Investigations on the synthesis and stability of η^3-bonded cycloheptadienyl complexes of molybdenum

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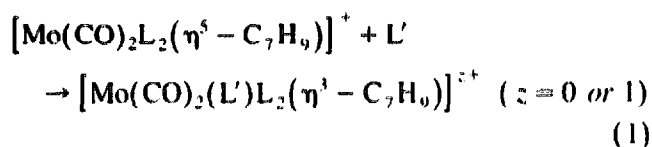
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Abstract

The trihapto bonded cycloheptadienyl complexes [MoX(CO)$_2$L$_2$(η^3-C$_7$H$_9$)] (X = Cl, L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe) 1, L$_2$ = Ph$_2$PCH$_2$PPh$_2$ (dppm) 2; X = NCO, L$_2$ = dppe 3) have been synthesised by reaction of [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)][BF$_4$] with LiCl or KNCO in acetone. Spectroscopic investigations indicate that 1–3 possess an asymmetric structure with one end of the bidentate phosphine ligand located *trans* to the C$_7$H$_9$ ring. In solution in acetonitrile [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)]$^+$ may exist in equilibrium with the adducts [Mo(CO)$_2$(NCMe)L$_2$(η^3-C$_7$H$_9$)]$^+$ with the composition of any mixture temperature and L$_2$ dependent. Variable temperature ^{31}P-NMR studies on [Mo(CO)$_2$(dppe)(η^5-C$_7$H$_9$)][BF$_4$] in CD$_3$CN reveal that the proportion of [Mo(CO)$_2$(NCMe)(dppe)(η^3-C$_7$H$_9$)]$^+$ present is increased as the temperature is lowered. The new complexes [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)][BF$_4$] (L$_2$ = Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe) 4 or 1,1,1-*tris*(diphenylphosphinomethyl)ethane (triphos) 5) have been prepared, the latter as an isomer mixture. Complex 4 remains unchanged in acetonitrile but infrared and variable temperature ^{31}P-NMR studies on 5 in acetonitrile establish the partial formation of [Mo(CO)$_2$(NCMe)(triphos)(η^3-C$_7$H$_9$)]$^+$. © 1997 Elsevier Science S.A.

Keywords: Molybdenum; Cycloheptadienyl; Hapticity; Allyl

1. Introduction

In a series of recent publications, we have described the synthesis and reactivity of molybdenum complexes of cycloheptadienyl (C$_7$H$_9$) [1,2] and cyclooctadienyl (C$_8$H$_{11}$) [3] ligands. These 'open' dienyl systems, incorporated into a cyclic hydrocarbon ring, have the potential to bond either trihapto or pentahapto to the co-ordinating metal centre and, as we have demonstrated for selected derivatives, there is a delicate balance in stability between η^5 and η^3 bonding modes. As an extension of our previous investigations, we now describe a series of reactions of the general type (equation 1)

$$\left[Mo(CO)_2L_2(\eta^5 - C_7H_9)\right]^+ + L'$$

$$\rightarrow \left[Mo(CO)_2(L')L_2(\eta^3 - C_7H_9)\right]^{z+} \quad (z = 0 \ or \ 1)$$

$$(1)$$

which probe further the effect of the identity of ligands

L' and L$_2$ upon the formation and stability of trihapto bonded cycloheptadienyl complexes

2. Results and discussion

2.1. Synthesis and structure of [MoX(CO)$_2$L$_2$(η^3-C$_7$H$_9$)] (X = Cl, L$_2$ = dppe, dppm; X = NCO, L$_2$ = dppe)

Our previous investigations on $\eta^5 \rightarrow \eta^3$ hapticity interconversion in cycloheptadienylmolybdenum complexes have focused on the formation of the cationic η^3-C$_7$H$_9$ adducts [Mo(CO)$_2$(L')L$_2$(η^3-C$_7$H$_9$)]$^+$ [L' = NCMe or CNBu^t, L$_2$ = dppe, dppm or 2,2'-bipyridyl (bipy)] [1,2]. However, with the exception of [Mo(CO)$_2$(CNBu^t)(bipy)(η^3-C$_7$H$_9$)][BF$_4$], these complexes are relatively unstable with respect to reversion to η^5-C$_7$H$_9$ products, either by loss of L' and regeneration of starting material (L' = NCMe) or by ligand substitution (L' = CNBu^t). In a new strategy to prepare stable trihapto bonded cycloheptadienylmolybdenum complexes the synthesis of the neutral adducts

