Synthesis, Structure and Reactivity of Bicycloheptatrienyl-bridged Dimolybdenum Complexes: Crystal Structure of $[Mo_2(CO)_4(\mu\text{-}I)(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]$†

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Thermal rearrangement of bicycloheptatriene, $C_{14}H_{14}$, followed by reaction with 1 equivalent of $[CPh_3][PF_6]$ at −20 °C afforded the cycloheptatriene-substituted cycloheptatrienyl cation, $[C_{14}H_{13}][PF_6]$ as a mixture of two isomers differing in the position of the CH_2 group on the cycloheptatriene ring. Treatment of $[C_{14}H_{13}][PF_6]$ with a further equivalent of $[CPh_3][PF_6]$ afforded the bicycloheptatrienyl dication $[C_{14}H_{12}][PF_6]_2$ which reacts with $[Mo(CO)_3(NCMe)_3]$ to give the bicycloheptatrienyl bridged bimetallic $[Mo_2(CO)_6(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **1**. Reaction of $[C_{14}H_{13}][PF_6]$ with $[Mo(CO)_3(NCMe)_3]$ leads to co-ordination at the cycloheptatrienyl ring and formation of $[Mo(CO)_3(\eta^7\text{-}C_{14}H_{13})][PF_6]$ **2** which is the precursor to $[MoI(CO)_2(\eta^7\text{-}C_{14}H_{12})][PF_6]$ **5** which contains an unco-ordinated, pendant cycloheptatrienyl ring. Complex **5** reacts with $[Mo(CO)_3(NCMe)_3]$ to give doubly bridged $[Mo_2(CO)_4(\mu\text{-}I)(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]$ **7**. X-Ray crystallographic characterisation of **7** reveals two crystallographically distinct cations both of which exhibit a twisted conformation of the bicycloheptatrienyl ligand. Reaction of **1** with $Na[Mn(CO)_5]$ results in conversion of the carbon–carbon bond which links the bridgehead carbons, from a single to a double bond and isolation of heptafulvalene-bridged $[Mo_2(CO)_6(\mu\text{-}\eta^6:\eta^6\text{-}C_{14}H_{12})]$ **8**. The acetonitrile derivative $[Mo_2(CO)_4(NCMe)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][BF_4]_2$ **11**, formed in a two-step synthesis from **1**, is activated towards $\eta^7 \longrightarrow \eta^3$ hapticity interconversion by comparison with $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)][BF_4]$, and when **11** is dissolved in acetonitrile at room temperature, the major product is $[Mo_2(CO)_4(NCMe)_6(\mu\text{-}\eta^3:\eta^3\text{-}C_{14}H_{12})][BF_4]_2$ **13**. Cyclic voltammetric investigations on $[Mo_2(NCMe)_2(Ph_2PCH_2CH_2PPh_2)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **15** reveal two discrete, reversible oxidations with ΔE° = 130 mV, indicating a limited degree of intermetallic electronic communication through the bicycloheptatrienyl ligand.

The use of linked ring systems, such as fulvalene [5-(cyclopenta-2,4-dienylidene)cyclopenta-1,3-diene] or biphenyl, to act as bridges between two metal centres is a growing area of interest in organometallic chemistry. Two properties of fulvalene- or biphenyl-bridged bimetallics have become the focus of a series of investigations. First, these ligands result in modified reactivity of the dimetal centre as exemplified[1,2] by the fulvalene complexes $[Mo_2(CO)_6(\mu\text{-}\eta^5:\eta^5\text{-}C_{10}H_8)]$ and $[Ru_2(CO)_4(\mu\text{-}\eta^5:\eta^5\text{-}C_{10}H_8)]$. Secondly the linked π systems of the cyclopentadienyl or arene rings promote communication between the two co-ordinated metal centres and complexes such as $[Mn_2(CO)_4(\mu\text{-}dppm)(\mu\text{-}\eta^5:\eta^5\text{-}C_{10}H_8)]$ and $[Cr_2(CO)_4(\mu\text{-}dppm)(\mu\text{-}\eta^6:\eta^6\text{-}C_{12}H_{10})]$ (dppm = $Ph_2PCH_2PPh_2$) can be oxidised to mixed-valence systems which exhibit significant intermetallic electronic communication.[3–6] A novel departure in the chemistry of linked ring, bimetallic complexes would be to extend investigations to complexes of the bicycloheptatrienyl ligand $C_{14}H_{12}$ thus completing the series of linked, five-, six- and seven-membered rings. However most previous reports on the free ligand, the dication $C_{14}H_{12}{}^{2+}$, are not encouraging; they involve either low-yield syntheses of the dication with reactive counter-anions such as $[PCl_6]^-$[7] or alternatively require the relatively inaccessible heptafulvalene, $C_{14}H_{12}$ as starting material.[8] We now describe an improved synthesis of the bicycloheptatrienyl dication, isolable as the bis(hexafluorophosphate) salt, and its subsequent co-ordination to two $Mo(CO)_3$ units. Following syntheses of a range of bicycloheptatrienyl bridged bimetallics, we describe examples of modified reactivity and demonstrate intermetallic, electronic communication between two co-ordinated molybdenum units, linked by the $C_{14}H_{12}$ ligand. We also report the first X-ray structural study on the bicycloheptatrienyl framework, an investigation made possible by the additional stability conferred through metal co-ordination.

Results and Discussion

Ligand Syntheses and Coordination.—Our primary target complex for this work was $[Mo_2(CO)_6(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})]^{2+}$ **1**, Scheme 1. Complex **1** may be considered as a ring-substituted derivative of the monometallic cycloheptatrienyl complex $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ and should permit exploitation of the well established reactivity of the $Mo(CO)_3$ unit in our investigations; as in biphenyl-linked bimetallics, the physical size of the $C_{14}H_{12}$ ligand may be predicted to preclude formation of alternative species in which the two metal centres are linked by a Mo–Mo bond. Our initial approach to **1** involved hydride abstraction from the bicycloheptatriene bridged complex $[Mo_2(CO)_6(\mu\text{-}\eta^6:\eta^6\text{-}C_{14}H_{14})]$ which is readily accessible by an analogous synthesis to that reported for the chromium derivative.[9] Although hydride abstraction of the *endo* hydrogens on the bridgehead carbons cannot proceed, studies on monometallic, ring-substituted cycloheptatriene complexes $[M(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}R)C_7H_7\}]$ (M = Cr or Mo, R = Me, Ph *etc.*) have established that thermal rearrangement of the co-ordinated cycloheptatriene ligand leads to isomers with ring CH_2 groups accessible to hydride abstraction with the trityl cation $CPh_3{}^+$.[10,11] However an analogous strategy involving thermolysis of $[Mo_2(CO)_6(\mu\text{-}\eta^6:\eta^6\text{-}C_{14}H_{14})]$ in refluxing octane followed by reaction of the product with

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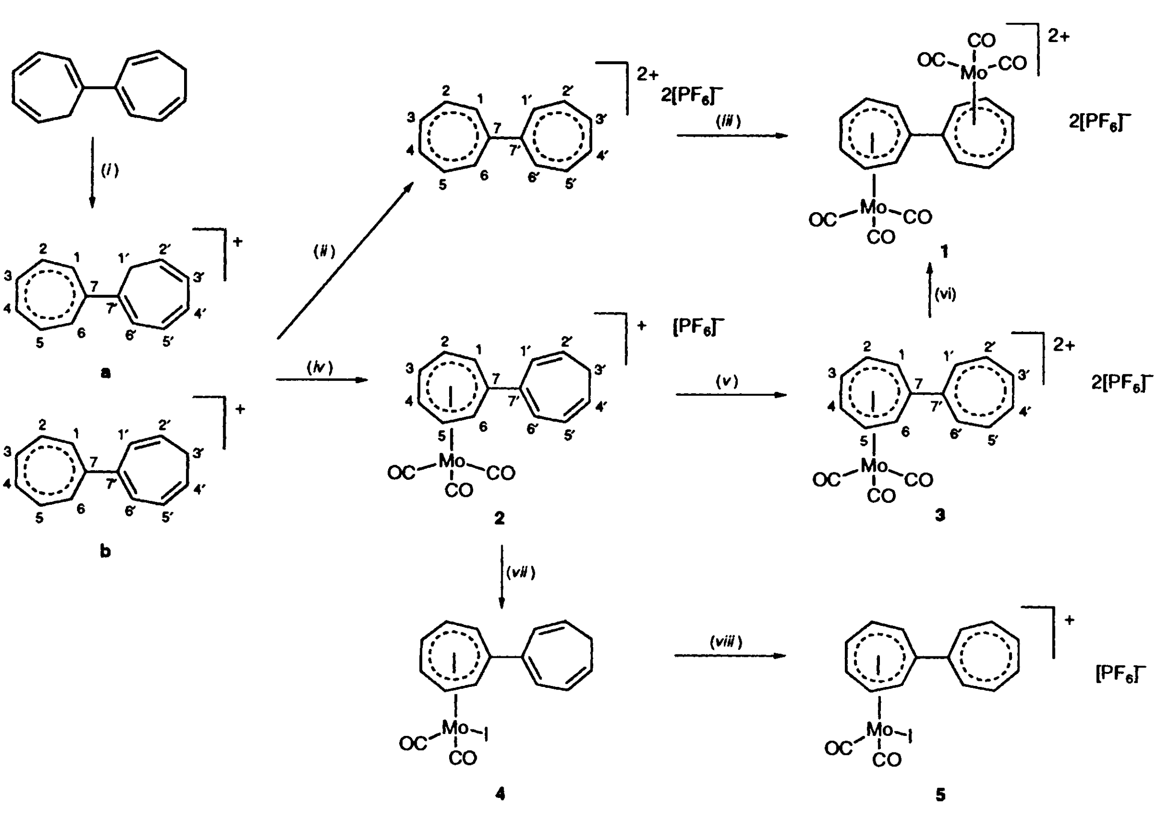
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 *Reagents and conditions*: (*i*) $[CPh_3][PF_6]$, 1 equivalent, stir in CH_2Cl_2, −20 °C, 1 h; (*ii*) $[CPh_3][PF_6]$, 1 equivalent, reflux in CH_2Cl_2, 1 h; (*iii*) $[Mo(CO)_3(NCMe)_3]$, 2 equivalents, stir in thf, 15 min; (*iv*) $[Mo(CO)_3(NCMe)_3]$, 1 equivalent, stir in thf, 15 min, product as mixture of **2a** and **2b**; (*v*) $[CPh_3][PF_6]$, 1 equivalent, reflux in CH_2Cl_2, 3.5 h; (*vi*) $[Mo(CO)_3(NCMe)_3]$, 1 equivalent, stir in CH_2Cl_2, 15 min; (*vii*) NaI, stir in acetone, 1 h, product as a mixture of **4a** and **4b**; (*viii*) $[CPh_3][PF_6]$, 1 equivalent, stir in CH_2Cl_2, 0 °C, 1 h

CPh_3^+ was unproductive. We therefore turned our attention to direct co-ordination of the $Mo(CO)_3$ unit to the preformed bicycloheptatrienyl ligand, exploiting the method that we have developed previously for the direct co-ordination of the $Mo(CO)_3$ fragment from $[Mo(CO)_3(NCMe)_3]$ to substituted cycloheptatrienyl cations.[11]

