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Investigations on the trigonal twist process in the pseudooctahedral complexes $[MX(CO)_2(P–P)(\eta^3\text{-}R)]$ (M = Mo or W; X = halide or pseudohalide; P–P = bidentate P-donor ligand; R = cycloheptatrienyl, cyclohexenyl or cyclooctenyl)

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Abstract

A series of complexes $[MX(CO)_2(P–P)(\eta^3\text{-}R)]$ [M = Mo or W; X = halide, NCO or NCS; P–P = $Ph_2P(CH_2)_nPPh_2$ ($n = 1-3$)] have been prepared. Variable temperature $^{31}P\{^1H\}$-NMR investigations reveal the operation of a trigonal twist fluxional process in complexes where R = cycloheptatrienyl (C_7H_7), cyclohexenyl (C_6H_9) or cyclooctenyl (C_8H_{13}) with $\Delta G^{\ddagger}_{C}$ (the free energy of activation at the temperature of coalescence) strongly R-dependent. Using the cycloheptatrienyl complexes $[MX(CO)_2\{Ph_2P(CH_2)_nPPh_2\}(\eta^3\text{-}C_7H_7)]$ detailed investigations have been made to establish the effect on $\Delta G^{\ddagger}_{C}$ of variation of *X*, *n* and M. © 2002 Published by Elsevier Science B.V.

Keywords: Allyl ligand; Cycloheptatrienyl; Molybdenum; Fluxionality; Trigonal twist process

1. Introduction

Complexes of the general formulation $[MX(CO)_2(P–P)(\eta^3\text{-}R)]$ (M = Mo or W; X = halide or pseudohalide; P–P = bidentate P-donor ligand; R = allyl [1,2], pentadienyl [3], hexadienyl [4], cycloheptatrienyl [5,6], cycloheptadienyl [7], cyclooctadienyl [8]) are an important class of compounds in the organometallic chemistry of molybdenum and tungsten. X-ray structural studies on selected, diverse examples reveal the adoption of a common pseudooctahedral structure with an asymmetric ligand arrangement [2,3,6] in which one phosphorus donor atom of the chelate P–P ligand is located *trans* to the η^3-R group. This leaves the two carbonyls, the halide ligand and the second phosphorus essentially coplanar. In a seminal study on the allyl derivatives $[MX(CO)_2(P–P)(\eta^3\text{-}C_3H_5)]$ [P–P = $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$, dppe) or $Ph_2PCH{=}CHPPh_2$], Faller et al. [2] employed variable temperature NMR methods to infer the operation of a trigonal twist rearrangement process in these complexes. The mechanism of the trigonal twist involves rotation of the triangular face formed by the two phosphorus atoms and the ligand X with respect to the face formed by the two carbonyls and the R (allyl) ligand. More recently we, [5,9] and others [10], have demonstrated the operation of an equivalent process in cycloheptatrienyl complexes of general formulation $[MX(CO)_2(P–P)(\eta^3\text{-}C_7H_7)]$, albeit with a rather higher free energy of activation.

The asymmetric structure of complexes of general formulation $[MX(CO)_2(P–P)(\eta^3\text{-}R)]$ affords the potential for regio- and stereo-selective synthesis [11] but progress in this endeavour would require both recognition and control of any trigonal twist process. The objectives of the work in the current paper are therefore twofold. First, since investigations to date have been restricted to allyl and cycloheptatrienyl complexes, we set out to explore the generality of the trigonal twist rearrangement in complexes with a variety of η^3-R

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ligands. Secondly, we have attempted to quantify the effect of variation of R, X, P–P, and M upon the free energy of activation of the trigonal twist process. The existing data for η^3-C_3H_5 complexes [2] give some indication of these effects but the very low free energies of activation observed for these complexes did not permit a full investigation (for example, values for free energies of activation are restricted to X = I). In fact the identity of R has a very significant effect upon the free energy of activation $\Delta G^{\ddagger}_{C}$ and, taking an extreme case as an example, for the two complexes [MoI(CO)$_2$(dppe)(η^3-R)] (R = C_3H_5 [2] or C_7H_7 [5]), $\Delta G^{\ddagger}_{C}$ is ca. 20 kJ mol^{-1} greater for the cycloheptatrienyl derivative. The focus of our work in the quantification of the effects of X and P–P is therefore with η^3-cycloheptatrienyl complexes for which limiting low temperature $^{31}P\{^1H\}$-NMR spectra and coalescence temperatures are readily accessible for a wide range of ligands.

2. Results and discussion

2.1. Synthetic studies

The work described in this paper draws together the results of our previous investigations on η^3-cycloheptatrienyl complexes together with new synthetic and NMR spectroscopic work. A full listing of the complexes considered in this paper is given in Scheme 1 but of these, the following new complexes are reported. The cyclohexenyl (R = C_6H_9) and cyclooctenyl (R = C_8H_{13}) complexes [MoBr(CO)$_2$(dppe)(η^3-R)] (**1**, R = C_6H_9; **4**, R = C_8H_{13}) were prepared by treatment of the known precursors [MoBr(CO)$_2$(NCMe)$_2$(η^3-R)] (R = C_6H_9 [12]; R = C_8H_{13} [13]) with dppe in CH_2Cl_2 and isolated as yellow–orange solids. Halide substituted derivatives [MoX(CO)$_2$(dppe)(η^3-C_8H_{13})], **3**, X = I; **5**, X = Cl were prepared by reaction of **4** with Ag[BF$_4$] in acetone followed by treatment with KI or LiCl, respectively. The cyclohexenyl tungsten complex [WBr(CO)$_2$(dppe)(η^3-C_6H_9)] (**2**), was isolated as a yellow solid from the reaction of dppe with [WBr(CO)$_2$(NCMe)$_2$(η^3-C_6H_9)]. A series of cycloheptatrienylmolybdenum complexes [MoX(CO)$_2$(P–P)(η^3-C_7H_7)] [X = Br, **7**, P–P = dppe; **13**, P–P = $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp); X = NCO, **11**, P–P = dppm; **12**, P–P = dppp; **14**, P–P = $Me_2PCH_2CH_2PMe_2$ (dmpe)] were prepared by reaction of [MoX(CO)$_2$(η^7-C_7H_7)] with P–P in CH_2Cl_2 and isolated as red/purple solids. Finally the cycloheptatrienyltungsten complexes [WX(CO)$_2$(P–P)(η^3-C_7H_7)], (**16**, X = Br, P–P = dppe; **18**, X = NCO, P–P = dppp) were prepared by reaction of [WX(CO)$_2$(η-C_7H_7)] with P–P in CH_2Cl_2. Details of the characterisation of the new complexes **1**–**5**, **7**, **11**–**14**, **16** and **18** are presented in Table 1 (microanalytical, IR and mass spectroscopic data) and Table 2 (^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopic data). Also included in Table 2 are previously unreported $^{31}P\{^1H\}$-NMR data for [MoX(CO)$_2$(dppe)(η^3-C_7H_7)] (**9**, X = NCO; **10**, X = NCS) [6].

