the ^{13}C NMR chemical shifts of the remaining carbons in the chain exhibit more dependence upon the identity of the substituent on the butadiynyl chain – all values for the new complexes **1–6** fall within accepted ranges. The assignment of C_α to C_δ in Table 2 follows that generally accepted chemical shift ordering [1] and, in the case of **4**, is supported by the magnitude of $J(\text{P}-\text{C})$ values with $^4J_{\text{CP}} > ^3J_{\text{CP}}$, as reported for $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*]$ [3]. In addition to the observation of phosphorus–carbon coupling along the diynyl chain, the dppe complexes **4** and **6** exhibit two additional features indicative of interaction through the diynyl π -system. First, C_α is shifted to high field by replacement of SiMe_3 with H in common with FeCp^* and RuCp^* analogues. Second, and more exceptionally [29], there is a $^6J(\text{H}-\text{P})$ coupling (1.6 Hz) in **6** between the terminal H of the butadiynyl chain and ^{31}P of the dppe ligand.

The electrochemistry of complexes **1–6** was investigated by cyclic voltammetry at a platinum electrode in CH_2Cl_2 (details as in Table 1). Under these conditions, each of complexes **1**, **2** and **4–6**, undergoes a diffusion controlled ($i_p/v^{1/2}$ is constant for scan rates $v = 50\text{--}500\text{ mVs}^{-1}$), chemically reversible one-electron oxidation with the separation between cathodic and anodic peak potentials comparable to that determined for ferrocene under identical conditions. The E° values for one-electron oxidation are consistent with increased electron density at the metal centre in the order **2** < **4** < **1** (or $\text{Bu}^t\text{-dab} < \text{dppe} < \text{bipy}$) as previously determined for complexes of these ligands [23]. The data are also indicative of the butadiynyl ligand acting as an efficient π -donor group with E° values very similar to the bromide derivative in all three cases. The carbonyl–triphenylphosphine complex **3**, undergoes one-electron oxidation at a higher potential than the other systems in this investigation, consistent with the carbonyl acceptor group in the ligand set and moreover the process is not fully reversible with $i_p^{\text{C}}/i_p^{\text{A}} = 0.85$ at a scan rate of 100 mVs^{-1} .

It is instructive to compare the electrochemistry of the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ complexes **4** and **6** with that of the FeCp^* and RuCp^* analogues. Direct comparisons of E°

values between different studies are impeded by differing preferences for working and reference electrodes and supporting electrolyte but the electrochemical data presented in Table 3 have been adjusted to a standard value for the $\text{FeCp}_2/\text{FeCp}_2^+$ couple of 0.54 V (the reference value in the current work) to permit a reasonable comparison. Two points emerge which suggest that synthetic redox studies on butadiynyl complexes of the $\text{MoL}_2(\eta\text{-C}_7\text{H}_7)$ system will lead to unprecedented isolation of metal-stabilised butadiynyl radicals [30,31]. First, the E° values for the $\text{Mo}(\eta\text{-C}_7\text{H}_7)$ complexes are to negative potential of both RuCp^* and FeCp^* analogues in accord with previous measurements on the related alkynyl derivatives $[\text{M}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-L})]$ ($\text{M} = \text{Mo}$, $\text{L} = \text{C}_7\text{H}_7$; $\text{M} = \text{Fe}$ or Ru , $\text{L} = \text{Cp}^*$) [32]. Second, the chemical reversibility of the one-electron oxidation processes is enhanced by the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ auxiliary such that not only does the C_4SiMe_3 derivative **4** exhibit a fully reversible one-electron oxidation but also, exceptionally, so does the unprotected C_4H derivative **6**; moreover the same observation is made for the $\text{Bu}^t\text{-dab}$ derivatives **2** and **5**. In agreement with electrochemical data for $\text{Fe}(\text{dppe})\text{Cp}^*$ and $\text{Ru}(\text{dppe})\text{Cp}^*$ derivatives, the magnitude of the redox potential E° is essentially unaffected by replacement of the protected C_4SiMe_3 ligand with desilylated C_4H .