In our first synthesis of the free ligand, $C_{14}H_{12}^{2+}$, we followed the recently reported route developed by Neuenschwander and co-workers[12] which involves thermal rearrangement of bicycloheptatriene, $C_{14}H_{14}$, followed by hydride abstraction with 2 equivalents of $[CPh_3][BF_4]$. However, attempts to obtain **1** by reaction of the product so obtained with $[Mo(CO)_3(NCMe)_3]$ were unsuccessful. We therefore re-examined the synthesis of $C_{14}H_{12}^{2+}$ with a view to improving both yield and purity. One problem in the reported synthesis of $C_{14}H_{12}^{2+}$ is in carrying out the reaction of thermally rearranged $C_{14}H_{14}$ with CPh_3^+ in precisely stoichiometric quantities, given that the thermolysis product may contain impurities resulting from decomposition. Critically, in our experience, the reaction of $[Mo(CO)_3(NCMe)_3]$ with cycloheptatrienyl cations is adversely affected by, and extremely sensitive to, traces of the trityl cation in the reaction mixture. We therefore developed a two-stage synthesis of the bicycloheptatrienyl dication, *via* the intermediate monocation $C_{14}H_{13}^+$. Treatment of thermally rearranged bicycloheptatriene, $C_{14}H_{14}$, with 1 equivalent of $[CPh_3][PF_6]$ in CH_2Cl_2 at −20 °C resulted in the precipitation of high yields of $[C_{14}H_{13}][PF_6]$ as a bright orange solid. Details of the characterisation of $[C_{14}H_{13}][PF_6]$, and of subsequently described complexes, are given in Tables 1 (microanalytical, infrared and mass spectroscopic data) and 2 (^1H and ^{13}C NMR data). In principle, $C_{14}H_{13}^+$ can exist as four different isomers which differ in the location of the sp^3 hybridised carbon in the cycloheptatriene ring. In the event, only two isomers were observed: **a** in which the CH_2 group on the cycloheptatriene ring is located at the 1′ position adjacent to the bridgehead, and **b** in which the CH_2 group is located at the 3′ position. We were unable to effect complete separation of **a** from **b**, but **a** was more soluble in CH_2Cl_2 permitting enrichment of a sample of $[C_{14}H_{13}][PF_6]$ to 80% **b** and thus facilitating the NMR assignments given in Table 2. The second stage in the synthesis of $[C_{14}H_{12}][PF_6]_2$ was carried out by reaction of $[C_{14}H_{13}][PF_6]$ (as an isomeric mixture of **a** and **b**) with 1 equivalent of $[CPh_3][PF_6]$ in refluxing CH_2Cl_2 leading to the precipitation of $[C_{14}H_{12}][PF_6]_2$, as an orange solid in moderate yield. This compound is a highly reactive species which could not be successfully recrystallised but its identity was confirmed by the ^1H NMR spectrum which exhibits one multiplet resonance centred at δ 9.45 (CD_3CN) consistent with a highly deshielded aromatic system and with literature reports.[7,8]

Analytically pure samples of $[C_{14}H_{12}][PF_6]_2$, prepared by the two-step synthesis described above, were orange in contrast to the black product previously assigned as $[C_{14}H_{12}][BF_4]_2$, and we therefore proceeded to reinvestigate the reaction of $[C_{14}H_{12}][PF_6]_2$ with $[Mo(CO)_3(NCMe)_3]$. Stirring of a suspension of $[C_{14}H_{12}][PF_6]_2$ with $[Mo(CO)_3(NCMe)_3]$ in thf resulted in the rapid formation of $[Mo_2(CO)_6(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})]^{2+}$ **1**, as an orange precipitate. Co-ordination of the $C_{14}H_{12}^{2+}$ ligand by two $Mo(CO)_3$ units results in a significant increase in stability so permitting recrystallisation of **1** and characterisation by both ^1H and ^{13}C NMR spectroscopy. The NMR spectra **1** are typical of those observed for ring substituted cycloheptatrienyl complexes of the type $[Mo(CO)_3(\eta\text{-}C_7H_6R)]^+$;[11] in the ^1H NMR spectrum, the protons adjacent to the bridgehead ($H^{1,1'}$, $H^{6,6'}$) appear as a doublet signal and all resonances are shielded with respect to $[C_{14}H_{12}][PF_6]_2$ as a result of $Mo(CO)_3$ co-ordination. In the IR spectrum of **1**, two carbonyl bands are observed with wavenumbers typical of the $Mo(CO)_3$ unit co-ordinated to a cycloheptatrienyl ion but shifted to slightly high wavenumber

Table 1 Microanalytical, infrared and mass spectroscopic data

Compound	Analysis[a] (%) C	H	Infrared[b] ν(CO) (cm⁻¹)	Mass spectral data[c] (*m*/*z*)
$[C_{14}H_{13}][PF_6]$	51.2 (51.5)	4.1 (4.0)		181 (M^+)
$[C_{14}H_{12}][PF_6]_2$	36.0 (35.8)	2.6 (2.6)		181 (M^+)
1	31.1 (28.9)	1.4 (1.5)	2079s, 2040m[d]	683 ($[M + PF_6]^+$), 628 ($[M + PF_6 - 2CO]^+$), 599 ($[M + PF_6 - 3CO]^+$), 574 ($[M + PF_6 - 4CO]^+$)
2	40.7 (40.3)	2.8 (2.6)	2071s, 2022m[d]	363 (M^+), 335 ($[M - CO]^+$), 279 ($[M - 3CO]^+$)
3	32.6 (31.4)	2.2 (1.9)	2091s, 2059m, 2047m[e]	362 (M^+), 278 ($[M - 3CO]^+$)
4	41.9 (41.8)	2.9 (2.8)	2014s, 1968m	462 (M^+), 434 ($[M - CO]^+$), 406 ($[M - 2CO]^+$)
5	31.8 (31.8)	2.1 (2.0)	2035s, 2020s, 1992s, 1977s[e]	461 (M^+), 405 ($[M - 2CO]^+$)
6	28.9 (29.1)	1.6 (1.5)	2079m, 2034s, 1995w	639 (M^+), 609 ($[M - CO]^+$), 581 ($[M - 2CO]^+$), 553 ($[M - 3CO]^+$), 500 ($[M - 5CO]^+$)
7	28.8 (28.6)	1.6 (1.6)	2044s, 2034s, 1990m	611 (M^+), 583 ($[M - CO]^+$), 555 ($[M - 2CO]^+$), 529 ($[M - 3CO]^+$), 500 ($[M - 4CO]^+$)
8	44.0 (44.5)	1.9 (2.2)	1985s, 1926m, 1892m	541 (M^+), 511 ($[M - CO]^+$)
9	29.3 (29.3)	1.6 (1.6)	2018s, 1976m	
10	34.1 (33.6)	1.9 (1.9)	2021s, 1979m	615 ($[M - CO]^+$), 588 ($[M - 2CO]^+$), 563 ($[M - Br]^+$), 535 ($[M - Br - CO]^+$)
11	36.0 (35.7)	2.7 (2.4)[f]	2041s, 2005m	565 (M^+), 535 ($[M - CO]^+$), 507 ($[M - 2CO]^+$), 451 ($[M - 4CO]^+$)
14	40.1 (39.7)	3.5 (3.3)		702 ($[M + PF_6]^+$)
15	54.1 (54.6)	4.5 (4.3)[g]		1398 ($[M + PF_6]^+$), 1207 ($[M - NCMe]^+$)

[a] Calculated values in parentheses. Cationic complexes as $[PF_6]$ salts except for **11** as $[BF_4]$ salt. [b] Solution spectra in CH_2Cl_2 unless stated otherwise, s = strong, m = medium, w = weak intensity. [c] By FAB mass spectroscopy, *m*/*z* values for monometallic complexes based on ^{98}Mo. [d] In acetone. [e] KBr disc. [f] N, 3.6 (3.8)%. [g] N, 2.1 (1.8)%.

of those observed for $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][PF_6]$ [ν(CO) (acetone) 2076, 2027 cm⁻¹] under identical conditions.

As a second strategy to bimetallic complexes of the bicycloheptatrienyl ligand, we also investigated the co-ordination of the cycloheptatriene substituted cycloheptatrienyl ion $C_{14}H_{13}^+$ with $Mo(CO)_3$. Treatment of a suspension of $[Mo(CO)_3(NCMe)_3]$ in thf with $[C_{14}H_{13}][PF_6]$ resulted in the rapid precipitation of $[Mo(CO)_3(\eta^7\text{-}C_{14}H_{13})][PF_6]$ **2**, as a bright orange solid. In principle, **2** offers two potential co-ordination sites for $Mo(CO)_3$ co-ordination (at either or both of the cycloheptatrienyl and cycloheptatriene rings) but spectroscopic data for **2** (both IR and NMR spectra) are consistent with exclusive co-ordination to the cycloheptatrienyl ring of $C_{14}H_{13}^+$ and moreover attempts further to co-ordinate the pendant cycloheptatriene ring of **2** were unsuccessful. In accord with the isomerism found for the precursor $C_{14}H_{13}^+$, complex **2** was also formed as an isomeric mixture, **2a** and **2b**, differing in the location of the CH_2 group on the unco-ordinated, pendant cycloheptatriene ring (at the 1′ and 3′ positions respectively). The NMR data reported in Table 2 are for **2b**; spectral assignment was facilitated by the selective synthesis of **2b** from a sample of $[C_{14}H_{13}][PF_6]$ enriched in isomer **b**.

Although the pendant cycloheptatriene ring of **2** appears unreactive towards metal co-ordination, it can be activated by hydride abstraction to give a pendant cycloheptatrienyl group. A further consequence of this approach is that isomerism associated with the cycloheptatriene ring of **2** is removed. Two strategies leading to the monometallic bicycloheptatrienyl complexes $[Mo(CO)_3(\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **3**, and $[MoI(CO)_2(\eta^7\text{-}C_{14}H_{12})][PF_6]$ **5**, were adopted. Direct treatment of **2** (as a mixture of **2a** and **2b**) with 1 equivalent of $[CPh_3][PF_6]$ in refluxing CH_2Cl_2 resulted in the gradual precipitation of **3** as an orange solid. The dicationic complex $[Mo(CO)_3(\eta^7\text{-}C_{14}H_{12})]^{2+}$, resembles $[Mo_2(CO)_6(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})]^{2+}$, but in **3** one cycloheptatrienyl ring is left unprotected by metal co-ordination and this is reflected in its poor stability (in common with the free ligand $[C_{14}H_{12}][PF_6]_2$, complex **3** could not be successfully recrystallised). The ¹H NMR spectrum **3** in $(CD_3)_2CO$ exhibits two groups of resonances, those around δ 9.7–10.0 are assigned to the pendant, unco-ordinated cycloheptatrienyl ring whilst resonances in the range δ 6.9–7.5 are consistent with a $Mo(CO)_3$ co-ordinated ring. The strong electron withdrawing effect of the pendant cycloheptatrienyl ring of **3** is evident from the IR spectral data, the symmetric stretching band at 2091 cm⁻¹ is at a remarkably high wavenumber for complexes of the type $[Mo(CO)_3(\eta^7\text{-}C_7H_6R)]^+$. In contrast to the pendant cycloheptatriene complex **2**, complex **3** is reactive to further metal co-ordination. Reaction of a suspension of $[Mo(CO)_3(NCMe)_3]$ in CH_2Cl_2 with **3** resulted in the precipitation of low yields of the bimetallic complex **1**. Clearly this alternative synthesis of **1** is unattractive by comparison with direct reaction of the dicationic ligand $C_{14}H_{12}^{2+}$ with 2 equivalents of $[Mo(CO)_3(NCMe)_3]$, but the feasibility of co-ordination onto a pendant cycloheptatrienyl ring has been demonstrated and the reaction also suggests a route to heterobimetallic complexes of the bicycloheptatrienyl ligand.