Complex	M	X	P-P	R
1	Mo	Br	dppe	C_6H_9
2	W	Br	dppe	C_6H_9
3	Mo	I	dppe	C_8H_{13}
4	Mo	Br	dppe	C_8H_{13}
5	Mo	Cl	dppe	C_8H_{13}
6	Mo	I	dppe	C_7H_7
7	Mo	Br	dppe	C_7H_7
8	Mo	Cl	dppe	C_7H_7
9	Mo	NCO	dppe	C_7H_7
10	Mo	NCS	dppe	C_7H_7
11	Mo	NCO	dppm	C_7H_7
12	Mo	NCO	dppp	C_7H_7
13	Mo	Br	dppp	C_7H_7
14	Mo	NCO	dmpe	C_7H_7
15	W	I	dppe	C_7H_7
16	W	Br	dppe	C_7H_7
17	W	Cl	dppe	C_7H_7
18	W	NCO	dppp	C_7H_7

Scheme 1. Numbering scheme for complexes [MX(CO)$_2$(P–P)η^3-R].

2.2. Spectroscopic studies

2.2.1. Variable temperature $^{31}P\{^1H\}$-NMR investigations

The principal method that we have employed to investigate the fluxional properties of [MX(CO)$_2$(P–P)(η^3-R)] is variable temperature $^{31}P\{^1H\}$-NMR spectroscopy. Typically these complexes exhibit limiting low temperature $^{31}P\{^1H\}$ spectra consisting of a doublet of doublets pattern arising from the two inequivalent, coupled phosphorus environments. As the temperature is increased, $^{31}P\{^1H\}$-NMR spectra of complexes in which the trigonal twist process is operative display coalescence of the two discrete phosphorus resonances as the environments are averaged by the fluxional process. A full list of the complexes considered in this investigation together with the essential data for calculation of $\Delta G^{\ddagger}_{C}$ ($\delta\nu$, the chemical shift separation in Hz of the two phosphorus environments in the limiting low temperature spectrum and T_C the coalescence temperature) is presented in Table 3. Our earlier investigations [5,9] utilized a field of 32 MHz for $^{31}P\{^1H\}$-NMR investigations whereas the new work reported in this paper employs a field of 121.5 MHz. These details are also made clear in Table 3 so that inappropriate comparisons of $\delta\nu$ and T_C are avoided. As far as possible we have used $CDCl_3$ as the standard solvent for our variable temperature $^{31}P\{^1H\}$ investigations but in cases where limiting low temperature spectra were expected to be below −40 °C, CD_2Cl_2 was preferred since this avoided extensive precipitation of the sample.

The free energies of activation at the temperature of coalescence, $\Delta G^{\ddagger}_{C}$, presented in Table 3, were deter-

Table 1
Microanalytical, infrared and mass spectroscopic data

Complex	Colour	Yield	Analysis (%) [a]			Infrared [b] ν(CO)(cm^{-1})	Mass spectral data [c]
			C	H	N		
1 $[MoBr(CO)_2(dppe)(\eta^3-C_6H_9)]$	Yellow–orange	44	57.7 (57.4)	4.7 (4.6)		1931, 1844	712 (M^+), 654 ($[M-3H-2CO]^+$), 633 ($[M-Br]^+$), 603 ($[M-Br-CO-2H]^+$), 575 ($[M-Br-2CO-2H]^+$), 496 ($[M-Br-2CO-C_6H_9]^+$)
2 $[WBr(CO)_2(dppe)(\eta^3-C_6H_9)]$	Yellow	92	51.6 (51.1)	4.5 (4.1)		1923, 1835	798 (M^+), 739 ($[M-3H-2CO]^+$), 718 ($[M-Br]^+$), 688 ($[M-Br-CO-2H]^+$), 660 ($[M-Br-2CO-2H]^+$)
3 $[MoI(CO)_2(dppe)(\eta^3-C_8H_{13})]$	Orange	40	54.5 (55.0)	5.0 (4.7)		1935, 1840	661 ($[M-I]^+$) [d]
4 $[MoBr(CO)_2(dppe)(\eta^3-C_8H_{13})]$	Yellow–orange	83	58.5 (58.5)	5.1 (5.0)		1932, 1837	661 ($[M-Br]^+$), 633 ($[M-Br-CO]^+$) [d]
5 $[MoCl(CO)_2(dppe)(\eta^3-C_8H_{13})]$	Yellow–orange	32	62.0 (62.2)	5.3 (5.3)		1929, 1833	660 ($[M-Cl]^+$) [d]
7 $[MoBr(CO)_2(dppe)(\eta^3-C_7H_7)]$	Purple–red	80	58.3 (58.3)	4.5 (4.3)		1936, 1855	643 ($[M-Br]^+$), 615 ($[M-Br-CO]^+$), 587 ($[M-Br-2CO]^+$)
11 $[Mo(NCO)(CO)_2(dppm)(\eta^3-C_7H_7)]$	Purple	62	62.7 (62.8)	4.7 (4.3)	2.0 (2.1)	2215 (νNCO) 1939, 1862	629 ($[M-NCO]^+$), 612 ($[M-2CO]^+$), 601 ($[M-NCO-CO]^+$), 573 ($[M-NCO-2CO]^+$) [d]
12 $[Mo(NCO)(CO)_2(dppp)(\eta^3-C_7H_7)]$	Red	63	63.3 (63.7)	4.8 (4.7)	2.0 (2.0)	2217 (νNCO) 1932, 1853	657 ($[M-NCO]^+$), 643 ($[M-2CO]^+$), 601 ($[M-NCO-2CO]^+$), 552 ($[M-C_7H_7-2CO]^+$)
13 $[MoBr(CO)_2(dppp)(\eta^3-C_7H_7)]$	Orange–red	86	59.5 (58.8)	4.8 (4.5)		1940, 1852	657 ($[M-Br]^+$), 629 ($[M-Br-CO]^+$), 601 ($[M-Br-2CO]^+$)
14 $[Mo(NCO)(CO)_2(dmpe)(\eta^3-C_7H_7)]$	Purple	30	44.1 (43.9)	5.4 (5.3)	3.2 (3.2)	2215 (νNCO) 1929, 1847	394 ($[M-NCO]^+$), 381 ($[M-2CO]^+$), 339 ($[M-NCO-2CO]^+$)
16 $[WBr(CO)_2(dppe)(\eta^3-C_7H_7)]$	Orange–red	88	51.9 (51.9)	4.0 (3.8)		1930, 1848	808 (M^+), 752 ($[M-2CO]^+$), 729 ($[M-Br]^+$), 717 ($[M-C_7H_7]^+$), 673 ($[M-Br-2CO]^+$), 662 ($[M-2CO-C_7H_7]^+$)
18 $[W(NCO)(CO)_2(dppp)(\eta^3-C_7H_7)]$	Red	37	56.0 (56.6)	3.7 (4.2)	1.7 (1.8)	2226 (νNCO) 1927, 1845	785 (M^+), 743 ($[M-NCO]^+$), 729 ($[M-2CO]^+$), 694 ($[M-C_7H_7]^+$), 652 ($[M-C_7H_7-NCO]^+$), 638 ($[M-2CO-C_7H_7]^+$)