X   L₂
1   Cl   dppe
2   Cl   dppm
3   NCO   dppe

L₂
dppe
dppm
4   dmpe
5   triphos
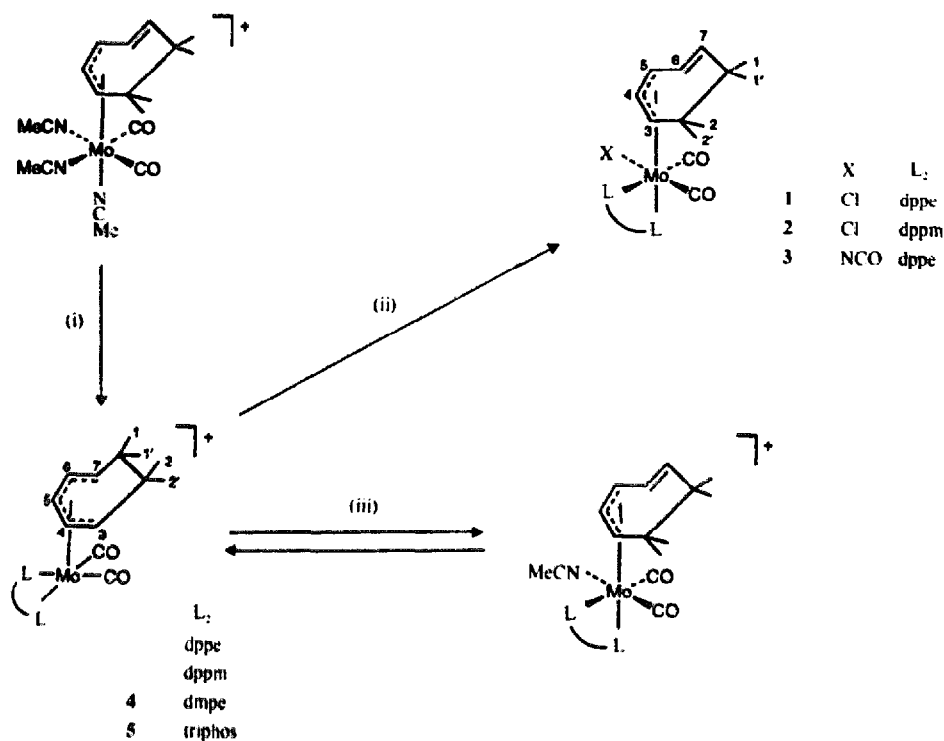
Scheme 1. Reagents and conditions: (i) L₂ = dppe, dppm, dmpe or triphos, stir in CH₂Cl₂; (ii) L₂ = dppe or dppm, stir in acetone with LiCl or KNCO; (iii) L₂ = dppe or triphos only, stir in NCMe.

[MoX(CO)₂L₂(η³-C₇H₉)] (X = Cl or NCO; L₂ = dppe, dppm or bipy) was explored.

Reaction of [Mo(CO)₂L₂(η³-C₇H₉)][BF₄] (L₂ = dppe or dppm) with LiCl in acetone resulted in the rapid formation of the neutral chloride adducts [MoCl(CO)₂L₂(η³-C₇H₉)] (L₂ = dppe 1 or dppm 2, Scheme 1) which were isolated as red solids following work up. An analogous reaction proceeds between [Mo(CO)₂(bipy)(η³-C₇H₉)][BF₄] and LiCl but the very low solubility of the resulting product precluded satis-

factory purification and characterisation. However, the general preparative procedure can be extended to other anionic ligands (X) and treatment of an acetone solution of [Mo(CO)₂(dppe)(η³-C₇H₉)][BF₄] with KNCO led to the formation of [Mo(NCO)(CO)₂(dppe)(η³-C₇H₉)], 3 which was isolated as a pink-red solid. In contrast to many of the cationic, η³-C₇H₉ complexes previously reported, 1–3 are relatively stable with respect to reversion to η⁵-C₇H₉ products, either through dissociation of ligand X or substitution of CO by X. Characterisation

Table 1
Microanalytical, infrared and mass spectroscopic data

Complex	Analysis(%) [a]		Infrared [b]	Mass spectral data [c]
	C	H	ν(CO) (cm⁻¹)	
1 [MoCl(CO)₂(dppe)(η³-C₇H₉)]	62.1 (61.9)	4.9 (4.9)	1932, 1841	645 ([M−Cl]⁺), 617 ([M−Cl−CO]⁺), 587 ([M−Cl−2CO−2H]⁺)
2 [MoCl(CO)₂(dppm)(η³-C₇H₉)]	61.5 (61.4)	4.7 (4.7)	1934, 1848	631 ([M−Cl]⁺), 601 ([M−Cl−CO−2H]⁺), 573 ([M−Cl−2CO−2H]⁺)
3 [Mo(NCO)(CO)₂(dppe)(η³-C₇H₉)]	63.1 (63.1)	4.9 (4.8) [d]	1929, 1842 [e]	687 (M⁺), 645 ([M−NCO]⁺), 631 ([M−2CO]⁺), 617 ([M−NCO−CO]⁺), 587 ([M−NCO−2CO−2H]⁺)
4 [Mo(CO)₂(dmpe)(η³-C₇H₉)][BF₄]	37.4 (37.3)	5.1 (5.2)	1998, 1903	397 (M⁺), 369 ([M−CO]⁺), 339 ([M−2CO−2H]⁺)
5 [Mo(CO)₂(triphos)(η³-C₇H₉)][BF₄]	62.8 (62.7)	4.9 (5.0)	2009, 1985 (sh) 1912	871 (M⁺), 843 ([M−CO]⁺), 813 ([M−2CO−2H]⁺)