The second approach to bicycloheptatrienyl complexes with an unco-ordinated, pendant cycloheptatrienyl ring involved the synthesis of $[MoI(CO)_2(\eta^7\text{-}C_{14}H_{12})][PF_6]$ **5** which proved to be much more stable than **3** and therefore a more suitable precursor to bimetallics. Rather than form **5** *via* the intermediacy of unstable **3**, we chose to modify the molybdenum centre of $[Mo(CO)_3(\eta^7\text{-}C_{14}H_{13})][PF_6]_2$ **2**, prior to hydride abstraction from the pendant cycloheptatriene ring. Treatment of an acetone solution of **2** with NaI gave a green solution from which high yields of neutral $[MoI(CO)_2(\eta^7\text{-}C_{14}H_{13})]$ **4** were isolated. NMR spectroscopic data for **4** were similar to those of its precursor **2** with resonances indicative of co-ordinated cycloheptatrienyl and unco-ordinated, pendant cycloheptatriene rings. Interpretation of the NMR data was again complicated by two isomeric forms (**4a** and **4b**) but assignments were achieved with the aid of a sample enriched in **4b**. Hydride abstraction from **4** with $[CPh_3][PF_6]$ proceeded smoothly at 0 °C in CH_2Cl_2 leading to the precipitation of high yields of **5** as a purple solid. The identity of **5** as a complex with an unco-ordinated, pendant cycloheptatrienyl ring is confirmed by the ¹H NMR spectrum which exhibits a strongly deshielded multiplet resonance centred at δ 9.52 in $(CD_3)_2CO$.

Properties and Reactions of Bicycloheptatrienyl-bridged Bimetallic Complexes.—It is well established that bimetallic

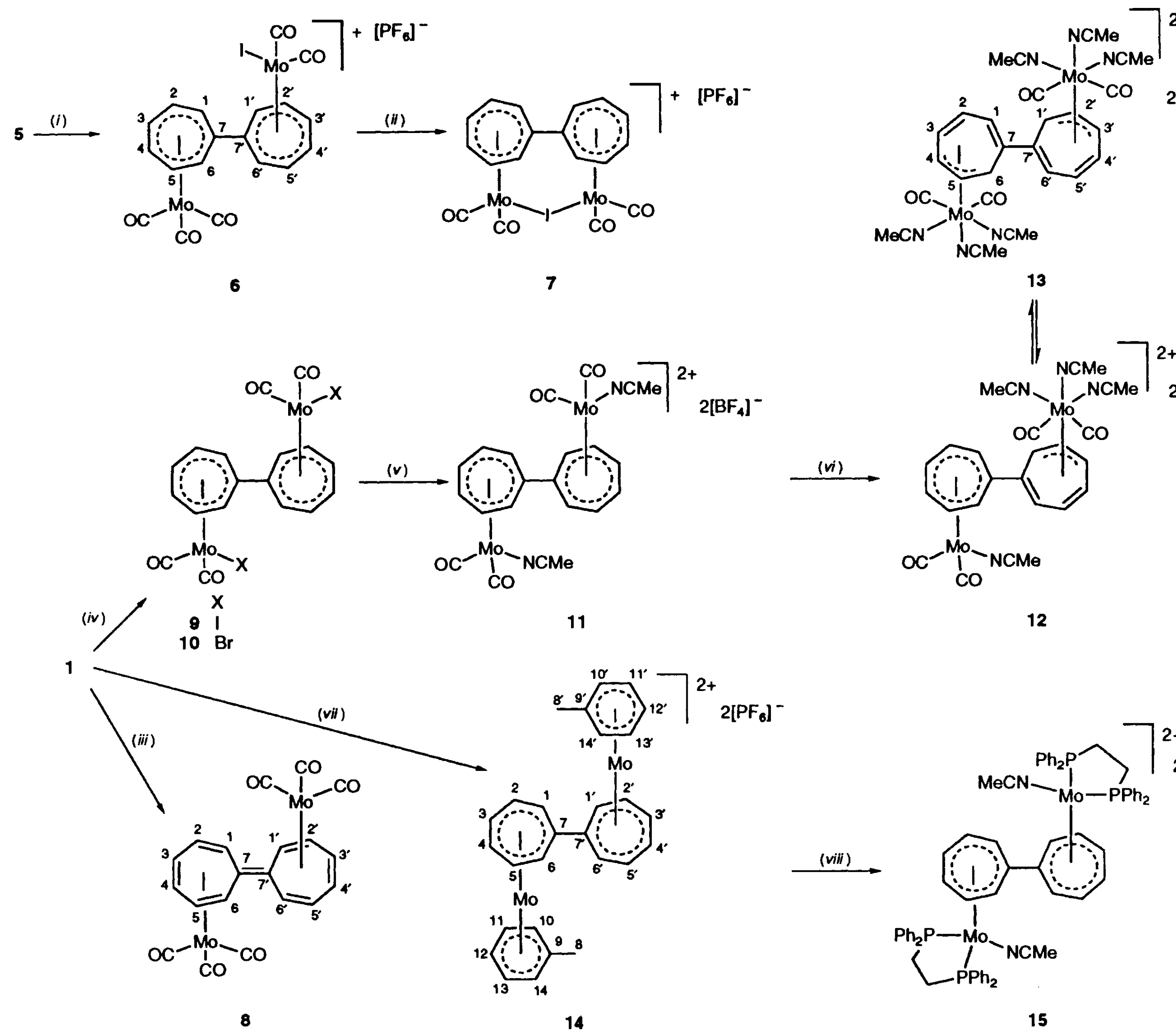
Table 2 Proton and ^{13}C NMR spectral data[a]

Compound	$^1H(\delta)$	$^{13}C(\delta)$
$[C_{14}H_{13}][PF_6]$ **a**	CH_2 at position 1′: 9.56 (m, 2 H, $H^{1,6}$), 9.22 (m, 4 H, H^{2-5}), 7.49 [d, 1 H, $H^{6'}$, $J(H^{6'}-H^{5'})$ 5.9], 7.16 [m, 1 H, $H^{4'}$, $J(H^{4'}-H^{3'})$ 5.4], 7.08 [m, 1 H, $H^{5'}$, $J(H^{5'}-H^{4'})$ 11.1], 6.67 [m, $H^{3'}$, $J(H^{3'}-H^{2'})$ 9.2], 6.09 [m, 1 H, $H^{2'}$, $J(H^{2'}-H^{1'})$ 7.1], 3.21 [d, 2 H, $H^{1'}$, $J(H^{1'}-H^{2'})$ 7.1]	
$[C_{14}H_{13}][PF_6]$ **b**	CH_2 at position 3′: 9.60 (m, 2 H, $H^{1,6}$), 9.39 (m, 4 H, H^{2-5}), 7.80 [d, 1 H, $H^{6'}$, $J(H^{6'}-H^{5'})$ 6.1], 6.83 [d, 1 H, $H^{1'}$, $J(H^{1'}-H^{2'})$ 9.6], 6.70 [m, 1 H, $H^{5'}$, $J(H^{5'}-H^{4'})$ 9.4], 6.00 (m, 2 H, $H^{2',4'}$), 2.63 [at, 2 H, $H^{3'}$, $J(H^{3'}-H^{2'}) \approx J(H^{3'}-H^{4'})$ 6.9]	170.1 (C^7), 153.7, 153.2 (C^{1-6}), 142.9 ($C^{7'}$) 140.3, 129.5, 128.4, 126.1, 126.0 ($C^{1',2',4'-6'}$), 28.7 ($C^{3'}$)
$[C_{14}H_{12}][PF_6]_2$[b]	9.45 (m, 12 H, $H^{1-6,1'-6'}$)	
1	7.35 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 7.5], 6.83 (m, 8 H, $H^{2-5,2'-5'}$)	208.5 (CO), 117.1 ($C^{7,7'}$), 103.3, 101.9, 98.7 ($C^{1-6,1'-6'}$)
2b	CH_2 at position 3′: 7.54 [d, 1 H, $H^{6'}$, $J(H^{6'}-H^{5'})$ 5.9], 6.76 (m, 6 H, H^{1-6}), 6.58 [d, 1 H, $H^{1'}$, $J(H^{1'}-H^{2'})$ 9.6], 6.51 [m, 1 H, $H^{5'}$, $J(H^{5'}-H^{4'})$ 9.0], 5.83 (m, 2 H, $H^{2',4'}$), 2.52 [at, 2 H, $H^{3'}$, $J(H^{3'}-H^{2'}) \approx J(H^{3'}-H^{4'})$ 6.9]	208.2 (CO), 139.7 ($C^{7'}$), 135.3, 126.8, 126.7, 126.2, 124.9 ($C^{1',2',4'-6'}$), 123.5 (C^7), 101.4, 100.7, 100.4 (C^{1-6}), 28.4 ($C^{3'}$)
3	9.97 [d, 2 H, $H^{1',6'}$, $J(H^{1'}-H^{2'} = H^{6'}-H^{5'})$ 8.6], 9.69 (br, 4 H, $H^{2'-5'}$), 7.47 [d, 2 H, $H^{1,6}$, $J(H^1-H^2 = H^6-H^5)$ 8.2], 6.88 (m, 4 H, H^{2-5})	
4a[c]	CH_2 at position 1′: 6.77 (m, 2 H, $H^{5',6'}$), 6.39 (m, 1 H, $H^{4'}$), 6.07 (d, 2 H, $H^{1,6}$, $J(H^1-H^2 = H^6-H^5)$ 8.5], 5.88 (m, 2 H, $H^{2,5}$), 5.71 (m, 4 H, $H^{2',3,3',4}$), 2.85 (d, 2 H, $H^{1'}$, $J(H^{1'}-H^{2'})$ 7.1]	213.5 (CO), 132.2 ($C^{7'}$), 132.3, 129.6, 127.4, 126.5, 121.7 ($C^{2'-6'}$), 112.8 (C^7), 94.6, 93.9, 93.3 (C^{1-6}), 32.5 ($C^{1'}$)
4b[c]	CH_2 at position 3′: 7.23 [d, 1 H, $H^{6'}$, $J(H^{6'}-H^{5'})$ 5.9], 6.50 [d, 1 H, $H^{1'}$, $J(H^{1'}-H^{2'})$ 9.7], 6.39 (m, 1 H, $H^{5'}$), 6.02 [d, 2 H, $H^{1,6}$, $J(H^1-H^2 = H^6-H^5)$ 8.4], 5.88 (m, 2 H, $H^{2,5}$), 5.71 (m, 4 H, $H^{2',3,4,4'}$), 2.46 [at, 2 H, $H^{3'}$, $J(H^{3'}-H^{2'}) \approx J(H^{3'}-H^{4'})$ 6.9]	213.5 (CO), 141.6 ($C^{7'}$), 131.7, 127.2, 126.1, 123.9, 123.2 ($C^{1',2',4'-6'}$), 114.1 (C^7), 94.7, 93.8, 93.6 (C^{1-6}), 28.0 ($C^{3'}$)
5	9.52 (m, 6 H, $H^{1'-6'}$), 6.50 [d, $H^{1,6}$, $J(H^1-H^2 = H^6-H^5)$ 7.6], 6.03 (m, 4 H, H^{2-5})	213.4 (CO), 167.7 ($C^{7'}$), 157.1, 154.7, 153.3 ($C^{1'-6'}$), 107.8 (C^7), 105.1, 93.0, 92.6 (C^{1-6})
6	7.10 [d, 2 H, $H^{1,6}$, $J(H^1-H^2 = H^6-H^5)$ 8.4], 6.82 (m, 4 H, H^{2-5}), 6.53 [d, 2 H, $H^{1',6'}$, $J(H^{1'}-H^{2'} = H^{6'}-H^{5'})$ 8.3], 6.02 (m, 2 H, $H^{3',4'}$), 5.95 (m, 2 H, $H^{2',5'}$)	213.7 [CO, MoI$(CO)_2$], 207.6 [CO, Mo$(CO)_3$], 121.8 (C^7), 107.1 ($C^{7'}$), 103.9, 102.3, 101.4, (C^{1-6}), 99.2, 93.2, 91.8 ($C^{1'-6'}$)
7	7.48 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 8.8], 6.52 (m, 4 H, $H^{2,2',5,5'}$), 5.74 (m, 4 H, $H^{3,3',4,4'}$)	214.4 (CO), 122.7 ($C^{7,7'}$), 104.8, 92.0, 90.0 $C^{1-6,1'-6'}$)
8[d]	4.95 (m, 4 H, $H^{3,3',4,4'}$), 4.12 (m, 4 H, $H^{2,2',5,5'}$), 3.36 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 9.7]	
9	6.36 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 8.4], 5.93 (m, 4 H), 5.84 (m, 4 H), $H^{2-5,2'-5'}$	214.8 (CO), 112.0 ($C^{7,7'}$), 101.0, 94.4, 92.9 ($C^{1-6,1'-6'}$)
10	6.32 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 8.1], 5.82 (m, 8 H, $H^{2-5,2'-5'}$)	
11[c]	6.13 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 7.9], 5.50 (m, 8 H, $H^{2-5,2'-5'}$), 2.05 (s, 6 H, CH_3CN)	214.2 (CO), 132.8 (CH_3CN), 114.9 ($C^{7,7'}$), 99.5, 95.5, 95.2 ($C^{1-6,1'-6'}$), 4.8 (CH_3CN)
12[b]	6.46 [d, 2 H, $H^{1',6'}$, $J(H^{1'}-H^{2'} = H^{6'}-H^{5'})$ 9.8], 5.79 (m, 8 H, $H^{1-6,2',5'}$), 4.37 [m, 2 H, $H^{3',4'}$, $J(H^{3'}-H^{2'} = H^{4'}-H^{5'})$ 5.6]	
13[b]	6.13 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 9.3], 5.38 (br, 4 H, $H^{2,2',5,5'}$), 4.67 (br, 4 H, $H^{3,3',4,4'}$)	
14[e]	6.39 (d, 4 H, $H^{10,10',14,14'}$, $J(H^{10,10'}-H^{11,11'} = H^{14,14'}-H^{13,13'})$ 5.8], 6.34 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 7.6], 6.27 (m, 4 H, $H^{11,11',13,13'}$), 6.20 (m, 2 H, $H^{12,12'}$), 5.89 (m, 4 H, $H^{2,2',5,5'}$), 5.63 (m, 4 H, $H^{3,3',4,4'}$), 2.21 (s, 6 H, CH_3)	117.2 ($C^{9,9'}$), 106.8 ($C^{7,7'}$), 101.5, 99.7, 98.6 ($C^{10-14,10'-14'}$), 90.2, 86.2, 84.8 ($C^{1-6,1'-6'}$), 20.7 ($C^{8,8'}$)
15[e]	7.36 (m, 20 H, C_6H_5), 5.80 [d, 4 H, $H^{1,1',6,6'}$, $J(H^{1,1'}-H^{2,2'} = H^{6,6'}-H^{5,5'})$ 7.8], 4.99 (br, 4 H), 4.67 (m, 4 H, $H^{2-5,2'-5'}$), 2.34 (m, 8 H, $Ph_2PC_2\mathit{H}_4PPh_2$), 1.35 (s, 6 H, CH_3CN)	135.1–128.7 [$(\mathit{C}_6H_5)_2PC_2H_4P(\mathit{C}_6H_5)_2$)], 104.4 ($C^{7,7'}$), 90.4, 87.2, 85.8 ($C^{1-6,1'-6'}$), 26.3 [at, $(C_6H_5)_2P\mathit{C}_2H_4P(C_6H_5)_2$], 3.1 ($CH_3CN$)