2.3. Structural studies

The principal structural feature of interest in these complexes is the geometry of the butadiynyl ligand and the consequence of variation of the metal centre, supporting ligands and the diynyl R substituent upon this geometry. In general, the effect of metal-coordination is small but some variation is observed with respect to carbon–carbon bond distances and curvature (deviation from linearity) of the C_4 chain. All co-ordinated butadiynyl ligands exhibit a distinct short–long–short CC bond sequence as observed for buta-1,3-diyne itself [$1.2176(14)$, $1.384(2)\text{ \AA}$] [33]. However, electron-rich metal centres coupled with SiMe_3 butadiynyl substituents, appear to result in elongation of $\text{C}_\alpha\text{-C}_\beta$ and $\text{C}_\gamma\text{-C}_\delta$ and contraction of $\text{C}_\beta\text{-C}_\gamma$, as exemplified by $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*]$ ($\text{M} = \text{Fe}$, Ru , see Table 5). These changes may be due to an increase in cumulenic character of the C_4 fragment but they have also been attributed simply to the effect of an extension of the conjugation pathlength [19]. By contrast, in $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*]$, the $\text{C}_\alpha\text{-C}_\beta$ distance is found to be foreshortened by comparison with free buta-1,3-diyne. Curvature in the C_4 chain is generally attributed to “crystal packing forces”. Deviations from linearity are expressed by the parameter $\Sigma(\text{bend})$, this being the sum of the deviations from 180° for the angles along the chain, $\text{M}-\text{C}_\alpha-\text{C}_\beta$, $\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma$, etc.; typical values for four angle systems (C_4R , $\text{R} \neq \text{H}$) lie in the region $13\text{--}17^\circ$.

The X-ray crystal structures of $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)]$, **1** and $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$, **6**, together with the crystallographic numbering schemes

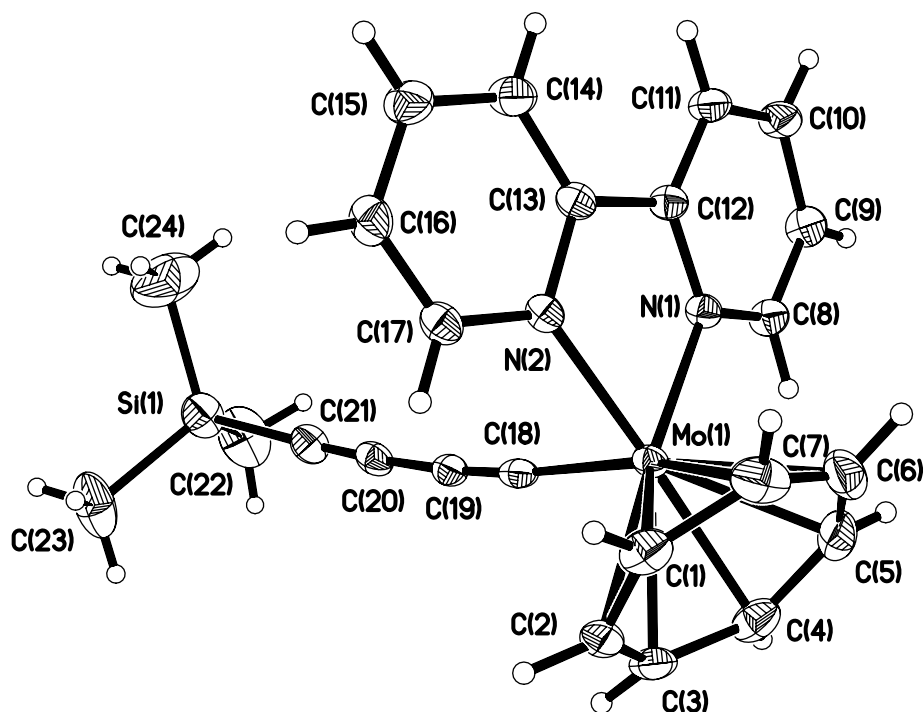


Fig. 1. Molecular structure of complex 1.

are illustrated in Figs. 1 and 2, respectively, important bond lengths and angles are given in Table 4. Key comparisons between the structures of **1** and **6** and those of related butadiynyl complexes are presented in Table 5. Consider-