[a] Calculated values in parentheses.
[b] Solution spectra in CH₂Cl₂.
[c] By FAB mass spectroscopy, m/z values based on ⁹⁸Mo.
[d] N. 2.0 (2.0)%.
[e] ν(CN) 2219 cm⁻¹.

details for **1–3** and of subsequently described complexes are presented in Table 1 (microanalytical, infrared and mass spectroscopic data) and 2 (^{1}H-, ^{13}C- and ^{31}P-NMR data). The typical spectroscopic properties, indicative of trihapto bonded cycloheptadienyl complexes, are exhibited by **1–3**. Thus, formation from [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)][BF$_4$] is accompanied by a shift in the average ν(CO) to lower wavenumber and, in the ^{13}C-NMR spectra three signals in the range 90–70 ppm

are indicative of the three co-ordinated allyl carbons (C$^{3-5}$). Detailed assignment of the ^{1}H- and ^{13}C-NMR spectra of [MoCl(CO)$_2$(dppe)(η^3-C$_7$H$_9$)] 1, was accomplished with the aid of [^{1}H–^{1}H]COSY and [^{1}H–^{13}C]HETCOR experiments.

Attempts to obtain crystals of **1–3**, suitable for X-ray characterisation were unsuccessful but these complexes are members of an extensive general class of organometallic compounds [MoX(CO)$_2$L$_2$(η^3-allyl)] (X

Table 2
Proton, ^{13}C- and ^{31}P-NMR spectral data [a]

Complex	^{1}H NMR data	^{13}C NMR data	^{31}P NMR data
1	7.75–7.11 [m, 20H, Ph (dppe)]; 5.91 [dd, 1H, H^6, J(H^6–H^7) 11, J(H^6–H^5) 6]; 5.45 [m, 1H, H^7]; 5.14 [dd, 1H, H^5]; 4.91 [br, 1H, H^3]; 3.97 [at, 1H, H^4, J(H^4–H^5) 7, J(H^4–H^3) 8]; 2.94 [m, 2H, CH$_2$, dppe]; 2.46–2.23 [m, 4H, CH$_2$, dppe and H$^{2,2'}$]; 2.10, br, 1H; 1.59, br, 1H [H$^{1,1'}$]	227.5, 224.6 [m, CO]; 135.5–127.8 [Ph, dppe and C^{6,7}]; 87.2 [C^4]; 81.3, 79.5 [C^{3,5}]; 30.6 [C^2] 28.6 [C^1]; 26.1, [m, CH$_2$, dppe]	49.5, d, J(P–P) 11 46.6, d, J(P–P) 11 [b]
2	7.63–7.15 [m, 20H, Ph (dppm)]; 6.14 [dd, 1H, H^6, J(H^6–H^7) 11, J(H^6–H^5) 6]; 5.44 [m, 1H, H^7]; 5.18 [br, 1H, H^5]; 5.10 [br, 1H, H^3]; 4.40 [m, 1H, CH$_2$, dppm]; 4.19 [t, 1H, H^4, J(H^4–H^5) 8, J(H^4–H^3) 8]; 4.02 [m, 1H, CH$_2$, dppm]; 2.54, br, 1H; 2.28, br, 1H; 2.17, br, 1H; 1.63, br, 1H [H$^{1,1',2,2'}$] [d]	229.2 [dd, CO, J(P–C) 10, 15]; 226.2 [dd, CO, J(P–C) 4, 10]; 134.2–127.6 [Ph, dppm and C^{6,7}]; 87.4, 80.3, 79.8 [C$^{3-5}$]; 35.2, [t, CH$_2$, dppm, J(P–C) 19]; 31.1, 28.6 [C^{1,2}] [c]	Major isomer: 6.2, d, J(P–P) 12; –10.4, d, J(P–P) 12 Minor isomer: 10.0, –9.8 [c,e]
3	7.74–7.21 [m, 20H, Ph (dppe)]; 5.90 [dd, 1H, H^6, J(H^6–H^7) 11, J(H^6–H^5) 6]; 5.47 [m, 1H, H^7]; 5.07 [dd, 1H, H^5]; 4.74 [br, 1H, H^3]; 3.81 [t, 1H, H^4, J(H^4–H^5) 8, J(H^4–H^3) 8]; 2.74 [m, 2H, CH$_2$, dppe]; 2.44–2.10, m, 5H, 1.63, br, 1H [CH$_2$, dppe and H$^{1,1',2,2'}$]	229.0 [dd, CO, J(P–C) 10, 17]; 224.2 [dd, CO, J(P–C) 4, 10]; 134.8–129.1 [Ph, dppe and C^{6,7}]; 86.0, 82.1, 77.8 [C$^{3-5}$]; 31.1, 29.1 [C^{1,2}]; 26.2 [m, CH$_2$, dppe]	48.8, d, J(P–P) 17 46.0, d, J(P–P) 17 [c]
4	5.93 [br, 1H, H^5]; 5.23, br, 2H; 4.72, br, 2H [H^{1,4,6,7}]; 2.31–1.82, br, 7H; 1.51, br, 1H [CH$_2$, dmpe and H$^{1',2,2'}$]; 1.69 [at, 12H, CH$_3$, dmpe] [c]	226.9 [CO]; 100.1, 98.1 [C^{3,7}]; 33.0 [C^{1,2}]; 29.7 [at, CH$_2$, dmpe]; 18.2, br; 16.2, br [CH$_3$, dmpe] [c]	47.8, d, J(P–P) 40 41.6, d, J(P–P) 40 [c,f]
5	7.74–7.06 [m, 30H, Ph (triphos)]; 6.05, 5.93 [1H, H^5] [f]; 4.86, br, 2H; 4.05, br, 2H [H^{1,4,6,7}]; 2.92, 2.63, 2.51, 1.98, 1.93 [br, m, 6H, CH$_2$ (triphos)]; 1.84 [4H, H$^{1',2,2'}$]; 0.41, s; 0.19, s [3H, CH$_3$ (triphos)] [g]	230.9 [br, CO]; 138.6–128.2 [Ph, triphos]; 100.8, 99.9, 98.8 [C$^{1-7}$]; 46.8, br, 45.2, br, 41.7, br, 40.7, br, 37.9 [d, J(P–C) 14], 37.3 [d, J(P–C) 14], [CH$_2$, triphos], 33.1, 31.6, 29.9 [C(Me)(CH$_2$PPh$_2$)$_3$, and CH$_2$ triphos]. 31.0 [C^{1,2}]	27.4, d, J(P–P) 57 26.4, d, J(P–P) 57 20.5, d, J(P–P) 57 20.3, d, J(P–P) 58 –31.9, –32.8 [c,f]