[a] 300 MHz ^1H NMR spectra, 75 MHz ^{13}C NMR spectra; s = singlet, d = doublet, t = triplet, at = apparent triplet, m = multiplet; chemical shifts downfield from $SiMe_4$, coupling constants J in Hz, in $(CD_3)_2CO$ solution unless stated otherwise; numbering as in Schemes 1 and 2, ^1H NMR assignments made with the aid of $^1H-^1H$ double irradiation experiments. [b] In CD_3CN. [c] In $CDCl_3$. [d] In C_6D_6. [e] In CD_2Cl_2.

complexes in which the two metal centres are bridged by a linked ring system exhibit novel reactivity and cooperative effects between metal centres, not observed for analogous monometallic or unbridged bimetallic complexes. The following discussion sets out to illustrate how the reactivity and properties of the tricarbonylmolybdenum and related metal centres in bicycloheptatrienyl bridged complexes are modified by comparison with the well established chemistry of $[Mo(CO)_3(\eta^7-C_7H_7)]^+$ and its substituted derivatives.

Our first example demonstrates modified reactivity of the $Mo(CO)_3$ group promoted by the proximate positions of two molybdenum centres as dictated by the bicycloheptatrienyl framework. To extend the range of the bimetallic, bicycloheptatrienyl bridged complexes available for investigation, we examined $Mo(CO)_3$ co-ordination onto the pendant cycloheptatrienyl ring of $[MoI(CO)_2(\eta^7-C_{14}H_{12})][PF_6]$ **5**. Reaction of a suspension of **5** and $[Mo(CO)_3(NCMe)_3]$ in tetrahydrofuran (thf) resulted in the formation of a mixture of two bimetallic products: the expected product $[Mo_2I(CO)_5(\mu-\eta^7:\eta^7-C_{14}H_{12})][PF_6]$ **6** (Scheme 2) and a second, more soluble material subsequently identified as the doubly bridged complex $[Mo_2(CO)_4(\mu-I)(\mu-\eta^7:\eta^7-C_{14}H_{12})][PF_6]$ **7**. The intermediacy of **6** in the formation of **7** was demonstrated by complete conversion of an isolated sample of **6** into **7** by heating in thf at 60 °C. The spectroscopic data for complex **6** are consistent with a superposition of the two separate halves of the molecule; NMR data for the rings attached to the $Mo(CO)_3$ and $MoI(CO)_2$ closely resemble data for the co-ordinated rings in **3** and **5** respectively. By contrast the spectroscopic data for **7** reveal a complex of high symmetry with only four signals attributable to the bicycloheptatrienyl framework in the ^{13}C NMR spectrum. In the IR spectrum, the pattern and



Scheme 2 *Reagents and conditions*: (*i*) $[Mo(CO)_3(NCMe)_3]$, 1 equivalent, stir in thf, 15 min; (*ii*) thf, 60 °C, 1 h; (*iii*) $Na[Mn(CO)_5]$, stir in thf, −78 °C then ambient, 1 h; (*iv*) NaX (X = I or Br), stir in acetone, −78 °C then ambient, 1.5 h; (*v*) X = Br, $Ag[BF_4]$, 2 equivalents, stir in NCMe, 30 min, then stir in CH_2Cl_2, 1 h; (*vi*) stir in NCMe; (*vii*) toluene, reflux, 7 h; (*viii*) NCMe, reflux, 15 min, then dppe, 2 equivalents, NCMe, reflux 2 h

wavenumbers of the carbonyl stretching frequencies are atypical of isolated $MoI(CO)_2$ or $Mo(CO)_3$ units found in complexes **1**–**6**. On the basis of these data and mass spectroscopic data, consistent with a tetracarbonyl complex, **7** was formulated as the doubly bridged bimetallic $[Mo_2(CO)_4(\mu\text{-}I)(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]$, this structural assignment being subsequently confirmed by a single-crystal X-ray study.

The crystal structure of **7** contains two crystallographically distinct cations A and B which have very similar gross structures. These are illustrated in Fig. 1 together with the atomic numbering schemes adopted and important bond lengths and angles are presented in Table 3. The proposed structure of **7**, in which the two metal centres are bridged by both $C_{14}H_{12}$ and iodide ligands in a molecule with approximate two-fold symmetry, is confirmed. The molybdenum to mean cycloheptatrienyl ring plane distances lie in the range 1.62–1.64 Å, comparable with simple cycloheptatrienyl complexes $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$ (1.658 Å)[13] and $[Mo(\sigma\text{-}C_6H_5)(CO)_2(\eta^7\text{-}C_7H_7)]$ (1.654 Å)[14] and the intermetallic molybdenum–molybdenum separations are 4.562 (A) and 4.568 Å (B) so precluding any significant, direct interaction between the metal centres. However the principal features of structural interest in **7** are dictated by the bicycloheptatrienyl ligand framework, the X-ray crystallographic characterisation of which is unprecedented. The salient structural feature of **7** is the twisted conformation of the bicycloheptatrienyl ligand with interplanar angles between best ring planes of 39.8 (A) and 35.5° (B); a view along the molybdenum–molybdenum axis of molecule A is shown in Fig. 2. This twisted conformation of the linked ring system appears to be a consistent feature in related doubly bridged bimetallics and may serve to avoid a strictly *cis* orientation of the two metal centres. The twist angles observed in the current study are intermediate between corresponding angles observed for $[Cr_2(CO)_4(\mu\text{-}Me_2PPMe_2)(\mu\text{-}\eta^6:\eta^6\text{-}C_{12}H_{10})]$ (27.5°)[6] at one extreme and $[Cr_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^6:\eta^6\text{-}C_{12}H_{10})]$ (50.8°)[5] and $[Mn_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^5:\eta^5\text{-}C_{10}H_8)]$ (65.4°)[3] at the other end of the range. A further aspect of note in the bicycloheptatrienyl ligand is the rather long inter-ring bond [C(13)–C(23) 1.53(1) (A), C(33)–C(43) 1.52(1) Å (B)] by comparison with the corresponding parameter in the biphenyl complexes $[Cr_2(CO)_4(\mu\text{-}Me_2PPMe_2)(\mu\text{-}\eta^6:\eta^6\text{-}C_{12}H_{10})]$[1.477(5) Å][6] and $[Cr_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^6:\eta^6\text{-}C_{12}H_{10})]$ (1.459 Å).[5]

The formation of iodo-bridged **7** from **6** provides an example of modified reactivity promoted by the bicycloheptatrienyl ligand. Although the two metal centres in **6** might be expected to adopt a preferred *trans* conformation, rotation about the inter-ring bond of the bicycloheptatrienyl ligand should be facile, so permitting the two metal centres to be placed in close proximity. In this *cis* arrangement, and with the intermetallic

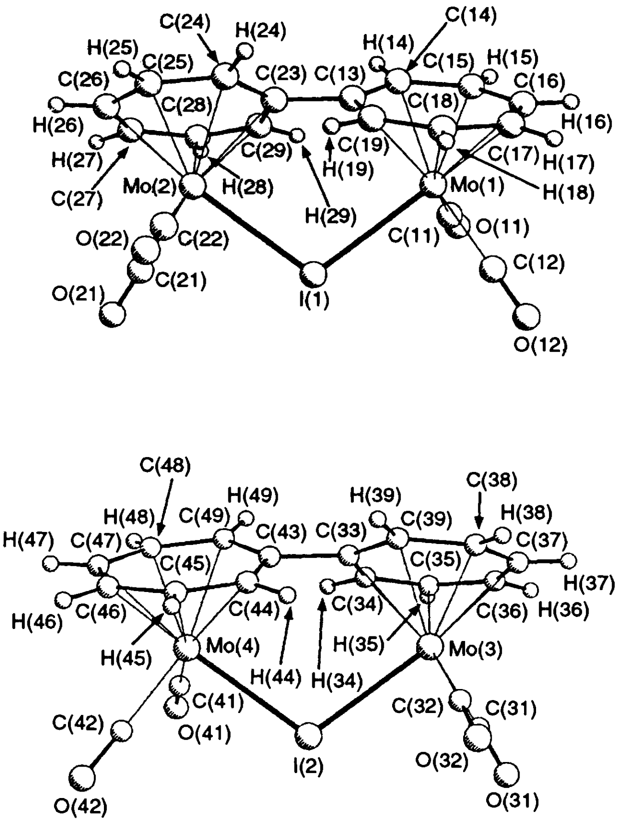


Fig. 1 Molecular structure of complex **7** showing the crystallographic numbering scheme for the two independent cations A and B present in the crystal structure