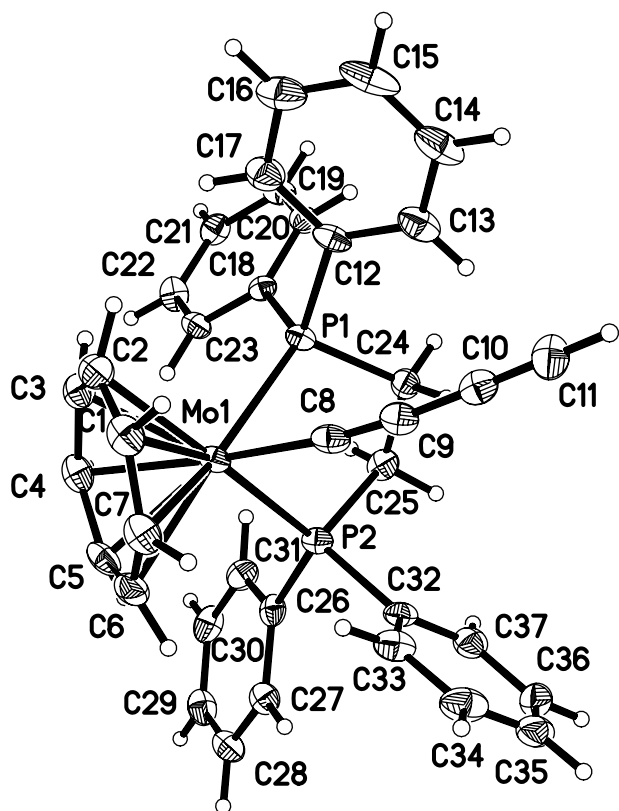


Fig. 2. Molecular structure of complex 2.

ing first, bond lengths along the C₄ chain, both **1** and **6** fall within normal values. For **1**, the carbon–carbon bond lengths along the chain are almost identical to free buta-1,3-diyne and do not show the lengthening of C_α–C_β and shortening of C_β–C_γ observed for [RuC≡CC≡CSiMe₃](dppe)Cp*] [5]. For **6**, the C_α–C_β and C_β–C_γ are again comparable with those of free buta-1,3-diyne in contrast with the C₄H ligand of [RuC≡CC≡CH](dppe)Cp*] for which significant shortening of C_α–C_β is observed. The Mo–C_α distance in **6** (2.114(3) Å) is shorter than the corresponding distance in **1** (2.135(2) Å) and is also probably shorter than Mo–C_α in the related alkynyl complex [Mo(C≡CPh)(dppe)(η-C₇H₇)] (2.138(5) Å) [34].

A remarkable feature of the current structural work is the extent of curvature in the C₄SiMe₃ chain of **1**; the magnitude of Σ(bend) taken over the four angle system is 23°. A possible explanation for this large deviation is given by the crystal packing diagram (Fig. 3). The packing is dominated by a π–π stacking interaction between the bipyridine rings of adjacent molecules and this imposes a head-to-head interaction between diyne chains with closest intermolecular contacts H(23 A) ⋯ H(6), 2.58 Å; H(23 A) ⋯ H(22C), 2.63 Å and C(20) ⋯ H(14), 2.74 Å. The close approach of opposing SiMe₃ end groups results in a large distortion in the C_γ–C_δ–Si angle (170.3(2)°) and this is largely responsible for the unusually high value of Σ(bend).

One final issue, informed by the structure of **1**, is the capacity of the 2,2'-bipyridine ligand to act as a π-acceptor in this complex – the ready substitution of the bipyridine ligand in **1** with dppe to give **4** suggests that any metal to ligand π-retrodonation is relatively minor in **1**.