[a] 300 MHz ^{1}H-, 75 MHz ^{13}C-, 121.5 MHz ^{31}P-NMR spectra in CDCl$_3$ at ambient temperature unless stated otherwise; s = singlet, d = doublet, t = triplet, at = apparent triplet, m = multiplet, br = broad; chemical shifts (^{1}H and ^{13}C) downfield from SiMe$_4$, coupling constants in Hz; numbering as in Scheme 1.
[b] In toluene-d_8.
[c] In CD$_2$Cl$_2$.
[d] 500 MHz ^{1}H spectrum.
[e] At –70°C, J(P–P) in minor isomer not resolved.
[f] At –80°C.
[g] Two discrete resonances associated with two isomers.

= halide or pseudohalide; L_2 = bidentate phosphorus-donor ligand; η^3-allyl = C_3H_5, [4], pentadienyl, [5], cycloheptatrienyl [6,7] etc.) which exhibit a common pseudo-octahedral ligand arrangement with one phosphorus of the bidentate P-donor ligand located *trans* to the allyl ligand. An analogous structure for complexes 1-3, as illustrated in Scheme 1, is therefore suggested and is corroborated by the ^{13}C- and ^{31}P-NMR spectroscopic data. Further by analogy with [MoX(CO)$_2$L$_2$(η^3-allyl)] (L_2 = dppm or dppe; η^3-allyl = C_3H_5 or C_7H_7), complexes 1-3 might be predicted to be fluxional by two discrete mechanisms: (i) a trigonal twist process which interconverts inequivalent phosphorus environments *cis* and *trans* to the η^3-C_7H_9 ring [4,6] and (ii) rotation of the η^3-C_7H_9 ligand with respect to the asymmetric metal centre. The most direct and simple probe with which to explore these effects is variable temperature ^{31}P-NMR spectroscopy. The ^{31}P-NMR spectra of the dppe complexes 1 and 3 are essentially invariant with temperature. At room temperature both exhibit doublet of doublets spectra indicative of inequivalent phosphorus atoms with resonances closely similar, both in chemical shift and separation to the limiting low temperature ^{31}P-NMR spectra of the cycloheptatrienyl analogues [MoX(CO)$_2$(dppe)(η^3-C_7H_7)] (for example, X = Cl, [6], δ^{31}P (CDCl$_3$, -20°C) 48.3, 45.1, J(P-P) 12). The low temperature ^{31}P-NMR spectra of 1 and 3 were little changed except for some broadening of the low field signal and a high temperature investigation on 1 in toluene-d_8 again demonstrated retention of a sharp doublet of doublets spectrum up to 60°C. It therefore seems improbable that a trigonal twist process operates in complexes 1 and 3. In distinction to 1 and 3, NMR spectra of the dppm derivative 2 exhibit complex variable temperature behaviour. In the ^{31}P-NMR spectrum of 2, at 20°C, two broad resonances, [δ^{31}P (CD$_2$Cl$_2$) 0.7, -3.2] and a shoulder on the high field resonance at δ = -4.2 are observed. However, on cooling to -70°C the spectrum resolves into four resonances (see Table 2) indicative of two distinct complexes, each with two inequivalent phosphorus atoms, and present in an approximate ratio of 2.0:1 as determined from integration of the spectrum. Further evidence for the existence of two low temperature forms of 2 is provided by ^{13}C-NMR data. In contrast with the dppe analogues 1 and 3, the ambient temperature ^{13}C-NMR spectrum of 2 revealed some broadening of the co-ordinated allyl resonances and cooling to -50°C effected resolution into two discrete sets of allyl carbons (C$^{1-5}$) distinguished by differing intensity (δ^{13}C, 125.7 MHz, (CD$_2$Cl$_2$, -50°C), major isomer: 87.8, 82.2, 77.5; minor isomer: 86.2, 83.5, 73.1). These results concur with our parallel investigations on the cyclooctadienyl complexes [MoBr(CO)$_2$L$_2$(η^3-C_8H_{11})] (L_2 = dppm or dppe; C_8H_{11} = η^3-2,5-C_8H_{11} or η^3-2,4-C_8H_{11}) which exhibit
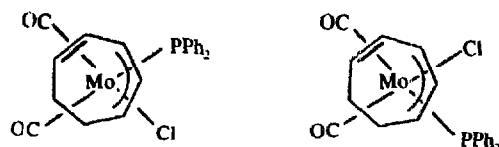