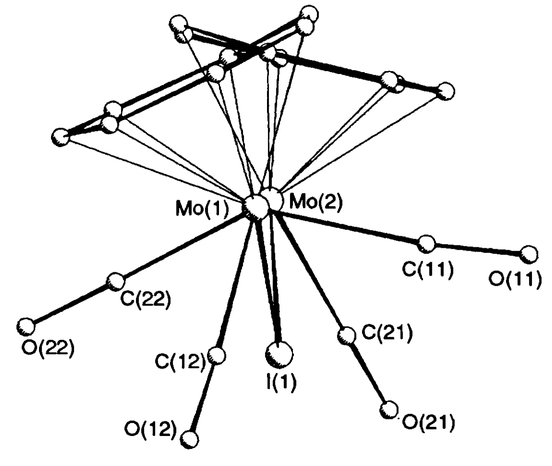


Fig. 2 View of **7** (molecule A) along the molybdenum–molybdenum axis

separation controlled by the bicycloheptatrienyl framework, we propose that the iodo ligand of the $MoI(CO)_2$ group can displace CO from the cationic $Mo(CO)_3$ unit leading to the iodo bridge. Our attempts to form an analogous iodo-bridged complex with isolated cycloheptatrienyl rings, $[Mo_2(CO)_4(\eta^7\text{-}C_7H_7)_2(\mu\text{-}I)]^+$, by reaction of $[MoI(CO)_2(\eta^7\text{-}C_7H_7)]$ with $[MoL(CO)_2(\eta^7\text{-}C_7H_7)]^+$ (L = CO or NCMe[15]) were totally without success, so demonstrating the importance of the linked ring system although a related iodo-bridged bimetallic $[M_2(CO)_6(\eta\text{-}C_5H_5)_2(\mu\text{-}I)]^+$ (M = Mo or W) has been implicated as an intermediate in the formation of $[MI(CO)_3(\eta\text{-}C_5H_5)]$ from $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and I_2.[16] Disappointingly, the dominant reaction type of **7** is cleavage of the iodo bridge; in the simplest case reaction of **7** with NaI yields $[Mo_2I_2(CO)_4(\mu\text{-}\eta^7{:}\eta^7\text{-}C_{14}H_{12})]$, a complex more readily obtained from $[Mo_2(CO)_6(\mu\text{-}\eta^7{:}\eta^7\text{-}C_{14}H_{12})]^{2+}$ (see below).

The remainder of the complexes to be discussed are derived from the dimolybdenum hexacarbonyl complex **1** as shown in Scheme 2. The intermetallic separation of > 4.5 Å observed in **7** tends to preclude the formation of metal–metal bonds between metal centres attached to the bicycloheptatrienyl framework and accordingly our attempts to reduce **1** to metal–metal bonded species were unsuccessful. However **1** does undergo reduction at the ligand framework with conversion of the carbon–carbon bond which links the bridgehead carbons from a single to a double bond. Thus reaction of **1** with $Na[Mn(CO)_5]$ in thf led to formation of the heptafulvalene complex $[Mo_2(CO)_6(\mu\text{-}\eta^6{:}\eta^6\text{-}C_{14}H_{12})]$ **8**, the chromium analogue of which has been synthesised previously, starting from $[Cr(CO)_3(NCMe)_3]$ and heptafulvalene.[17] The synthesis of **8** from **1** and $Na[Mn(CO)_5]$ mirrors the formation of bicycloheptatriene bridged $[Mo_2(CO)_6(\mu\text{-}\eta^6{:}\eta^6\text{-}C_{14}H_{14})]$ from reaction of $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ with $Na[Mn(CO)_5]$;[18] both reactions result in ligand-centred carbon–carbon bond formation. Interestingly, we were also able to synthesise heptafulvalene by reaction of the bicycloheptatrienyl dication $C_{14}H_{12}{}^{2+}$ with $Na[Re(CO)_5]$ in contrast to previous unsuccessful attempts to obtain heptafulvalene by reduction of $C_{14}H_{12}{}^{2+}$ with zinc.[12]

A further example of modification in reactivity promoted by the bicycloheptatrienyl ligand is provided by an investigation on $\eta^7 \longleftrightarrow \eta^3$ hapticity interconversion at the linked seven-membered rings. We have previously reported a series of studies which illustrate interconversion of the bonding mode of the cycloheptatrienyl ligand between η^7 and η^3 hapticity types when co-ordinated to appropriate Mo and W centres.[15,19] Most pertinently we have demonstrated that in acetonitrile, at 20 °C, the complex $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)]^+$ exists in equilibrium with $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ in the approximate ratio 65 : 35 ($\eta^7{:}\eta^3$).[15,20] In the current work, we set out to explore how linking the two metal centres through the bicycloheptatrienyl ligand would affect preferred hapticity in an otherwise identical system.

The synthesis of $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)]^+$ is carried out in a two-step process[15] starting from $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ *via* the intermediate $[MoI(CO)_2(\eta^7\text{-}C_7H_7)]$ and a parallel strategy was adopted for the synthesis of the bimetallic, bicycloheptatrienyl analogue $[Mo_2(CO)_4(NCMe)_2(\mu\text{-}\eta^7{:}\eta^7\text{-}C_{14}H_{12})][BF_4]$ **11**. Reaction of $[Mo_2(CO)_6(\mu\text{-}\eta^7{:}\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **1** with an excess of NaX (X = I or Br) in acetone at −78 °C and subsequent warming to room temperature led to formation of the green halogenocarbonyl complexes $[Mo_2X_2(CO)_4(\mu\text{-}\eta^7{:}\eta^7\text{-}C_{14}H_{12})]$ (X = I **9** or Br **10**) *via* an unidentified red intermediate. By comparison with their monometallic analogues $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$, complexes **9** and **10** exhibit considerably reduced solubility but almost identical carbonyl stretching frequencies in their infrared spectra. In the second step of the synthesis, treatment of the bromo complex **10** with $Ag[BF_4]$ in acetonitrile and subsequent dissolution of the crude reaction product in CH_2Cl_2 led to isolation of the required acetonitrile complex **11** as a green solid. The equivalence of the two metal centres in **11** is clearly demonstrated by the relative simplicity of the ^1H and ^{13}C NMR spectra which also confirm the presence of the NCMe ligand. The IR spectrum of **11** in CH_2Cl_2 shows two carbonyl stretching frequencies [ν(CO) (CH_2Cl_2) 2041, 2005 cm^{-1}] closely comparable with those observed for $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)]^+$ [ν(CO) (CH_2Cl_2) 2036, 1993 cm^{-1}][15] and typical of an η^7-co-ordinated molybdenum centre. An investigation of $\eta^7 \longleftrightarrow \eta^3$ hapticity interconversion in the bicycloheptatrienyl system was carried out simply by observing the infrared, ^1H and ^{13}C NMR spectra of a solution of **11** in acetonitrile. The results are compatible with a two component equilibrium mixture consisting of the $\eta^7{:}\eta^3$ complex **12** and $\eta^3{:}\eta^3$ bonded **13** (Scheme 2) and not including the starting

Table 3 Selected bond lengths (Å) and angles (°) for the independent cations A and B of complex **7**

A				B			
Mo(1)–I(1)	2.842(5)	O(11)–C(11)	1.17(1)	Mo(3)–I(2)	2.837(4)	O(31)–C(31)	1.13(1)
Mo(2)–I(1)	2.851(8)	O(12)–C(12)	1.13(1)	Mo(4)–I(2)	2.842(3)	O(32)–C(32)	1.14(1)
Mo(1)–C(11)	2.00(1)	O(21)–C(21)	1.12(1)	Mo(3)–C(31)	2.01(1)	O(41)–C(41)	1.13(1)
Mo(1)–C(12)	2.00(1)	O(22)–C(22)	1.16(1)	Mo(3)–C(32)	2.02(1)	O(42)–C(42)	1.13(1)
Mo(1)–C(13)	2.30(1)	C(13)–C(14)	1.38(1)	Mo(3)–C(33)	2.330(9)	C(33)–C(34)	1.44(1)
Mo(1)–C(14)	2.322(9)	C(13)–C(19)	1.44(1)	Mo(3)–C(34)	2.298(9)	C(33)–C(39)	1.39(1)
Mo(1)–C(15)	2.262(9)	C(13)–C(23)	1.53(1)	Mo(3)–C(35)	2.31(1)	C(33)–C(43)	1.52(1)
Mo(1)–C(16)	2.30(1)	C(14)–C(15)	1.42(1)	Mo(3)–C(36)	2.28(1)	C(34)–C(35)	1.40(1)
Mo(1)–C(17)	2.267(9)	C(15)–C(16)	1.40(1)	Mo(3)–C(37)	2.28(1)	C(35)–C(36)	1.40(2)
Mo(1)–C(18)	2.311(9)	C(16)–C(17)	1.37(1)	Mo(3)–C(38)	2.25(1)	C(36)–C(37)	1.37(2)
Mo(1)–C(19)	2.31(1)	C(17)–C(18)	1.42(1)	Mo(3)–C(39)	2.335(9)	C(37)–C(38)	1.38(2)
Mo(2)–C(21)	2.05(1)	C(18)–C(19)	1.39(1)	Mo(4)–C(41)	2.03(1)	C(38)–C(39)	1.43(1)
Mo(2)–C(22)	2.01(1)	C(23)–C(24)	1.39(1)	Mo(4)–C(42)	2.02(1)	C(43)–C(44)	1.40(1)
Mo(2)–C(23)	2.301(9)	C(23)–C(29)	1.43(1)	Mo(4)–C(43)	2.320(8)	C(43)–C(49)	1.40(1)
Mo(2)–C(24)	2.340(9)	C(24)–C(25)	1.43(1)	Mo(4)–C(44)	2.257(9)	C(44)–C(45)	1.38(1)
Mo(2)–C(25)	2.26(1)	C(25)–C(26)	1.40(1)	Mo(4)–C(45)	2.30(1)	C(45)–C(46)	1.41(1)
Mo(2)–C(26)	2.30(1)	C(26)–C(27)	1.40(1)	Mo(4)–C(46)	2.28(1)	C(46)–C(47)	1.39(2)
Mo(2)–C(27)	2.30(1)	C(27)–C(28)	1.42(1)	Mo(4)–C(47)	2.29(1)	C(47)–C(48)	1.39(2)
Mo(2)–C(28)	2.31(1)	C(28)–C(29)	1.38(1)	Mo(4)–C(48)	2.247(9)	C(48)–C(49)	1.42(1)
Mo(2)–C(29)	2.29(1)			Mo(4)–C(49)	2.326(9)		
Mo(1)–I(1)–Mo(2)	106.5(2)	C(15)–C(16)–C(17)	126(1)	Mo(3)–I(2)–Mo(4)	107.1(1)	C(35)–C(36)–C(37)	129(1)
I(1)–Mo(1)–C(11)	89.5(4)	C(16)–C(17)–C(18)	129.7(9)	I(2)–Mo(3)–C(31)	85.8(3)	C(36)–C(37)–C(38)	127(1)
I(1)–Mo(1)–C(12)	87.2(4)	C(17)–C(18)–C(19)	129.0(9)	I(2)–Mo(3)–C(32)	83.5(3)	C(37)–C(38)–C(39)	131(1)
I(1)–Mo(1)–C(13)	84.7(3)	C(13)–C(19)–C(18)	129.1(9)	I(2)–Mo(3)–C(33)	85.0(2)	C(33)–C(39)–C(38)	127.8(9)
C(11)–Mo(1)–C(12)	84.7(7)	Mo(2)–C(21)–O(21)	180(1)	C(31)–Mo(3)–C(32)	80.3(5)	Mo(4)–C(41)–O(41)	177(1)
I(1)–Mo(2)–C(21)	86.4(4)	Mo(2)–C(22)–O(22)	179(1)	I(2)–Mo(4)–C(41)	83.1(3)	Mo(4)–C(42)–O(42)	177.6(9)
I(1)–Mo(2)–C(22)	87.0(3)	C(13)–C(23)–C(24)	116.0(8)	I(2)–Mo(4)–C(42)	90.7(3)	C(33)–C(43)–C(44)	117.4(7)
I(1)–Mo(2)–C(23)	84.4(3)	C(13)–C(23)–C(29)	117.2(8)	I(2)–Mo(4)–C(43)	84.6(2)	C(33)–C(43)–C(49)	117.4(8)
C(21)–Mo(2)–C(22)	84.2(5)	C(24)–C(23)–C(29)	126.8(8)	C(41)–Mo(4)–C(42)	81.6(4)	C(44)–C(43)–C(49)	125.0(9)
Mo(1)–C(11)–O(11)	174(1)	C(23)–C(24)–C(25)	127.8(8)	Mo(3)–C(31)–O(31)	175(1)	C(43)–C(44)–C(45)	130.7(9)
Mo(1)–C(12)–O(12)	177(2)	C(24)–C(25)–C(26)	130.7(9)	Mo(3)–C(32)–O(32)	175.1(9)	C(44)–C(45)–C(46)	128.6(9)
C(14)–C(13)–C(19)	126.1(8)	C(25)–C(26)–C(27)	126.7(9)	C(34)–C(33)–C(39)	126.7(9)	C(45)–C(46)–C(47)	129(1)
C(14)–C(13)–C(23)	117.0(8)	C(26)–C(27)–C(28)	128.5(9)	C(34)–C(33)–C(43)	116.0(8)	C(46)–C(47)–C(48)	127(1)
C(19)–C(13)–C(23)	116.9(8)	C(27)–C(28)–C(29)	129.5(9)	C(39)–C(33)–C(43)	117.0(8)	C(47)–C(48)–C(49)	129(1)
C(13)–C(14)–C(15)	128.5(9)	C(23)–C(29)–C(28)	129.4(9)	C(33)–C(34)–C(35)	129(1)	C(43)–C(49)–C(48)	130.0(9)
C(14)–C(15)–C(16)	131(1)			C(34)–C(35)–C(36)	129(1)		