[a] Calculated values in parentheses.
[b] Solution spectra in CH_2Cl_2.
[c] By FAB mass spectroscopy unless stated otherwise, m/z values based on ^{98}Mo, ^{184}W and ^{79}Br.
[d] By electrospray mass spectroscopy.

Table 2
^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR data for [$MoX(CO)_2R'_2P(CH_2)_nPR'_2(\eta^3$-R)] [a]

Complex	^{1}H-NMR data			^{13}C-NMR data				^{31}P-NMR data		
	R	$R'_2P(CH_2)_nPR'_2$		CO	R	$R'_2P(CH_2)_nPR'_2$		$\delta\,^{31}$P	J(P–P) (Hz)	T (K)
		R′	CH_2			R′	CH_2			
1	(−40 °C), C*H* protons: 4.52, 1H, m, 4.30, 1H, br, 3.71, 1H, m; CH_2 protons: 2.07–1.76, m, 5H (4H, CH_2), 1.05, 1H, br, 0.47, 1H, br	7.82–7.17	3.00, m, 2H, 2.40, m, 1H, 2.07–1.76, m, 5H (1H, dppe)	(−30°C) 224.7, dd {7, 14} 220.5, dd {13, 32}	81.3, 71.2, 66.2, *C*H; 22.6, 22.0, 18.4, *C*H$_2$	135.8–127.7	26.7, m; 22.5, m	41.97 40.16	n.r.	213
2 [b]	(−40 °C), C*H* protons: 4.14, 1H, br, 4.07, 1H, br, 3.02, 1H, m; CH_2 protons: 2.13–1.73, m, 5H (4H, CH_2), 1.02, 1H, m, 0.37, 1H, m	7.80–7.30	3.16, m, 2H, 2.54, m, 1H, 2.13–1.73, m, 5H (1H, dppe)	213.7	72.6, br, 64.8, 56.0, br, *C*H; 22.1 br, 19.8, *C*H$_2$	132.3–127.7	28.0, br; 24.0, br	30.37 [205] 26.58 [176]	6.7	223
3 [c]	C*H* protons: 4.78, 2H, br; 4.54, 1H, t; CH_2 protons: 2.41, 2H, m; 2.15, 1H, m; 1.57, 7H, m	7.71–7.44	3.12, 2H, m; 2.41, 2H, m	225.4, m	83.6, 75.9 br, *C*H; 32.2, 27.5, 23.2, *C*H$_2$	135.3–127.8	26.5, br	42.63 41.01	14.1	203
4 [c]	C*H* protons: 4.62, 2H, br; 4.17, 1H, t; CH_2 protons: 2.42, 2H, m; 2.13, 1H, m; 1.54, 7H, m	7.71–7.38	3.02, 2H, m; 2.36, 2H, m	225.8, m	86.1, 77.2, *C*H; 32.4, 27.7, 23.2, *C*H$_2$	135.0–127.8	25.9, m	45.39 42.18	14.0	193
5 [c]	C*H* protons: 4.51, 2H, br; 3.92, 1H, t; CH_2 protons: 2.42, 2H, m; 2.12, 1H, m; 1.54, 7H, m	7.70–7.43	2.93, 2H, m; 2.29, 2H, m	226.1, m	87.0, 77.6, *C*H; 32.4, 27.6, 23.1, *C*H$_2$	134.5–127.7	25.5, m	47.54 44.23	15.9	188
7	5.43	7.65–7.30	3.17, 2.45, br	n.o.	106.1	133.7–128.2	28–24, br	45.91 43.87	13.4	223
9 [d]								44.72 43.43	15.3	223
10 [d]								48.84 47.82	16.4	233

Table 2 (*Continued*)