Table 4
Important bond lengths (Å) and angles (°)

| Complex 1 | | | |
|-------------------|------------|-------------------|----------|
| Mo(1)–N(1) | 2.1341(18) | N(1)–C(8) | 1.355(3) |
| Mo(1)–N(2) | 2.1417(18) | C(8)–C(9) | 1.373(3) |
| Mo(1)–C(18) | 2.135(2) | C(9)–C(10) | 1.394(3) |
| Mo(1)–C(1) | 2.256(2) | C(10)–C(11) | 1.378(3) |
| Mo(1)–C(2) | 2.297(2) | C(11)–C(12) | 1.395(3) |
| Mo(1)–C(3) | 2.269(2) | C(12)–N(1) | 1.367(3) |
| Mo(1)–C(4) | 2.289(2) | C(12)–C(13) | 1.450(3) |
| Mo(1)–C(5) | 2.263(2) | N(2)–C(13) | 1.366(3) |
| Mo(1)–C(6) | 2.318(2) | C(13)–C(14) | 1.393(3) |
| Mo(1)–C(7) | 2.316(2) | C(14)–C(15) | 1.373(3) |
| C(18)–C(19) | 1.207(3) | C(15)–C(16) | 1.390(3) |
| C(19)–C(20) | 1.382(3) | C(16)–C(17) | 1.373(3) |
| C(20)–C(21) | 1.214(3) | C(17)–N(2) | 1.359(3) |
| C(21)–Si(1) | 1.834(2) | | |
| N(1)–Mo(1)–N(2) | 73.92(7) | C(18)–C(19)–C(20) | 175.6(2) |
| N(1)–Mo(1)–C(18) | 85.60(7) | C(19)–C(20)–C(21) | 176.4(2) |
| N(2)–Mo(1)–C(18) | 84.98(7) | C(20)–C(21)–Si(1) | 170.3(2) |
| Mo(1)–C(18)–C(19) | 174.51(16) | | |
| Complex 6 | | | |
| Mo(1)–P(1) | 2.4726(7) | Mo(1)–C(5) | 2.313(2) |
| Mo(1)–P(2) | 2.4578(6) | Mo(1)–C(6) | 2.315(3) |
| Mo(1)–C(8) | 2.114(3) | Mo(1)–C(7) | 2.280(2) |
| Mo(1)–C(1) | 2.288(3) | C(8)–C(9) | 1.223(4) |
| Mo(1)–C(2) | 2.310(3) | C(9)–C(10) | 1.369(4) |
| Mo(1)–C(3) | 2.288(3) | C(10)–C(11) | 1.198(4) |
| Mo(1)–C(4) | 2.355(3) | | |
| P(1)–Mo(1)–P(2) | 78.45(2) | Mo(1)–C(8)–C(9) | 174.6(2) |
| P(1)–Mo(1)–C(8) | 74.83(7) | C(8)–C(9)–C(10) | 175.2(3) |
| P(2)–Mo(1)–C(8) | 85.75(7) | C(9)–C(10)–C(11) | 178.8(3) |

The complex $[\text{Mo}(\text{OPr}^i)_2(\text{bipy})_2]$ provides typical structural parameters for a molybdenum 2,2'-bipyridine complex in which the bipy ligand does function as a good π -acceptor group [35]. In terms of Mo–N distances, those observed for **1** [2.134(2), 2.142(2) Å] are longer than those of $[\text{Mo}(\text{OPr}^i)_2(\text{bipy})_2]$ [2.107(2), 2.115(2), 2.123(2) and 2.126(2) Å] but much shorter than typical values in molybdenum bipyridine complexes (for example $[\text{Mo}(\text{CO})_2(\text{bipy})(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$, 2.237(4), 2.222(4) Å) [36]. However, inspection of the bond lengths within the bipyridine ligand of **1** (Table 4) reveals that the distortions in geometry associated with the ligand acting as a π -acceptor group in $[\text{Mo}(\text{OPr}^i)_2(\text{bipy})_2]$ are not significant for **1**. Therefore, the replacement of the bipyridine ligand