material **11**. Moreover, at 20 °C the principal component of the equilibrium mixture is the $\eta^3:\eta^3$ species **13** (approximate ratio **12**:**13** = 35:65 as determined from ^{1}H NMR integrals) in contrast to the predominance of the η^7-bonded [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)]$^+$ in the analogous monometallic system.

In principle the bicycloheptatrienyl complex **11**, dissolved in acetonitrile, has scope for a three-component equilibrium system between the $\eta^7:\eta^7$ bonded **11**, $\eta^7:\eta^3$ bonded **12** and $\eta^3:\eta^3$ bonded **13**, and the interpretation of the spectra, outlined below, is guided by experience drawn from the two-component equilibrium [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_6$R)]$^+$ $\rightleftharpoons$ [Mo(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_6$R)]$^+$ (R = H, Me or C$_6$H$_4$Me-4).[15,20] For these particular mononuclear complexes, the principal features characteristic of $\eta^7 \longrightarrow \eta^3$ 'ring slip' are: (*i*) a colour change from green to orange yellow, (*ii*) a shift to lower wavenumber of the averaged carbonyl stretching frequencies by *ca.* 90 cm^{-1}, (*iii*) in the ^{13}C NMR spectrum, a shift to low field in the CO resonances (from δ 216.9 to 224.9 where R = H)[20] and (*iv*) in the ^{1}H NMR spectrum, a shift to high field and broadening of the cycloheptatrienyl ring resonances (the broadening is probably associated with a 1,2-shift of the metal centre around the η^3-bonded cycloheptatrienyl ring).[21,22] When green [Mo$_2$(CO)$_4$(NCMe)$_2$(μ-$\eta^7:\eta^7$-C$_{14}$H$_{12}$)][BF$_4$]$_2$ **11** was dissolved in acetonitrile an orange-yellow solution resulted which exhibited three carbonyl stretching frequencies [ν(CO) (MeCN) 2013m, 1958s, 1883m cm^{-1}] indicative of a mixture of η^7- and η^3-bonded molybdenum centres. The high wavenumber band at 2013 cm^{-1} is shifted quite considerably from that of **11** (in CH$_2$Cl$_2$) and is almost certainly more correctly assigned to the $\eta^7:\eta^3$ product **12**. Hydrogen-1 and ^{13}C NMR spectra of the equilibrium mixture were obtained by dissolving a sample of **11** in CD$_3$CN. The ^{13}C NMR spectrum so obtained exhibits broad and difficult to assign resonances for the bicycloheptatrienyl carbons but in the carbonyl carbon region, three sharp resonances were observed, two in the region typical of an η^3-bonded Mo centre (at δ 224.8 and 224.5) and one resonance at δ 217.1 indicative of an η^7-bonded centre. The peak heights of the resonances at δ 217.1 and 224.5 are essentially identical whilst that at 224.8 is approximately twice the height of the resonance at δ 224.5. These data are indicative of a two-component equilibrium system with the resonance at δ 224.8 assigned to the $\eta^3:\eta^3$ complex **13** and resonances at δ 224.5 and 217.1 assigned to $\eta^7:\eta^3$ bonded **12**. The presence of significant quantities of a third component, $\eta^7:\eta^7$-bonded **11** would require either an additional resonance around δ 217 or, in the case of overlapping signals, different signal intensities to those described. These conclusions are supported by the ^{1}H NMR data of which selected spectra are illustrated in Fig. 3. The room-temperature ^{1}H NMR spectrum of the equilibrium mixture [Fig. 3(*a*)] shows six groups of signals which were assigned with the aid of ^{1}H–^{1}H double irradiation experiments and variable-temperature studies (see below). The doublet at δ 6.13, due to protons adjacent to the bridgehead, and the two broad and shielded resonances centred at δ 5.38 and 4.67 can be assigned to the symmetrical $\eta^3:\eta^3$ complex **13** whilst the remaining resonances are due to $\eta^7:\eta^3$-bonded **12**; the protons of the η^3-bonded ring of **12** exhibit a broad range of chemical shifts (δ 6.46, 5.79, 4.37) as in **13**. As shown by Fig. 3(*b*) (0 °C) and 3(*c*) (60 °C), the position of equilibrium between **12** and **13** is temperature dependent with the proportion of the $\eta^3:\eta^7$ complex **12** being decreased by cooling and increased on heating to 60 °C; a similar high-temperature preference for the

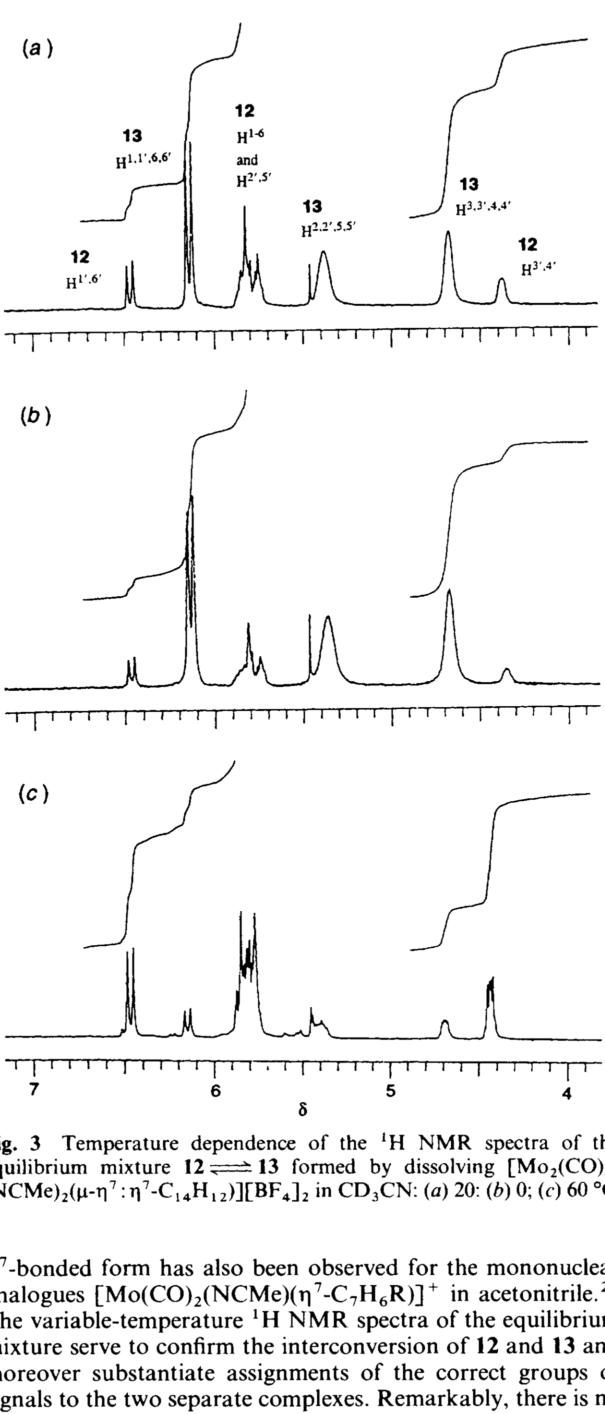


Fig. 3 Temperature dependence of the ^1H NMR spectra of the equilibrium mixture **12** $\rightleftharpoons$ **13** formed by dissolving $[Mo_2(CO)_4(NCMe)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][BF_4]_2$ in CD_3CN: (*a*) 20; (*b*) 0; (*c*) 60 °C

η^7-bonded form has also been observed for the mononuclear analogues $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+$ in acetonitrile.[20] The variable-temperature ^1H NMR spectra of the equilibrium mixture serve to confirm the interconversion of **12** and **13** and moreover substantiate assignments of the correct groups of signals to the two separate complexes. Remarkably, there is no evidence for significant quantities of the third possible component of the equilibrium mixture, $\eta^7:\eta^7$ bonded **11** even at elevated temperatures which promote the η^7-bonding mode. Variable-temperature studies also support assignments of the carbonyl carbon resonances; at −30 °C, the resonance at δ 224.8, assigned to $\eta^3:\eta^3$-bonded **13** is significantly strengthened in intensity at the expense of the other carbonyl resonances, consistent with an increased proportion of **13** at low temperature.

The striking result from these investigations on hapticity interconversion in bicycloheptatrienyl bridged bimetallics is the increased reactivity of the metal centres towards $\eta^7 \longrightarrow \eta^3$ ring slip. Not only is the $\eta^7:\eta^7$ complex **11** not observed in the equilibrium mixture but also the $\eta^3:\eta^3$ species **13** is the predominant component at room temperature; these observations contrast with the analogous monometallic systems $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_6R)]^+ \rightleftharpoons [Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_6R)]^+$. It is probable that in η^3-bonded cycloheptatrienyl ligands there is some charge localisation on the uncoordinated diene unit and we suggest that the $\eta^3:\eta^3$ bonded bicycloheptatrienyl ligand presents the opportunity for an extended unsaturated system through the linked rings as shown for **13** in Scheme 2. Such an arrangement may promote the η^3-bonding mode of the molybdenum centres although, as noted previously, in η^3-bonded cycloheptatrienyl complexes of Mo and W, a 1,2 metal shift serves to exchange the ring carbons attached to the metal centre[21] and therefore **13** as shown in Scheme 2 is only one representation of the structure.