Complex	^{1}H-NMR data			^{13}C-NMR data				^{31}P-NMR data		
	R	$R'_2P(CH_2)_nPR'_2$		CO	R	$R'_2P(CH_2)_nPR'_2$		$\delta\,^{31}$P	J(P–P) (Hz)	T (K)
		R′	CH_2			R′	CH_2			
11 [b]	5.32, t, {1.2}	7.56–7.33	4.26, m 4.09, m	n.o.	105.2	132.7–128.3	36.4, t, {18}	7.74 −6.54	n.r.	243
12 [e]	5.13	7.65–7.26	2.76, m, 2H; 2.37, m, 2H; 2.19, br, 1H; 1.41, m, 1H	225.3	105.8, br	134.0–128.5	26.5, 19.1	15.63 11.00	40.8	213
13	5.35	7.64–7.30	3.53, m, 2H; 2.36, br 3H; 1.37, m, 1H	n.o.	106.4	134.4–128.1	28–24, br	9.31 1.20	46.4	223
14	5.27, t {1.1}	1.59, d, {8} 1.52, d,{8}	1.86, m	n.o.	105.0	14.0, 12.1, br	27.3, m	40.34 30.86	29.3	223
16	5.14	7.66–7.41	3.15, br, 2H; 2.42, br, 2H	n.o.	102.1	132.9–128.2	27.4, br	32.84 [216] 27.34 [196]	3.0	233
18 [e]	4.89	7.64–7.26	2.79, m, 2H; 2.49, m, 2H; 2.25, br, 1H; 1.46, m, 1H	216.6	102.0, br	134.2–128.6	25.9, 19.3	−0.39 [200] −8.06 [172]	26.9	213

[a] ^{1}H-, 300 MHz; $^{13}C\{^1H\}$-, 75 MHz; $^{31}P\{^1H\}$-NMR spectra, 121.5 MHz; all signals singlets unless stated otherwise, d, doublet; t, triplet; m, multiplet; br, broad; n.o., not observed. Coupling constants in Hz indicated in parentheses: {} indicates J(P–H) or J(P–C), [] indicates $J(^{183}W–P)$, n.r. indicates not resolved. Chemical shifts downfield from $SiMe_4$, spectra recorded in $CDCl_3$ at ambient temperature unless stated otherwise.

[b] ^{1}H- and ^{13}C-NMR spectra in CD_2Cl_2.

[c] All spectra in CD_2Cl_2.

[d] ^{1}H- and ^{13}C-NMR data in Ref. [6].

[e] $^{31}P\{^1H\}$-NMR spectrum in CD_2Cl_2.

Table 3
Free Energies of activation, $\Delta G^{\ddagger}_{\mathrm{C}}$ for the Trigonal Twist process in $[\mathrm{MX(CO)_2(P–P)(\eta^3\text{-}R)}]$ [a]

Complex	Field (MHz)/solvent	T_C (K)	δv (Hz)	$\Delta G^{\ddagger}_{\mathrm{C}}$ (kJ mol^{-1})
1 $[\mathrm{MoBr(CO)_2(dppe)(\eta^3\text{-}C_6H_9)}]$	121.5/$\mathrm{CDCl_3}$	296	220	57.2
2 $[\mathrm{WBr(CO)_2(dppe)(\eta^3\text{-}C_6H_9)}]$	121.5/$\mathrm{CDCl_3}$	326	460	61.3
3 $[\mathrm{MoI(CO)_2(dppe)(\eta^3\text{-}C_8H_{13})}]$	121.5/$\mathrm{CD_2Cl_2}$	275	197	53.3
4 $[\mathrm{MoBr(CO)_2(dppe)(\eta^3\text{-}C_8H_{13})}]$	121.5/$\mathrm{CD_2Cl_2}$	248	390	46.4
5 $[\mathrm{MoCl(CO)_2(dppe)(\eta^3\text{-}C_8H_{13})}]$	121.5/$\mathrm{CD_2Cl_2}$	230	402	42.8
6 $[\mathrm{MoI(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$ [b]	32/$\mathrm{CDCl_3}$	318	78	64.4
7 $[\mathrm{MoBr(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CDCl_3}$	316	248	61.0
8 $[\mathrm{MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CDCl_3}$	302	304	57.6
9 $[\mathrm{Mo(NCO)(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CDCl_3}$	284	157	55.6
10 $[\mathrm{Mo(NCS)(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CDCl_3}$	301	124	59.7
11 $[\mathrm{Mo(NCO)(CO)_2(dppm)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CDCl_3}$	328	1734	58.1
12 $[\mathrm{Mo(NCO)(CO)_2(dppp)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CD_2Cl_2}$	266	561	49.1
13 $[\mathrm{MoBr(CO)_2(dppp)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CDCl_3}$	305	985	55.3
14 $[\mathrm{Mo(NCO)(CO)_2(dmpe)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CD_2Cl_2}$	297	1152	53.4
15 $[\mathrm{WI(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$ [b]	32/$\mathrm{CDCl_3}$	314	162	61.7
16 $[\mathrm{WBr(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CDCl_3}$	311	668	57.4
17 $[\mathrm{WCl(CO)_2(dppe)(\eta^3\text{-}C_7H_7)}]$ [b]	32/$\mathrm{CDCl_3}$	281	189	54.6
18 $[\mathrm{W(NCO)(CO)_2(dppp)(\eta^3\text{-}C_7H_7)}]$	121.5/$\mathrm{CD_2Cl_2}$	260	932	46.9

[a] T_C and δv determined by variable temperature $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectroscopy. $\Delta G^{\ddagger}_{\mathrm{C}}$ calculated by Eq. (1).
[b] Data from Ref. [5].

mined assuming an equally populated two-site system and a transmission coefficient κ of unity. On the basis of these assumptions, the Eyring equation can be simplified to Eq. (1) which has been employed in this work for the calculation of $\Delta G^{\ddagger}_{\mathrm{C}}$ [14].

$$\Delta G^{\ddagger}_{\mathrm{C}} = 19.14\ T_{\mathrm{C}}[9.972 + \log(T_{\mathrm{C}}/\delta v)]\ \mathrm{J\ mol^{-1}}. \qquad (1)$$

We estimate that although δv can be determined with good accuracy, measurement of T_C carries a maximum error of ± 5 °C with a consequent error in $\Delta G^{\ddagger}_{\mathrm{C}}$ of ca. ± 1 kJ mol^{-1}. Thus we suggest that a difference in $\Delta G^{\ddagger}_{\mathrm{C}}$ values between two complexes of more than 2 kJ mol^{-1} represents an effect for consideration. In accord with our error estimation, duplicate determinations on complexes **8** and **9** gave values of $\Delta G^{\ddagger}_{\mathrm{C}}$ consistent to within 1 kJ mol^{-1}.