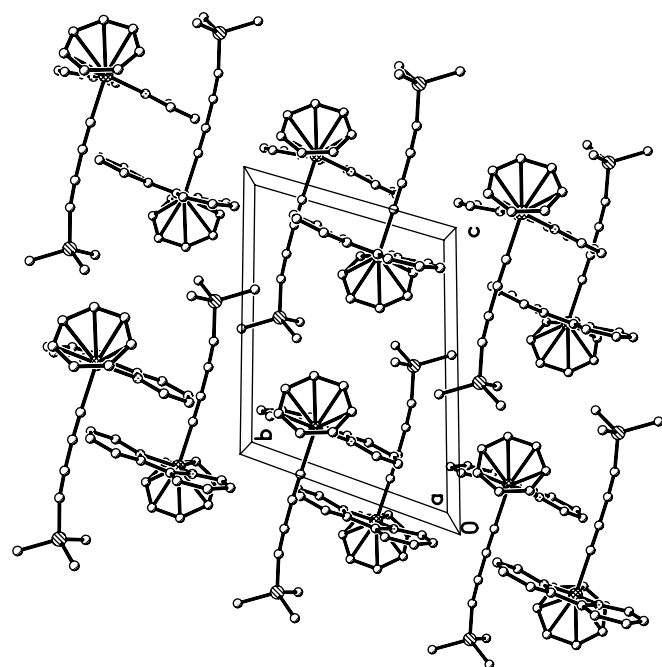


Fig. 3. Packing diagram for complex **1**.

in complex **1** with dppe, a key result of this paper, might be rationalised in terms of the enhanced π -acceptor capability of dppe vs. bipy in these cycloheptatrienylmolybdenum complexes.

3. Conclusions

Syntheses of several molybdenum diynyl complexes containing the electron-rich supporting auxiliary $\text{MoL}_2(\eta\text{-C}_7\text{H}_7)$, ($\text{L}_2 = \text{bipy}$, $\text{Bu}^t\text{-dab}$, dppe) have been developed. Spectroscopic and structural investigations confirm that the properties of the new complexes complement those of analogous diynyl derivatives of the isoelectronic $\text{M}(\text{dppe})\text{Cp}^*$ systems ($\text{M} = \text{Fe}$ or Ru). However, electrochemical data for the cycloheptatrienyl molybdenum complexes reveal highly electron-rich metal centres which support chemically reversible one-electron oxidation processes on the electrochemical time-scale, even with unprotected C_4H ligands. The $\text{MoL}_2(\eta\text{-C}_7\text{H}_7)$ auxiliary is therefore a system of a second row transition metal which also exhibits a very strong electron donor capacity and the

Table 5
Comparison of structural parameters for the butadiynyl ligand in selected complexes^a

| Complex | M–C _α (Å) | C _α –C _β (Å) | C _β –C _γ (Å) | C _γ –C _δ (Å) | C _δ –Si (Å) | Σ(bend) ^o |
|---|----------------------|------------------------------------|------------------------------------|------------------------------------|------------------------|----------------------|
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)]$ | 2.135(2) | 1.207(3) | 1.382(3) | 1.214(3) | 1.834(2) | 23.2 |
| $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ | 1.875(3) | 1.226(4) | 1.374(4) | 1.220(4) | 1.821(3) | 16.8 |
| $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ | 1.983(2) | 1.231(2) | 1.371(2) | 1.222(3) | 1.822(2) | 13.5 |
| $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ | 2.114(3) | 1.223(4) | 1.369(4) | 1.198(4) | – | 11.4 |
| $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ | 2.015(4) | 1.186(5) | 1.387(6) | 1.193(6) | – | 16.8 |

^a Data from this work (Mo complexes) or Ref. [5] (Fe and Ru complexes).

potential to stabilise diyanyl and diyndiyl complexes in a range of oxidation states. Applications of the cycloheptatrienyl molybdenum auxiliary to the isolation of metal-stabilised diyanyl radicals and as an end-cap in all-carbon bridged complexes are evident and are currently under investigation.

4. Experimental

4.1. 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(bipy)(η -C₇H₇)] [23], [MoBr(Bu^t-dab)(η -C₇H₇)] [23] and [MoBr(CO)(PPh₃)(η -C₇H₇)] [37] were prepared by published procedures. NMR spectra were recorded on Varian Inova 300 (300 MHz ¹H, 75 MHz ¹³C{¹H}) or Varian Inova 400 (400 MHz ¹H, 100 MHz ¹³C{¹H}) spectrometers. Infrared spectra were obtained on a Perkin Elmer FT RX1 spectrometer and mass spectra were recorded using Kratos Concept 1S (FAB spectra), Micromass Platform II (ES spectra) or Micromass/Waters Tof Spec 2E (MALDI spectra) instruments. Cyclic voltammetric studies were carried out using an EG&G model 270/283 electrochemical system; the working and counter electrodes were platinum and the reference electrode was Ag/AgCl. Test solutions were made up with 1×10^{-3} mol dm⁻³ complex and 0.1 mol dm⁻³ [NBu₄]⁺[PF₆]⁻ as supporting electrolyte. All potentials are quoted vs. the Ag/AgCl reference electrode; under these conditions *E*^o for the couple [FeCp₂]/[FeCp₂]⁺ is 0.54 V. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Manchester.