The remainder of the discussion will focus upon an example of intermetallic, electronic communication promoted by the bicycloheptatrienyl framework. Some of the most comprehensive and relevant investigations on intermetallic, electronic communication in ligand-bridged complexes have been carried out on bimetallic chromium biphenyl systems containing identical metal centres.[5,6] Cyclic voltammetric studies on these complexes provide an estimate of the extent of electronic communication between metal centres by the magnitude of ΔE°, where ΔE° is the difference in potentials at which redox processes for the two discrete, but identical metal centres are observed. Typically, mono-bridged species such as $[Cr_2(CO)_6(\mu\text{-}\eta^6:\eta^6\text{-}C_{12}H_{10})]$ exhibit Class II mixed-valence behaviour with ΔE° around 200 mV whereas doubly bridged complexes such as $[Cr_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^6:\eta^6\text{-}C_{12}H_{10})]$ have ΔE° values in excess of 500 mV indicating the possibility of complete electron delocalisation and Class III mixed-valence behaviour.[5] Intermetallic, electronic communication may occur either through a direct metal–metal interaction or through the bridging ligand but, in the case of biphenyl (and bicycloheptatrienyl) bridged systems, the bridging ligand must have an important role given the large intermetallic separation governed by the ligand framework.

The design of a complex to illustrate intermetallic communication through the bicycloheptatrienyl ligand was governed by two factors. First, we chose not to mask any effect due to the bicycloheptatrienyl ligand and therefore investigated a complex in which the two metal centres are bridged only by this ligand. Secondly, in our experience with the redox chemistry of the cycloheptatrienylmolybdenum system, complexes which exhibit reversible redox behaviour allowing straightforward determination of E° values are restricted to diphosphine substituted complexes of the type $[MoX(L)_2(\eta^7\text{-}C_7H_7)]^{z+}$ [$z = 0$, X = halide, C≡CR *etc.*, $(L)_2 = \{P(OMe)_3\}_2$ or $Ph_2PCH_2CH_2PPh_2$ (dppe); $z = +1$, X = NCMe, $(L)_2$ = dppe].[23,24] These non-carbonyl containing derivatives are accessible from the sandwich complex $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)]^+$ [11,25] and therefore the synthesis of the equivalent bicycloheptatrienyl complex $[Mo_2(\eta^6\text{-}C_6H_5Me)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **14** was examined. Using a synthesis analogous to that of $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)]^+$ from $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$, complex **14** was prepared by reflux of a suspension of **1** in toluene. The formation of **14** proceeded more rapidly than for its mononuclear counterpart but also in much lower yield. In view of the small quantities of **14** obtained, the choice of a suitable redox active complex for investigation by cyclic voltammetry was restricted to those accessible from **14** in a one-step synthesis and, by analogy with the reactions of $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)]^+$,[26] the synthesis of $[Mo_2(NCMe)_2(dppe)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})]^{2+}$ **15** was effected by reflux of **14** with dppe in acetonitrile. We have established previously that the analogous mononuclear complex $[Mo(NCMe)(dppe)(\eta^7\text{-}C_7H_7)]^+$ undergoes a reversible one-electron oxidation with E° (MeCN) 0.37 V as determined by cyclic voltammetry and the 17-electron radical dication $[Mo(NCMe)(dppe)(\eta^7\text{-}C_7H_7)]^{2+}$ has been generated chemically, isolated, and fully characterised.[23] To date, the small quantities of **15** available have precluded analogous synthetic studies but cyclic voltammetric investigations on **15** have been carried out. The cyclic voltammogram of **15** {MeCN–0.2 mol dm^{-3} [NBu$^n_4$][BF$_4$], potentials *vs.* standard calomel electrode} exhibits two narrowly separated, reversible oxidations for which E° values are estimated as $E^\circ_1 = 0.41$ V for the 2+/3+ couple and $E^\circ_2 = 0.54$ V for the 3+/4+ couple. The ΔE° value of 130 mV is small but, nevertheless, the bridging bicycloheptatrienyl ligand has been shown by a well established procedure, to promote some limited intermetallic, electronic communication.

Experimental

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. Thermally rearranged bicycloheptatriene $C_{14}H_{14}$ was prepared from [C_7H_7][BF_4] in two steps by published procedures.[12,27] The chemicals dppe, Ag[BF_4] and [$Mn_2(CO)_{10}$] were supplied by Aldrich Chemical Co. 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were recorded on Bruker AC 300 E or Varian Associates XL 300 spectrometers. Infrared spectra were obtained on a Perkin-Elmer FT 1710 spectrometer and mass spectra using a Kratos Concept 1S instrument. Cyclic voltammetric studies were carried out, as described previously,[24] at a carbon working electrode using 0.2 mol dm^{-3} [NBu$^n_4$][BF$_4$] as supporting electrolyte. All potentials are referenced to an aqueous calomel electrode and, under these conditions, E° for the couple [Fe(η-C_5H_5)$_2$]–[Fe(η-C_5H_5)$_2$]$^+$ is 0.43 V in MeCN. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Syntheses.—[$C_{14}H_{13}$][PF_6]. A cooled (−20 °C) solution of thermally rearranged bicycloheptatriene (2.859 g, 15.71 mmol) in dichloromethane (35 cm^3) was treated with [CPh_3][PF_6] (5.50 g, 14.18 mmol) over a period of 15 min. A dark red solution was formed which was stirred at −20 °C for 1 h, resulting in the precipitation of the product, [$C_{14}H_{13}$][PF_6], as an orange solid. The product was collected by filtration (at −20 °C), washed [toluene (40 cm^3), diethyl ether (30 cm^3)] and dried; yield 3.34 g (72% based on [CPh_3][PF_6]).

[$C_{14}H_{12}$][PF_6]$_2$. Treatment of [$C_{14}H_{13}$][PF_6] (2.61 g, 8.00 mmol) in dichloromethane (25 cm^3) with a solution of [CPh_3][PF_6] (3.15 g, 8.12 mmol) in dichloromethane (25 cm^3) and reflux of the reaction mixture for 1 h led to the formation of [$C_{14}H_{12}$][PF_6]$_2$ as an orange precipitate. The precipitate was collected, washed (diethyl ether) and dried; yield 1.21 g (32%). Continued reflux of the reaction mixture mother-liquors for a further 2 h gave an additional 0.28 g of product; total yield 1.49 g (40%).

[$Mo_2(CO)_6$(μ-η^7:η^7-$C_{14}H_{12}$)][PF_6]$_2$ **1**. *Method* (*a*). A solution of $Mo(CO)_6$ (0.958 g, 3.63 mmol) in acetonitrile (40 cm^3) was refluxed for 6 h then evaporated to dryness. The resulting residue of [$Mo(CO)_3(NCMe)_3$] was suspended in thf (30 cm^3) and treated with [$C_{14}H_{12}$][PF_6]$_2$ (0.811 g, 1.73 mmol). Precipitation of the product as an orange-brown solid occurred after 5 min and the mother-liquors were removed after 15 min. The product was recrystallised twice from acetone–toluene to give **1** as an orange solid; yield 0.613 g (42% based on [$C_{14}H_{12}$][PF_6]$_2$).

Method (*b*). A solution of $Mo(CO)_6$ (0.394 g, 1.49 mmol) in acetonitrile (40 cm^3) was refluxed for 6 h then evaporated to dryness. The resulting residue of [$Mo(CO)_3(NCMe)_3$] was suspended in dichloromethane (25 cm^3) and treated with [$Mo(CO)_3$(η^7-$C_{14}H_{12}$)][PF_6]$_2$ **3** (0.887 g, 1.36 mmol). The reaction mixture developed a deep red coloration followed by the precipitation of the product as an orange solid. After 15 min, the mother-liquors were removed and the product **1** was washed (diethyl ether) then recrystallised from acetone–toluene; yield 0.120 g (11% based on **3**).

[$Mo(CO)_3$(η^7-$C_{14}H_{13}$)][PF_6] **2**. A solution of $Mo(CO)_6$ (1.644 g, 6.23 mmol) in acetonitrile (40 cm^3) was refluxed for 6 h then evaporated to dryness. The resulting residue of [$Mo(CO)_3(NCMe)_3$] was suspended in stirred thf (35 cm^3) and treated with [$C_{14}H_{13}$][PF_6] (1.848 g, 5.67 mmol). Precipitation of the product as a bright orange solid occurred after 5 min and the mother-liquors were removed after 15 min. Recrystallisation from acetone–diethyl ether gave [$Mo(CO)_3$(η^7-$C_{14}H_{13}$)][PF_6] as an orange solid; yield 1.148 g (40%).

[$Mo(CO)_3$(η^7-$C_{14}H_{12}$)][PF_6]$_2$ **3**. A suspension of [$Mo(CO)_3$(η^7-$C_{14}H_{13}$)][PF_6] **2** (1.957 g, 3.87 mmol) in dichloromethane (60 cm^3) was treated dropwise with a solution of [CPh_3][PF_6] (1.521 g, 3.92 mmol) in dichloromethane (25 cm^3). The reaction mixture was then refluxed resulting in progressive formation of the product as an orange precipitate. After 3.5 h, the precipitated [$Mo(CO)_3$(η^7-$C_{14}H_{12}$)][PF_6]$_2$ was separated by filtration, washed (dichloromethane then diethyl ether) and dried; yield 1.112 g (44%).

[$MoI(CO)_2$(η^7-$C_{14}H_{13}$)] **4**. Addition of NaI (0.266 g, 1.77 mmol) to a stirred solution of [$Mo(CO)_3$(η^7-$C_{14}H_{13}$)][PF_6] **2** (0.449 g, 0.89 mmol) in acetone (20 cm^3) gave a green solution. After 1 h solvent was removed and the resulting green residue recrystallised from dichloromethane–*n*-hexane to give **4** as a green-brown solid; yield 0.346 g (85%).

[$MoI(CO)_2$(η^7-$C_{14}H_{12}$)][PF_6] **5**. Treatment of a cooled (0 °C), stirred solution of [$MoI(CO)_2$(η^7-$C_{14}H_{13}$)] **4** (0.628 g, 1.37 mmol) in dichloromethane (15 cm^3), with a cooled (0 °C) solution of [CPh_3][PF_6] (0.595 g, 1.53 mmol) in dichloromethane (5 cm^3) resulted in the precipitation of the product **5** as a purple solid. After 1 h the product was separated by filtration, washed [toluene (40 cm^3) then diethyl ether (40 cm^3)] and dried; yield 0.503 g (61%).