2.2.2. Discussion

The sub-sections below consider in turn the effect of variation of R, X, P–P, and M upon the free energy of activation to a trigonal twist process in $[\mathrm{MX(CO)_2(P–P)(\eta^3\text{-}R)}]$. The values of $\Delta G^{\ddagger}_{\mathrm{C}}$ which form the basis of this discussion are summarised in Table 3.

2.2.2.1. Effect of R [R = cycloheptatrienyl (C_7H_7), cyclohexenyl (C_6H_9) or cyclooctenyl (C_8H_{13})]. Comparison of analogous allyl and cycloheptatrienyl complexes $[\mathrm{MX(CO)_2(P–P)(\eta^3\text{-}R)}]$ (R = $\mathrm{C_3H_5}$ or $\mathrm{C_7H_7}$) reveals that changes in the identity of R have the potential for a very large effect on the magnitude of $\Delta G^{\ddagger}_{\mathrm{C}}$ for the trigonal twist process. For example, in the case of $[\mathrm{MoI(CO)_2(dppe)(\eta^3\text{-}R)}]$ (R = $\mathrm{C_3H_5}$, $\Delta G^{\ddagger}_{\mathrm{C}} = 44.3$ kJ mol^{-1} [2]; R = $\mathrm{C_7H_7}$, $\Delta G^{\ddagger}_{\mathrm{C}} = 64.4$ kJ mol^{-1}) the difference in $\Delta G^{\ddagger}_{\mathrm{C}}$ is ca. 20 kJ mol^{-1}. It was therefore of considerable interest to investigate other R ligands to establish both the generality of the trigonal twist process and the effect of R on $\Delta G^{\ddagger}_{\mathrm{C}}$.

Variable temperature $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR investigations on the cyclohexenyl complexes $[\mathrm{MBr(CO)_2(dppe)(\eta^3\text{-}C_6H_9)}]$ (**1**, M = Mo; **2**, M = W) and the cyclooctenyl complexes $[\mathrm{MoX(CO)_2(dppe)(\eta^3\text{-}C_8H_{13})}]$ (**3**, X = I; **4**, X = Br; **5**, X = Cl) reveal behaviour characteristic of the operation of a trigonal twist process. It is clear therefore that this is a fairly general property of complexes of the type $[\mathrm{MX(CO)_2(P–P)(\eta^3\text{-}R)}]$ with examples now demonstrated for R = cycloheptatrienyl, cyclohexenyl, cyclooctenyl and allyl ($\mathrm{C_3H_5}$). However, it is important to note that these observations are not made for all possible identities of η^3-R ligands; in some cases variable temperature $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR methods fail to provide any evidence for a trigonal twist process. For example, our $^{31}\mathrm{P}\{^1\mathrm{H}\}$ investigations on the cycloheptadienyl complexes $[\mathrm{MoX(CO)_2(dppe)(\eta^3\text{-}C_7H_9)}]$ (X = Cl or NCO) [7] reveal temperature invariant spectra consisting of two discrete doublet resonances and similarly the 2-methylallyl complex $[\mathrm{MoCl(CO)_2(dppe)(\eta^3\text{-}2\text{-}Me–C_3H_4)}]$ has a temperature invariant doublet of doublets pattern in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum [15].

Using data for the molybdenum complexes $[\mathrm{MoBr(CO)_2(dppe)(\eta^3\text{-}R)}]$ (**1**, R = $\mathrm{C_6H_9}$; **4**, R = $\mathrm{C_8H_{13}}$; **7**, R = $\mathrm{C_7H_7}$) a clear ordering in $\Delta G^{\ddagger}_{\mathrm{C}}$ (R = $\mathrm{C_7H_7} > \mathrm{C_6H_9} > \mathrm{C_8H_{13}}$) is apparent with a very large decrease in $\Delta G^{\ddagger}_{\mathrm{C}}$ (ca. 11 kJ mol^{-1}) on replacement of the cyclohexenyl by the cyclooctenyl ligand. We attribute the relatively low $\Delta G^{\ddagger}_{\mathrm{C}}$ values observed for the cyclooctenyl complexes to the flexibility of the methylene groups of the cyclooctenyl ring allowing them to bend away from and so avoid interaction with the $MoX(CO)_2(dppe)$ group. To complete the series of ligands R it is necessary to make a direct comparison with data for allyl complexes $[MI(CO)_2(P\text{–}P)(\eta^3\text{-}C_3H_5)]$ which are available only as iodide derivatives. Comparison of $\Delta G^‡_C$ values for $[MoI(CO)_2(dppe)(\eta^3\text{-R})]$ (**3**, $R = C_8H_{13}$, $\Delta G^‡_C = 53.3$ kJ mol^{-1}; $R = C_3H_5$, $\Delta G^‡_C = 44.3$ kJ mol^{-1}) clearly establishes that it is the C_3H_5 ligand which promotes the lowest values of $\Delta G^‡_C$.

The data for the effect of R on the magnitude of $\Delta G^‡_C$ guided our choice of ligand R for the subsequent investigations on variation in X and P–P. Systems with accessible coalescence temperatures and limiting low temperature $^{31}P\{^1H\}$-NMR spectra generally exhibit $\Delta G^‡_C$ in the range 40–65 kJ mol^{-1} and to achieve this for a wide range of ligands X and P–P, it is necessary to select R to promote relatively high $\Delta G^‡_C$ values. In this way for example investigations on X = Cl, not possible for complexes such as $[MoCl(CO)_2(dppe)(\eta^3\text{-}C_3H_5)]$, are facilitated. Our choice of ligand R for subsequent studies was therefore between R = cyclohexenyl or cycloheptatrienyl and, in the event, $R = C_7H_7$ was selected because some data on the effect of variation of X and P–P were already available from our previous work [5].