4.2. Preparation of [Mo(C≡CC≡CSiMe₃)(bipy)-(η -C₇H₇)], **1**

A solution of Me₃SiC≡CC≡SiMe₃ (0.50 g, 2.58 mmol) in stirred, cooled (-78 °C) thf (25 cm³) was treated with MeLi–LiBr (2.5 cm³ of a 1.5 M solution in diethyl ether) and the reaction mixture was then allowed to warm to room temperature over a period of 2 h. The solution of LiC≡CC≡CSiMe₃ so prepared was transferred to a stirred solution of [MoBr(bipy)(η -C₇H₇)] (0.70 g, 1.65 mmol) in thf (40 cm³) at -78 °C. The reaction mixture was warmed to room temperature (30 min) and reaction continued for a further 1 h at room temperature and finally 30 min at 30 °C to give a red–purple solution. The entire reaction mixture was then transferred to an alumina-*n*-hexane chromatography column maintained at -20 °C and the product eluted as a purple band with *n*-hexane/CH₂Cl₂ (1:1). The band was collected, solvent removed *in vacuo* and the residue recrystallised from CH₂Cl₂-*n*-hexane to give **1** as a dark-purple solid, yield 0.60 g (78%).

4.3. Preparation of [Mo(C≡CC≡CSiMe₃)(Bu^t-dab)-(η -C₇H₇)], **2**

Complex **2** was prepared by a similar procedure to that described for **1** starting from Me₃SiC≡CC≡SiMe₃ (2.00 g, 10.31 mmol), MeLi–LiBr (7.0 cm³ of a 1.5 M solution in diethyl ether) and [MoBr(Bu^t-dab)(η -C₇H₇)] (2.50 g, 5.75 mmol). Recrystallisation of the crude product eluted from the column from diethyl-ether-*n*-hexane gave complex **2** as a purple solid, yield 2.10 g (77%).

4.4. Preparation of [Mo(C≡CC≡CSiMe₃)(CO)-(*PPh*₃)(η -C₇H₇)], **3**

The preparation of complex **3** was by an identical procedure to that described for **1**, starting from Me₃SiC≡CC≡SiMe₃ (1.28 g, 6.60 mmol), MeLi–LiBr (4.4 cm³ of a 1.5 M solution in diethyl ether) and [MoBr(CO)(PPh₃)-(η -C₇H₇)] (1.82 g, 3.30 mmol). The product **3** was obtained as a green–brown solid, yield 0.985 g (50%).

4.5. Preparation of [Mo(C≡CC≡CSiMe₃)(dppe)-(η -C₇H₇)], **4**

A mixture of [Mo(C≡CC≡CSiMe₃)(bipy)(η -C₇H₇)], (0.86 g, 1.86 mmol) and dppe (1.11 g, 2.79 mmol) was refluxed in toluene (40 cm³). The initial purple reaction mixture became green–brown and after 3 h solvent was removed. The residue was dissolved in CH₂Cl₂ and transferred to a *n*-hexane–celite chromatography column. Elution with *n*-hexane/CH₂Cl₂ (10:1) gave a green–brown band which was collected and evaporated to dryness. The residue was recrystallised from CH₂Cl₂-*n*-hexane to give **4** as a deep green solid, yield 0.93 g (71%).

4.6. Preparation of [Mo(C≡CC≡CH)(Bu^t-dab)-(η -C₇H₇)], **5**

A solution of [Mo(C≡CC≡CSiMe₃)(Bu^t-dab)(η -C₇H₇)], **2**, (0.50 g, 1.05 mmol) in 1:1 methanol/thf (50 cm³) was treated with KF (0.090 g, 1.55 mmol) and the reaction mixture was refluxed for 15 h. The resulting red solution was evaporated to dryness and the residue recrystallised from diethylether-*n*-hexane to give complex **5** as a red–purple solid, yield 0.295 g (69%).