Fig. 1. Suggested low temperature isomers of complex 2 (dppm ligand truncated to show only the PPh$_2$ group located in the equatorial plane).

analogous behaviour [8]. Our preferred explanation for these observations is based upon the combination of an asymmetric metal centre with a dienyl ligand deficient in a bisecting mirror plane. At low temperature, rotation of the dienyl ring with respect to the metal centre is terminated resulting in isomeric forms which differ in the orientation of the dienyl ligand with respect to the asymmetric metal centre. The isomeric forms may differ simply as rotamers about the Mo-C_7H_9 bond since it is probable that any two orientations are at least similar in energy. Alternatively, assuming the adoption of a single preferred orientation such as that normally observed in the solid state for the complexes [MoX(CO)$_2$L$_2$(η^3-allyl)], in which the two carbonyl ligands are directed towards the terminal carbons of the co-ordinated η^3-allyl group [9], two isomeric forms may still result as shown in Fig. 1 by the location of the Cl ligand *syn* or *anti* with respect to the double bond of the dienyl ligand.

2.2. Effect of variation of temperature and L_2 on the stability of acetonitrile adducts [Mo(CO)$_2$(NCMe)L$_2$(η^5-C_7H_9)]$^+$

The reaction of cationic η^5-dienyl complexes [Mo(CO)$_2$L$_2$(η^5-dienyl)]$^+$ with acetonitrile solvent to give adducts [Mo(CO)$_2$(NCMe)L$_2$(η^3-dienyl)]$^+$ is well established for a range of dienyl and L_2 ligands (dienyl = pentadienyl, C_5H_7 [10]; cycloheptadienyl, C_7H_9 [2]; cyclooctadienyl, C_8H_{11} [3]; L_2 = dppe, dppm, bipy). However the acetonitrile ligand in these adducts is relatively labile with respect to dissociation and accompanying regeneration of η^5-dienyls [Mo(CO)$_2$L$_2$(η^5-dienyl)]$^+$. This delicate balance in stability between η^5- and η^3-dienyl forms provides an ideal system with which to probe the effect of variation of both L_2 and dienyl ligand upon preferred hapticity. The results of such investigations, previously reported, can be summarised by the ordering: (L_2 = bipy > dppe > dppm; dienyl = $C_8H_{11} \geq C_5H_7 > C_7H_9$) with the first entry of each list most effective in promoting stability of the η^3-dienyl adduct [Mo(CO)$_2$(NCMe)L$_2$(η^3-dienyl)]$^+$. Thus cycloheptadienyl derivatives [Mo(CO)$_2$(NCMe)L$_2$(η^3-C_7H_9)]$^+$ are not isolable and

are observed only in solution in acetonitrile; moreover [Mo(CO)₂(NCMe)(dppm)(η^3-C₇H₉)][BF₄] is not formed, even under these conditions. The objectives of