2.2.2.2. Effect of X. In the cycloheptatrienylmolybdenum complexes $[MoX(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (**6**–**10**), only the ligand X (X = I, Br, Cl, NCO, NCS) is varied. As expected from the work [2] on $[MX(CO)_2(P\text{–}P)(\eta^3\text{-}C_3H_5)]$ the highest $\Delta G^‡_C$ is observed for X = I. However, study of the cycloheptatrienyl system also allowed calculation of $\Delta G^‡_C$ for X = Br or Cl and the results reveal a steady decrease in $\Delta G^‡_C$ of ca. 3 kJ mol^{-1} along the series I > Br > Cl. In fact the ligand X = NCO promotes the lowest value of $\Delta G^‡_C$ and this finding was utilised in the design of a series of complexes to examine the effect of the chelate phosphine ligand P–P (see below).

Having derived a series for X in the cycloheptatrienyl system we decided to check its validity for the cyclooctenyl system $[MoX(CO)_2(dppe)(\eta^3\text{-}C_8H_{13})]$ (X = I, Br, Cl) in which the absolute magnitude of $\Delta G^‡_C$ is much lower. Inspection of $\Delta G^‡_C$ values for cyclooctenyl complexes **3**–**5** confirms the ordering I > Br > Cl but the overall magnitude of the change from I = I to X = Cl is probably larger than that observed for the cycloheptatrienyl system. We conclude therefore that, whilst the ordering of $\Delta G^‡_C$ along the halide series I > Br > Cl is probably generally applicable to complexes of the type $[MX(CO)_2(P\text{–}P)(\eta^3\text{-R})]$, the absolute magnitude of the change in $\Delta G^‡_C$ along the series is dependent on the other variables M, P–P and R.

In general, we have not attempted to rationalise the effects of variation in M, X, P–P and R upon $\Delta G^‡_C$ because it is not possible to delineate the contributions of steric and electronic effects. It seems probable that an increase in the steric requirements of X, P–P or R will operate to increase $\Delta G^‡_C$ as is observed for the halide series X = Cl, Br or I but considerable caution must be exercised because of a superimposed electronic effect. Use of carbonyl stretching frequencies as a probe suggests that electron density at the metal centre increases slightly along the series I < Br < Cl [complexes **3**–**5** (Table 1) and **6**–**8**] and similarly NCS < NCO [ν(CO) (cm^{-1}, CH_2Cl_2): **10**, (X = NCS), 1940, 1865; **9**, (X = NCO), 1933, 1855] [6]. If steric factors for X = NCO, NCS are similar then it may be inferred that an increase in electron density at the metal centre correlates with a decrease in $\Delta G^‡_C$.

2.2.2.3. Effect of P–P. Ligands of the type $R'_2P(CH_2)_nPR'_2$ may affect $\Delta G^‡_C$ through the chain length (*n*) or the identity of R′ substituents attached to phosphorus. Previous studies with $[MoX(CO)_2(P\text{–}P)(\eta^3\text{-}C_3H_5)]$ suggest [2] that replacement of dppm (*n* = 1) by dppe (*n* = 2) decreases $\Delta G^‡_C$ by ca. 2.5 kJ mol^{-1}. In this work the effect of chain length was investigated further through the complexes **11**, **9** and **12** in which *n* is systematically increased from 1 to 3. To promote direct comparison, all other ligands in complexes **9**, **11** and **12** are identical; the ligand X was selected as NCO because this reduces $\Delta G^‡_C$ and permits measurement of T_C for the dppm derivative **11**. In fact, complex **11** is the first example of a dppm derivative of the cycloheptatrienyl system for which the trigonal twist process has been shown to operate. Previous attempts with derivatives where X = halide were unsuccessful due to decomposition of the complexes at the high temperatures required for investigation [5].

Examination of $\Delta G^‡_C$ values for the NCO complexes **9**, **11** and **12** reveals a non-linear decrease in $\Delta G^‡_C$ with increasing chain length *n*. The dppm derivative **11** exhibits the highest value of $\Delta G^‡_C$ (58.1 kJ mol^{-1}) and this decreases by ca. 3 kJ mol^{-1} in the dppe derivative **9**. A much larger decrease in $\Delta G^‡_C$ (ca. 6 kJ mol^{-1}) is observed on moving to the dppp derivative, **12**. Further to establish the large change in $\Delta G^‡_C$ from *n* = 2 to *n* = 3, the bromide derivative $[MoBr(CO)_2(dppp)(\eta^3\text{-}C_7H_7)]$ **13** was prepared for direct comparison with the dppe analogue **7** and again a decrease in $\Delta G^‡_C$ of ca. 6 kJ mol^{-1} is observed. Overall it is clear that the length of the bridging chain in the diphosphine has a very significant effect with $\Delta G^‡_C$ decreasing by ca. 10 kJ mol^{-1} along the series $n = 1 - 3$. In an attempt to assess the effect of the phosphine ligand substituents R′ we also synthesised the dmpe complex $[Mo(NCO)(CO)_2(dmpe)(\eta^3\text{-}C_7H_7)]$, (**14**). The substitution of phosphine phenyl substituents in **9** with the methyl substituents of **14** whilst keeping chain length (*n* = 2) constant has only a small effect (if any) on $\Delta G^‡_C$ (decrease of ca. 2 kJ mol^{-1}) although it is not possible to delineate the contribution of the differing steric and electronic effects of the Me and Ph substituents. In summary however, the dominant effect connected with the $R'_2P(CH_2)_nPR'_2$ ligand appears to be the bridging chain length and the flexibility imparted to the system as *n* is increased.