4.7. Preparation of [Mo(C≡CC≡CH)(dppe)(η -C₇H₇)], **6**

A solution of [Mo(C≡CC≡CSiMe₃)(dppe)(η -C₇H₇)], **4**, (0.739 g, 1.05 mmol) in thf (30 cm³) was treated with Bu₄ⁿNF (0.2 cm³ of a 1 M solution in thf) and stirred for 90 min. The resulting solution was evaporated to dryness and the residue, dissolved in CH₂Cl₂ was transferred to a *n*-hexane–celite chromatography column. Elution with *n*-hexane/CH₂Cl₂ (10:1) gave a deep brown band which

Table 6

Crystal data and refinement parameters for $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)]$, **1** and $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$, **6**

| Complex | 1 | 6 |
|---|---|--|
| Formula | $\text{MoC}_{24}\text{H}_{24}\text{N}_2\text{Si}$ | $\text{MoC}_{37}\text{H}_{32}\text{P}_2$ |
| Mass | 464.48 | 634.51 |
| Temperature (K) | 100(2) | 100(2) |
| λ (Å) | 0.71069 (Mo-K α) | 0.71073 (Mo-K α) |
| Crystal system | Triclinic | Orthorhombic |
| Space group | <i>P</i> -1 | <i>P</i> 2(1)2(1)2(1) |
| <i>a</i> (Å) | 9.945(5) | 11.6226(7) |
| <i>b</i> (Å) | 10.443(5) | 15.0351(9) |
| <i>c</i> (Å) | 12.693(5) | 16.8653(10) |
| α (°) | 67.788(5) | 90 |
| β (°) | 75.759(5) | 90 |
| γ (°) | 64.156(5) | 90 |
| <i>V</i> (Å ³); <i>Z</i> | 1093.1(9); 2 | 2947.2(3); 4 |
| Absorption coefficient (cm ⁻¹) | 6.66 | 5.79 |
| θ range (°) | 1.74–26.36 | 1.81–26.37 |
| Limiting indices (<i>h</i> , <i>k</i> , <i>l</i>) | ±12; ±13; ±15 | –12/14; –18/18; –21/19 |
| Total reflections | 8657 | 14681 |
| Independent reflections, <i>I</i> > 2 σ (<i>I</i>) | 4383 | 6021 |
| <i>R</i> ₁ | 0.0254 | 0.0266 |
| <i>wR</i> ₂ | 0.0636 | 0.0660 |
| Completeness to θ (%) | 98.0 | 99.9 |

was evaporated to dryness. Recrystallisation from CH_2Cl_2 gave the product, **6**, as a deep brown solid, yield 0.512 g (77%).

4.8. X-ray crystal structures of

$[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{bipy})(\eta\text{-C}_7\text{H}_7)]$, **1** and
 $[\text{Mo}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$, **6**

The majority of details of the structure analyses carried out on complexes **1** and **6** are given in Table 6. Single crystals of **1** were obtained as black plates by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of the complex and a crystal of dimensions 0.50 × 0.50 × 0.02 mm was selected for analysis. Single crystals of **6** were obtained as brown plates by vapour diffusion of pentane into a toluene solution of the complex and a crystal of dimensions 0.35 × 0.20 × 0.10 mm was selected for analysis. Data collection, cell refinement and data reduction were carried out with Bruker SMART and Bruker SAINT software; SIR—97 [38] (**1**) or SHELXS-97 [39] (**6**) were employed for the computing structure solution and SHELXL-97 [40] for the computing structure refinement. In each case an absorption correction was applied with the aid of the SADABS programme [41]. Both structures were solved by direct methods with refinement by full-matrix least squares based on *F*² and all non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions except for the aromatic H atoms in **1** which were located by difference Fourier techniques and refined isotropically.

Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC 297787 contains the supplementary crystallographic data for complex **1** and CCDC 297,788, the data for complex **6**. These may be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.05.011](https://doi.org/10.1016/j.jorganchem.2006.05.011).

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