the new work described herein were twofold: first to examine the effect of temperature on the relative stability of the trihapto bonded acetonitrile adducts and sec-
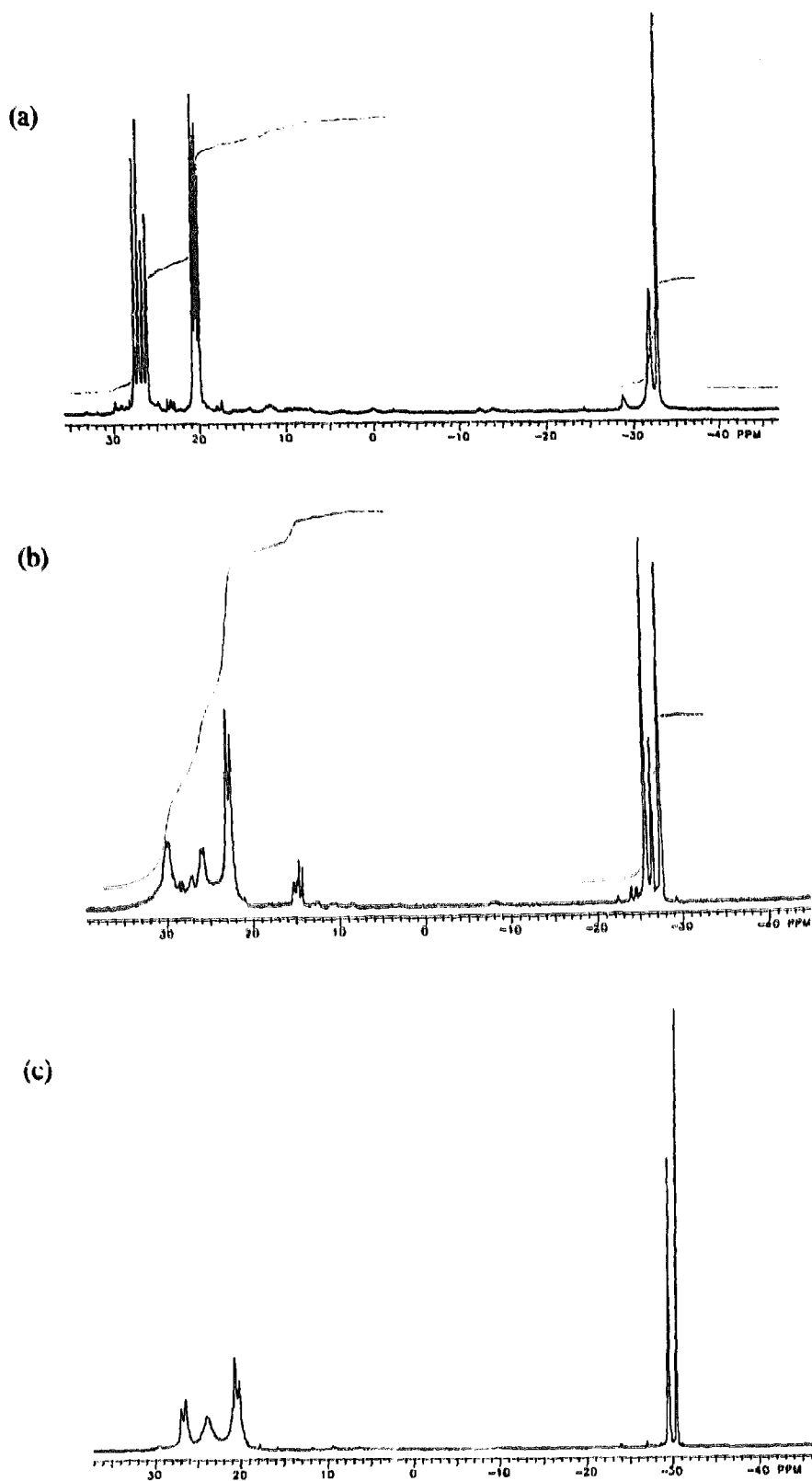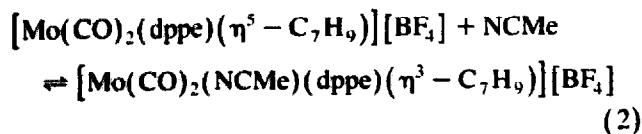
Fig. 2. ^{31}P-NMR spectra of complex 5. (a) In CD₂Cl₂ at −80°C; (b) in CD₃CN at −30°C; (c) in CD₂Cl₂ at −20°C.

ondly to extend our investigations to new complexes $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)]^+$ with an increased variety of ligands L_2.

$$[Mo(CO)_2(dppe)(\eta^5 - C_7H_9)][BF_4] + NCMe$$

$$\rightleftharpoons [Mo(CO)_2(NCMe)(dppe)(\eta^3 - C_7H_9)][BF_4] \quad (2)$$

We have previously described the equilibrium system (Equation 2) together with infrared, ^{13}C- and ^{31}P-NMR spectroscopic evidence for the assignment of the aceto-nitrile adduct [2]. In the closely related system involving cycloheptatrienylmolybdenum complexes (Equation 3)

$$[Mo(CO)_2(NCMe)(\eta^7 - C_7H_7)][BF_4] + 2NCMe$$

$$\rightleftharpoons [Mo(CO)_2(NCMe)_3(\eta^3 - C_7H_7)][BF_4] \quad (3)$$
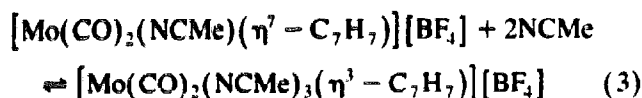
the position of equilibrium has been shown to be temperature dependent with low temperatures increasing the proportion of the $\eta^3\text{-}C_7H_7$ component present [7]. The possibility that the relative stability of $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)][BF_4]$ might also be enhanced by low temperature led to a re-examination of the variable temperature ^{31}P-NMR data for the reaction displayed in equation (2). Variable temperature ^{31}P-NMR investigations were carried out on 0.1 M solutions of $[Mo(CO)_2(dppe)(\eta^5\text{-}C_7H_9)][BF_4]$ dissolved in CD_3CN. The % $\eta^3:\eta^5$ ratios at 20°C, 0°C and -25°C were calculated on the basis of ^{31}P integrals of reso-nances previously assigned to η^5 and η^3 forms [2] although some difficulty was experienced in the accu-rate determination of integrals for the broad signals of the $\eta^3\text{-}C_7H_9$ component at room temperature. How-ever, the results (% $\eta^3:\eta^5$: 20°C, 32:68; 0°C, 38:62; -25°C, 58:42), based on two independent determina-tions, clearly establish an increase in the proportion of $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)][BF_4]$ present in the equilibrium mixture as temperature is decreased.