2.2.2.4. Effect of M (M = Mo or W). In the allyl complexes $[MI(CO)_2(P–P)(\eta^3-C_3H_5)]$, substitution of Mo by W leads to an increase in $\Delta G^{\ddagger}_C$ by 2–3 kJ mol^{-1} depending on the identity of P–P. A similar effect is evident from comparison of the cyclohexenyl complexes $[MBr(CO)_2(dppe)(\eta^3-C_6H_9)]$ (**1**, M = Mo; **2**, M = W) for which an increase in $\Delta G^{\ddagger}_C$ of ca. 4 kJ mol^{-1} is observed. The results for the cycloheptatrienyltungsten system were therefore unexpected in that they show a *decrease* in $\Delta G^{\ddagger}_C$ of ca. 3 kJ mol^{-1} through replacement of Mo by W. We have reasonable confidence in this conclusion because: (i) the difference in $\Delta G^{\ddagger}_C$ between analogous Mo and W complexes is larger than the estimated allowance for experimental error; and (ii) the effect is consistent for comparison of a complete series of halide complexes $[MX(CO)_2(dppe)(\eta^3-C_7H_7)]$ (X = I, Br, Cl; M = Mo, **6**–**8**; M = W, **15**–**17**). In addition to the dppe complexes **15**–**17**, we also examined $[W(NCO)(CO)_2(dppp)(\eta^3-C_7H_7)]$ **18**, to determine whether the observation extended to systems in which $\Delta G^{\ddagger}_C$ was much lower. Comparison of the $\Delta G^{\ddagger}_C$ values for $[M(NCO)(CO)_2(dppp)(\eta-C_7H_7)]$ (**12**, M = Mo; **18**, M = W) reveals a decrease of ca. 2 kJ mol^{-1} by substitution of Mo with W and, although the magnitude of the difference could be accounted for by experimental error, the trend is consistent with that observed for the dppe analogues. Finally, it should be noted that in complex **18**, the variables X, P–P and M are all set to promote the lowest value of $\Delta G^{\ddagger}_C$ and therefore the result of 47 kJ mol^{-1} may be taken as a very approximate guide to the minimum free energy of activation to the trigonal twist process in the cycloheptatrienyl complexes $[MX(CO)_2(P–P)(\eta^3-C_7H_7)]$.

2.2.2.5. H- and $^{13}C\{^1H\}$-NMR spectra. The ^{1}H- and $^{13}C\{^1H\}$-NMR data for the new complexes reported in this paper are summarised in Table 2. The generally broad appearance of the ambient temperature spectra is consistent with the operation of a trigonal twist process, with the broadening effect especially marked where coalescence temperatures T_C lie in the range 280–320 K (see Table 3). Typical observations are broadening of the ring (R ligand) resonances in both ^{1}H- and ^{13}C-NMR spectra, broadening of signals associated with methylene groups of the chelate phosphine and failure to observe the carbonyl carbon resonance in the ^{13}C-NMR spectrum. These observations are manifest in the majority of the cycloheptatrienyl complexes and in the cyclohexenyl complexes **1** and **2** for which the broadness of the ambient temperature ^{1}H-NMR spectra precluded attempts at assignment of ring protons. Fortunately, in the cycloheptatrienyl system spectral assignment is facilitated by a rapid 1,2-shift process which renders equivalent all seven protons and carbons of the $\eta^3-C_7H_7$ ring [16]. We have already demonstrated that for the cycloheptatrienyl complexes $[MX(CO)_2(P–P)(\eta^3-C_7H_7)]$, better resolved ^{1}H- and $^{13}C\{^1H\}$-NMR spectra can be obtained by employing variable temperature studies [5]. Although we considered it unnecessary to extend such investigations to the additional cycloheptatrienyl complexes reported in the current work, some points of interest do arise from the new cyclohexenyl and cyclooctenyl systems and these are discussed below.

Low temperature ^{1}H- and $^{13}C\{^1H\}$-NMR spectra have been acquired for the cyclohexenyl complexes **1** (^{1}H and ^{13}C) and **2** (^{1}H only) with the objective of obtaining fully assigned spectra. The low temperature spectra are indicative of an asymmetric structure with two discrete phosphorus environments and consistent with the solid state structure determined by X-ray crystallography on analogous complexes $[MX(CO)_2(P–P)(\eta^3-R)]$. Thus in **1** [−40 °C (^{1}H)/−30 °C (^{13}C)] all the ring protons/carbons are inequivalent and in the ^{13}C-NMR spectrum there are two separate carbonyl resonances each with couplings to two distinct phosphorus atoms. Moreover, there are two non-equivalent methylene carbons for the dppe ligand, each split into four lines by J(P–C) coupling. By contrast, the *ambient* temperature $^{13}C\{^1H\}$ spectrum of the tungsten derivative **2** exhibits discrete but very broad resonances for the cyclohexenyl ring carbons and methylene bridge carbons of the dppe ligand.

The ambient temperature ^{1}H- and $^{13}C\{H\}$-NMR spectra of the cyclooctenyl complexes $[MoX(CO)_2(dppe)(\eta^3-C_8H_{13})]$ (**3**, X = I; **4**, X = Br; **5**, X = Cl) demonstrate the opposite extreme of the effect of the trigonal twist process on such spectra. In these cases, coalescence temperatures are less than 280 K and the ring protons/carbons, dppe methylene protons/carbons and the carbonyl carbons exhibit fully averaged environments (for example in the $^{13}C\{^1H\}$-NMR spectra, only five cyclooctenyl ring carbons are observed). This is especially the case for the chloride derivative **5**, whereas the iodide derivative **3** (which has the higher coalescence temperature) displays quite significant broadening of these resonances.