[$Mo_2I(CO)_5$(μ-η^7:η^7-$C_{14}H_{12}$)][PF_6] **6**. A solution of $Mo(CO)_6$ (0.340 g, 1.29 mmol) in acetonitrile (40 cm^3) was refluxed for 6 h then evaporated to dryness. The resulting residue of [$Mo(CO)_3(NCMe)_3$] was suspended in thf (30 cm^3) and treated with [$MoI(CO)_2$(η^7-$C_{14}H_{12}$)][PF_6] **5** (0.712 g, 1.18 mmol). The brown reaction mixture was stirred for 15 min then added dropwise to rapidly swirling diethyl ether, leading to

Table 4 Structure analysis of complex **7**

Formula	$C_{18}H_{12}F_6IMo_2O_4P$
M	756.04
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	14.71(1)
b/Å	15.88(2)
c/Å	10.44(3)
α/°	109.3(1)
β/°	98.9(1)
γ/°	77.96(9)
U/Å^3	2241(8)
T/K	296
Z	4
D_c/g cm^{-3}	2.240
F(000)	1432
μ/cm^{-1}	25.98 (Mo-Kα)
Diffractometer	Rigaku AFC6S
Crystal dimensions/mm	0.12 × 0.22 × 0.40
λ/Å	0.710 69 (Mo-Kα)
θ range/°	1–25
Scan type	ω
Scan width/°	$1.13 + 0.30 \tan\theta$
Total data	8245
Unique data	7906
'Observed' data [$I > 3\sigma(I)$], N_0	4975
Least squares variables, N_v	577
*R**	0.038
*R'**	0.045
*S**	1.55
Difference map features/e Å^{-3}	+0.85, −0.75

* $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$.

the precipitation of a brown solid which was separated, washed (diethyl ether) and dried. Extraction with acetone and subsequent solvent removal gave an oily residue. Dissolution in dichloromethane and fractional precipitation from dichloromethane-diethyl ether gave, in the first fraction, $[Mo_2I(CO)_5(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]$ **6** which was isolated as an orange-brown solid [yield 0.130 g (14%)] and in the second fraction, $[Mo_2(CO)_4(\mu\text{-}I)(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]$ **7** as a green-brown solid; yield 0.047 g (5%) (Found; C, 29.0; H, 1.8. $C_{18}H_{12}F_6IMo_2O_4P$ requires C, 28.6; H, 1.6%).

$[Mo_2(CO)_4(\mu\text{-}I)(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]$ **7**. A solution of $[Mo_2I(CO)_5(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]$ **6** (1.198 g, 1.53 mmol) in thf (40 cm^3) was heated at 60 °C for 1 h, resulting in the precipitation of a green solid. The reaction mixture was then evaporated to dryness. Extraction of the residue with CH_2Cl_2 and recrystallisation from dichloromethane–diethyl ether gave **7** as a green solid; yield 0.508 g (44%).

$[Mo_2(CO)_6(\mu\text{-}\eta^6:\eta^6\text{-}C_{14}H_{12})]$ **8**. A solution of $[Mn_2(CO)_{10}]$ (0.261 g, 0.67 mmol) in thf (15 cm^3) was stirred over sodium amalgam [prepared from 0.26 g, 11.30 mmol Na in Hg (1.5 cm^3)] for 2 h to give a green-brown solution of $Na[Mn(CO)_5]$. The solution of $Na[Mn(CO)_5]$ was separated from the amalgam, cooled (−78 °C) and $[Mo_2(CO)_6(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **1** (0.551 g, 0.66 mmol) added. The stirred mixture was allowed to warm slowly to room temperature and, after 1 h, solvent was removed to give a dark red residue. The residue was washed (*n*-hexane) then recrystallised from diethyl ether–*n*-hexane to give **8** as a purple solid; yield 0.010 g (3%).

$[Mo_2I_2(CO)_4(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})]$ **9**. Addition of NaI (0.463 g, 3.09 mmol) to a cooled (−78 °C) solution of $[Mo_2(CO)_6(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **1** (0.224 g, 0.27 mmol) in acetone (20 cm^3) gave a red solution which, upon warming to room temperature, resulted in the formation of a green precipitate in green-brown mother-liquors. After 1.5 h, the reaction mixture was evaporated to dryness and the residue recrystallised from CH_2Cl_2–*n*-hexane to give the product **9** as a dark green solid; yield 0.051 g (26%). Similarly, the addition of NaBr (0.176 g, 1.71 mmol) to a cooled (−78 °C) solution of **1** (0.450 g, 0.54 mmol) in acetone (20 cm^3) gave $[Mo_2Br_2(CO)_4(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})]$ **10**, as a green solid after work up; yield 0.060 g (17%).

$[Mo_2(CO)_4(NCMe)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][BF_4]_2$ **11**. Addition of $Ag[BF_4]$ (0.201 g, 1.03 mmol) to a suspension of $[Mo_2Br_2(CO)_4(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})]$ **10** (0.300 g, 0.47 mmol) in acetonitrile (20 cm^3) resulted in a rapid colour change from green to orange. After 30 min the reaction mixture was filtered, then evaporated to dryness. The orange residue was dissolved in dichloromethane and stirred for 1 h yielding a green solution. Filtration, followed by recrystallisation from dichloromethane–diethyl ether gave **11** as a green solid; yield 0.189 g (55%).

$[Mo_2(\eta^6\text{-}C_6H_5Me)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **14**. An orange suspension of $[Mo_2(CO)_6(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **1** (0.461 g, 0.56 mmol) in toluene (50 cm^3) was refluxed for 7 h resulting in the formation of a green-brown precipitate, which was separated from the mother-liquors. Subsequent recrystallisation of the precipitate from dichloromethane–diethyl ether gave the product **14** as a pale green solid; yield 0.025 g (5%).

$[Mo_2(NCMe)_2(dppe)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **15**. Reflux of $[Mo_2(\eta^6\text{-}C_6H_5Me)_2(\mu\text{-}\eta^7:\eta^7\text{-}C_{14}H_{12})][PF_6]_2$ **14** (0.025 g, 0.03 mmol) in acetonitrile (40 cm^3) resulted in a colour change from green to red. After 15 min, treatment of the reaction mixture with dppe (0.023 g, 0.06 mmol) followed by a further 2 h reflux gave an orange solution of the product. Evaporation to dryness, followed by recrystallisation from dichloromethane–toluene then acetone–diethyl ether gave **15** as a pink solid; yield 0.010 g (22%).

X-Ray Crystal Structure Analysis of Complex 7.—The majority of details of the structure analysis carried out on complex **7** are given in Table 4; non-hydrogen atom positional parameters are listed in Table 5. Green, prismatic crystals of **7** were grown by slow diffusion of a hexane layer into a dichloromethane solution of the complex. Cell dimensions were

Table 5 Atomic coordinates for complex **7**

Atom	*x*	*y*	*z*
I(1)	0.522 60(4)	0.110 03(4)	0.437 14(7)
I(2)	0.287 17(4)	0.262 38(4)	0.280 95(8)
Mo(1)	0.655 46(5)	0.120 16(5)	0.274 22(8)
Mo(2)	0.548 97(5)	0.242 36(5)	0.695 82(8)
Mo(3)	0.207 20(5)	0.426 46(6)	0.224 27(9)
Mo(4)	0.142 74(5)	0.202 10(5)	0.361 71(8)
P(1)	0.237 4(2)	0.542 2(2)	0.770 2(3)
P(2)	0.045 1(2)	0.869 7(2)	0.181 6(3)
F(1)	0.278 7(4)	0.505 0(5)	0.894 2(6)
F(2)	0.141 4(4)	0.508 9(4)	0.762 5(6)
F(3)	0.198 1(4)	0.578 2(4)	0.644 6(6)
F(4)	0.334 5(3)	0.574 9(3)	0.777 3(6)
F(5)	0.198 5(4)	0.636 9(4)	0.872 0(6)
F(6)	0.277 2(4)	0.446 7(4)	0.666 2(6)
F(7)	−0.054 8(5)	0.849 1(6)	0.154(1)
F(8)	0.076 3(5)	0.790 3(7)	0.238(1)
F(9)	0.012 6(5)	0.960 6(6)	0.150(1)
F(10)	0.144 2(5)	0.892 0(7)	0.215(1)
F(11)	0.067(1)	0.821(1)	0.044(1)
F(12)	0.016(1)	0.924 6(8)	0.322(1)
O(11)	0.494 0(6)	0.203 6(9)	0.091(1)
O(12)	0.622(1)	−0.071(1)	0.084(2)
O(21)	0.346 0(6)	0.227 1(8)	0.743(1)
O(22)	0.615 0(7)	0.079 5(6)	0.819 3(9)
O(31)	0.377 9(6)	0.387 3(6)	0.054(1)
O(32)	0.365 9(5)	0.501 4(5)	0.447 4(8)
O(41)	0.172 3(7)	0.045 2(6)	0.084 7(9)
O(42)	0.288 5(5)	0.059 9(6)	0.471(1)
C(11)	0.551 3(7)	0.168(1)	0.156(1)
C(12)	0.633(1)	−0.001(1)	0.150(2)
C(13)	0.707 5(5)	0.224 3(5)	0.469 9(9)
C(14)	0.701 1(7)	0.261 2(6)	0.365(1)
C(15)	0.729 5(7)	0.218 0(7)	0.231(1)
C(16)	0.777 9(7)	0.131 2(6)	0.172(1)
C(17)	0.806 6(6)	0.064 6(6)	0.232(1)
C(18)	0.800 1(6)	0.067 1(6)	0.367(1)
C(19)	0.755 5(5)	0.135 8(6)	0.470 5(9)
C(21)	0.417 9(8)	0.232 6(8)	0.726(1)
C(22)	0.590 2(8)	0.138 7(7)	0.773(1)
C(23)	0.654 8(6)	0.281 4(5)	0.593 7(9)
C(24)	0.699 0(6)	0.276 9(6)	0.720(1)
C(25)	0.660 0(6)	0.309 3(7)	0.848(1)
C(26)	0.574 2(7)	0.362 6(7)	0.886(1)
C(27)	0.502 4(7)	0.394 5(7)	0.801(1)
C(28)	0.499 7(7)	0.381 2(7)	0.659(1)
C(29)	0.564 8(6)	0.330 8(6)	0.568 5(9)
C(31)	0.314 0(7)	0.399 9(8)	0.110(1)
C(32)	0.305 6(7)	0.477 4(7)	0.370(1)
C(33)	0.068 5(5)	0.402 2(6)	0.277(1)
C(34)	0.076 6(6)	0.361 3(6)	0.133(1)
C(35)	0.096 0(8)	0.399 8(9)	0.040(1)
C(36)	0.119 0(8)	0.485(1)	0.064(1)
C(37)	0.123 8(7)	0.554 8(9)	0.183(2)
C(38)	0.108 8(6)	0.556 0(6)	0.311(1)
C(39)	0.080 0(6)	0.490 0(6)	0.354(1)
C(41)	0.159 5(7)	0.101 3(7)	0.183(1)
C(42)	0.237 4(7)	0.112 4(7)	0.432(1)
C(43)	0.054 8(5)	0.340 0(5)	0.354(1)
C(44)	0.104 0(6)	0.349 3(6)	0.482(1)
C(45)	0.108 6(7)	0.301 2(6)	0.572(1)
C(46)	0.072 6(7)	0.221 3(7)	0.552(1)
C(47)	0.018 4(7)	0.175 0(7)	0.440(1)
C(48)	−0.010 7(6)	0.196 2(7)	0.319(1)
C(49)	−0.000 2(6)	0.273 5(6)	0.286(1)

determined using the setting angles of 14 carefully centred reflections in the range $28.71 < 2\theta < 34.44°$. An empirical absorption correction was applied to the data using the program DIFABS[28] and the data were also corrected for Lorentz and polarisation effects. A linear decay correction was applied, based on the intensities of three representative reflections which were measured after every 150 reflections and decayed by −0.35%. The structure was solved by direct methods and refined by full-matrix least squares. Hydrogen atoms were included in the structure-factor calculation in idealised positions (C–H = 0.95 Å) and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. The weighting scheme was $w = 4F_o^2/\sigma^2(F_o^2)$ with a p factor of 0.03 to weight down strong reflections. Neutral-atom scattering factors were taken from ref. 29 and all calculations were performed using the TEXSAN crystallographic software packages of Molecular Structure Corporation.[30]

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