To examine further the effect of L_2 variation, new complexes of the type $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)][BF_4]$ ($L_2 = $ dmpe **4** or 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) **5**) were prepared by treatment of cold (-78°C), CH_2Cl_2 solu-tions of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)][BF_4]$ with the appropriate phosphine followed by warming to room temperature and were isolated as red or pink solids respectively. Spectroscopic data for the dmpe derivative **4** are typical of those previously reported for $[Mo(CO)_2L_2(\eta^5\text{-}C_7H_9)][BF_4]$ ($L_2 = $ dppe or dppm) [1,2]. In common with dppe and dppm derivatives, the variable temperature ^{31}P-NMR spectrum of **4** in CD_2Cl_2 reveals a doublet of doublets pattern at -80°C which collapses to a sharp singlet at $+20$°C with a coales-cence temperature of approximately -5°C; this be-haviour is attributed to asymmetry in the relative orien-tations of the dienyl ring and metal centre at low

temperature. In principle, reaction of $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_9)][BF_4]$ with triphos could result in coordination of triphos as a tridentate ligand but spectroscopic data for the isolated product and in particular infrared active $\nu(CO)$ and the low tempera-ture ^{31}P-NMR spectrum in CD_2Cl_2 (Fig. 2a) unequivo-cally permit assignment to the $\eta^5\text{-}C_7H_9$, bidentate triphos formulation of $[Mo(CO)_2(triphos)(\eta^5\text{-}C_7H_9)][BF_4]$ **5**. Thus in the ^{31}P-NMR spectrum, reso-nances in the region 20–30 ppm are attributable to the two coordinated phosphorus atoms whilst resonances around -30 ppm are assigned to the pendant phosphine group; integration of the spectrum supports these con-clusions. Further examination of Fig. 2a reveals twice the number of resonances expected for the proposed structure. This observation may be rationalised by the existence of two isomeric forms, present in an approxi-mately 1:1 ratio and differing, we suggest, in the orien-tation of the pendant phosphine group with respect to the C_7H_9 ring (see Fig. 3); the complexity of reso-nances associated with the triphos ligand in the ^1H- and ^{13}C-NMR spectra of **5** is also consistent with the exis-tence of isomers. The variable temperature behaviour of the ^{31}P-NMR spectrum of **5** parallels that of **4** although coalescence temperatures for the coordinated phosphine resonances are isomer dependent. However, in the room temperature ^{31}P-NMR spectrum of **5**, there remain in the pendant phosphine region, two discrete resonances consistent with two non-interconvertible isomers.

The reactivity of complexes **4** and **5** towards NCMe addition accompanied by $\eta^5 \rightarrow \eta^3$ hapticity conversion at the C_7H_9 ring was investigated by infrared and variable temperature ^{31}P-NMR spectroscopy on aceto-nitrile solutions of the complexes. In the case of the dmpe derivative **4**, there was no evidence of any change. This result is consistent with investigations on the L_2 dependent stability of the pentadienyl complexes $[Mo(CO)_2(NCMe)L_2(\eta^3\text{-}C_5H_7)]^+$ which was deter-mined as $L_2 = $ dmpe $<$ dppe, an observation attributed to the differing electronic and steric properties of these two L_2 ligands [10]. By contrast, analogous investiga-tions on the triphos derivative **5** proved to be more absorbing. The infrared spectrum of **5** dissolved in acetonitrile revealed, in addition to $\nu(CO)$ assigned to unchanged **5**, new, weak bands at 1948 and 1866 cm^{-1}, almost identical to $\nu(CO)$ attributed to $[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_9)]^+$ (1946, 1868
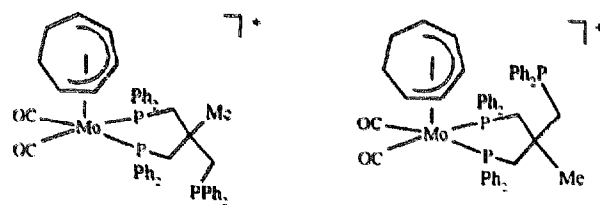

Fig. 3. Suggested isomeric forms of complex **5**.

cm^{-1} in NCMe [2]). Further evidence for the formation of the acetonitrile adduct [Mo(CO)$_2$(NCMe)(triphos)(η^3-C$_7$H$_9$)]$^+$, in equilibrium with 5 in acetonitrile, was provided by variable temperature ^{31}P-NMR studies. At $-30°$C, the ^{31}P-NMR spectrum of 5 in CD$_3$CN (Fig. 2b) exhibits three singlet signals in the pendant phosphine region (δ -25.6, -26.4, -27.5) and a complex set of signals in the coordinated phosphine region. Comparison with the CD$_2$Cl$_2$ spectrum, recorded at $-20°$C (Fig. 2c) suggests that, in CD$_3$CN at $-30°$C, a combination of 5 (as an isomer mixture) together with a trihapto-bonded acetonitrile adduct (δ -26.4 and ca. 15) is present. As the temperature was raised, the resonances attributed to the NCMe adduct decreased in intensity, consistent with a reduction in adduct stability with increase in temperature (as demonstrated above for the dppe analogue) and at 40°C only resonances due to 5 could be observed. It is not clear whether the observation of only three resonances in the fingerprint pendant phosphine region of the spectrum at $-30°$C is due to coincidental overlap of a fourth signal or alternatively isomer selectivity in the reaction of 5 with NCMe. A comparison between the stability of NCMe adducts formed from 5 and [Mo(CO)$_2$(dppe)(η^5-C$_7$H$_9$)]$^+$ based on ^{31}P-NMR integrals is therefore not made.

3. Experimental

3.1. General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complexes [Mo(CO)$_2$L$_2$(η^5-C$_7$H$_9$)][BF$_4$] (L$_2$ = dppm, [1] dppe [2]) and [Mo(CO)$_2$(NCMe)$_2$(η^5-C$_7$H$_9$)][BF$_4$] [1] were prepared by literature procedures and the chemicals dmpe and 1,1,1-tris(diphenylphosphinomethyl)ethane, (triphos) were obtained from 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 and 500 MHz ^{1}H-, 125.7 MHz ^{13}C-NMR spectra on a Varian Unity 500 instrument. 121.5 MHz ^{31}P-NMR spectra were obtained on Varian Associates XL 300 or Varian Unity Inova 300 spectrometers. Infrared spectra were obtained on a Perkin–Elmer FT 1710 spectrometer and mass spectra using a Kratos Concept 1S instrument. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

3.2. Preparation of [MoCl(CO)$_2$(dppe)(η^5-C$_7$H$_9$)] 1

Lithium chloride (0.28 g, 6.59 mmol) was added to a pink-red, stirred solution of [Mo(CO)$_2$(dppe)(η^5-

C$_7$H$_9$)][BF$_4$] (2.40 g, 3.29 mmol) in acetone (30 cm^3). After 50 min the resulting orange-brown solution was reduced to dryness in vacuo and the residue recrystallised from toluene-n-hexane to give 1 as a light red solid; yield 1.51 g (68%). A similar procedure, starting from [Mo(CO)$_2$(dppm)(η^5-C$_7$H$_9$)][BF$_4$] (0.50 g, 0.70 mmol) and LiCl (0.06 g, 1.41 mmol) stirred in acetone (20 cm^3) for 20 min., gave [MoCl(CO)$_2$(dppm)(η^3-C$_7$H$_9$)] 2, as a dark red solid; yield 0.12 g (26%).

3.3. Preparation of [Mo(NCO)(CO)$_2$(dppe)(η^5-C$_7$H$_9$)] 3

Potassium cyanate, KNCO (0.18 g, 2.22 mmol) was added to a stirred solution of [Mo(CO)$_2$(dppe)(η^5-C$_7$H$_9$)][BF$_4$] (1.50 g, 2.05 mmol) in acetone (20 cm^3). After 2 h the reaction mixture was reduced to dryness in vacuo and the residue recrystallised from toluene-n-hexane to give 3 as a pink-red solid; yield 1.21 g (86%).

3.4. Preparation of [Mo(CO)$_2$(dmpe)(η^5-C$_7$H$_9$)][BF$_4$] 4

A stirred solution of [Mo(CO)$_2$(NCMe)$_2$(η^3-C$_7$H$_9$)][BF$_4$] (0.29 g, 0.64 mmol) in CH$_2$Cl$_2$ (40 cm^3) was cooled to $-78°$C then treated with dmpe (0.10 g, 0.67 mmol). The reaction mixture was allowed to slowly warm and at $-20°$C a colour change from orange-brown to deep red occurred. The solution was then filtered, reduced in volume and diethylether added to give 4 as a light red solid; yield 0.24 g (78%). A similar procedure was employed for the preparation of [Mo(CO)$_2$(triphos)(η^3-C$_7$H$_9$)][BF$_4$] 5, from [Mo(CO)$_2$(NCMe)$_2$(η^3-C$_7$H$_9$)][BF$_4$] (0.95 g, 2.09 mmol) and triphos (1.61 g, 2.58 mmol), except that after warming to room temperature, the reaction was allowed to proceed for a further 30 min. Complex 5 was isolated as a pink solid; yield 1.58 g (79%).

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