3. Conclusions

Variable temperature $^{31}P\{^1H\}$-NMR investigations strongly support the operation of a trigonal twist fluxional process in complexes of the type $[MX(CO)_2$-

(P–P)(η^3-R)] [R = cycloheptatrienyl, cyclohexenyl, cyclooctenyl or allyl (C_3H_5)] but the process is not universal for all identities of R. Calculation of $\Delta G^{\ddagger}_{\mathrm{C}}$ for the molybdenum complexes [MoX(CO)$_2$(dppe)(η^3-R)] reveals a decrease in the order R = cycloheptatrienyl > cyclohexenyl > cyclooctenyl > allyl. Detailed investigations on the effect of variation of X and P–P on $\Delta G^{\ddagger}_{\mathrm{C}}$ were carried out on the cycloheptatrienyl complexes [MX(CO)$_2$(P–P)(η^3-C_7H_7)] which exhibited accessible values of $\Delta G^{\ddagger}_{\mathrm{C}}$ (45–65 kJ mol^{-1}) over a wide variation in ligands X and P–P. The complexes [MoX(CO)$_2$(dppe)(η^3-C_7H_7)] establish that $\Delta G^{\ddagger}_{\mathrm{C}}$ decreases in the order X = I > Br ≈ NCS > Cl > NCO whilst investigations on [Mo(NCO)(CO)$_2${Ph$_2$P-(CH$_2$)$_n$PPh$_2$}(η^3-C_7H_7)] show that $\Delta G^{\ddagger}_{\mathrm{C}}$ decreases significantly from $n = 1$ to $n = 3$. The variables M, X, P–P and R are not independent but the trends in $\Delta G^{\ddagger}_{\mathrm{C}}$ observed for the variation of X and P–P in the cycloheptatrienyl system appear to have some general validity. The effect on $\Delta G^{\ddagger}_{\mathrm{C}}$ of exchange of Mo for W is strongly R-dependent. Where R = cyclohexenyl or allyl, $\Delta G^{\ddagger}_{\mathrm{C}}$ increases on substitution of Mo by W but the reverse effect is observed for R = C_7H_7.

4. Experimental

4.1. General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The compounds [MoBr(CO)$_2$(NCMe)$_2$(η^3-C_6H_9)] [12], [MoBr(CO)$_2$(NCMe)$_2$(η^3-C_8H_{13})] [13] and [M(NCO)(CO)$_2$(η-C_7H_7)] (M = Mo or W) [17] were prepared by published procedures. Three hundred megahertz ^{1}H- and 75 MHz ^{13}C{^{1}H}-NMR spectra were recorded on Bruker AC 300 E, Varian Associates XL 300 or Varian Unity Inova 300 spectrometers; 121.5 MHz ^{31}P{^{1}H}-NMR spectra were recorded on the Varian Unity Inova 300 instrument. Infrared spectra were obtained on a Perkin–Elmer FT 1710 spectrometer and mass spectra were recorded using Kratos Concept 1S (FAB spectra) or Micromass Platform II (ES spectra) instruments. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

*4.2. Preparation of [MoBr(CO)$_2$(dppe)(η^3-C_6H_9)] (**1**)*

Reaction of [MoBr(CO)$_2$(NCMe)$_2$(η^3-C_6H_9)] (2.71 g, 6.86 mmol) with dppe (2.73 g, 6.86 mmol) in THF (60 cm^3) gave an orange solution which was stirred at room temperature (r.t.) for 24 h. The reaction mixture was then evaporated to dryness and the crude product recrystallised from CH_2Cl_2–hexane then toluene–diethyl ether to give **1** as a yellow–orange solid; yield 2.15 g (44%).

*4.3. Preparation of [WBr(CO)$_2$(dppe)(η^3-C_6H_9)] (**2**)*

A stirred solution of [W(CO)$_3$(NCMe)$_3$] (0.848 g, 2.17 mmol) in NCMe (30 cm^3) was treated with 3-bromocyclohexene (0.350 g, 2.17 mmol). After 40 min, precipitation of the product [WBr(CO)$_2$(NCMe)$_2$(η^3-C_6H_9)] as a pale yellow–green solid was complete; yield 0.923 g. The intermediate [WBr(CO)$_2$(NCMe)$_2$(η^3-C_6H_9)] (0.445 g, 0.92 mmol) in thf (30 cm^3) was treated with dppe (0.370 g, 0.093 mmol) and stirred at r.t. for 40 h. The solvent was then removed and the residue recrystallised from CH_2Cl_2–hexane then acetone–hexane to give **2** as a bright yellow solid; yield 0.678 g (92%).

*4.4. Preparation of [MoBr(CO)$_2$(dppe)(η^3-C_8H_{13})] (**4**)*

Reaction of [MoBr(CO)$_2$(NCMe)$_2$(η^3-C_8H_{13})] (0.350 g, 0.83 mmol) with dppe (0.329 g, 0.83 mmol) in CH_2Cl_2 (20 cm^3) gave an orange solution which was stirred at r.t. for 2 h. The solvent was then removed in vacuo and the residue recrystallised from CH_2Cl_2–hexane to give **4** as a yellow–orange solid; yield 0.510 g (83%).

*4.5. Preparation of [MoX(CO)$_2$(dppe)(η^3-C_8H_{13})] (**3**, X = I; **5**, X = Cl)*

A stirred solution of [MoBr(CO)$_2$(dppe)(η^3-C_8H_{13})] (0.370 g, 0.50 mmol) in AnalaR acetone (30 cm^3) was treated with Ag[BF$_4$] (0.120 g, 0.62 mmol). The solution was stirred for 30 min, filtered to remove the precipitate of AgBr and then KI (0.415 g, 2.5 mmol) was added. After stirring for 20 h the solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–hexane to give **3** as an orange solid; yield 0.158 g (40%). The chloride derivative [MoCl(CO)$_2$(dppe)(η^3-C_8H_{13})], **5** was prepared similarly from [MoBr(CO)$_2$(dppe)(η^3-C_8H_{13})] (0.200 g, 0.27 mmol), Ag[BF$_4$] (0.071 g, 0.36 mmol) and LiCl (0.057 g, 1.36 mmol) and isolated an orange–yellow solid; yield 0.060 g (32%).

*4.6. Preparation of [MX(CO)$_2$(P–P)(η^3-C_7H_7)] [M = Mo or W, X = Br or NCO, P–P = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1–3)], **7**, **11–13**, **16**, **18***

These complexes were prepared by a standard procedure starting from [MX(CO)$_2$(η-C_7H_7)] (M = Mo or W; X = Br or NCO). Reaction of a green solution of [MX(CO)$_2$(η-C_7H_7)] (ca. 0.50 g) in CH_2Cl_2 (20 cm^3)

with an equimolar quantity of $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–3) at r.t. gave a red–purple solution of the product $[MX(CO)_2(P–P)(\eta^3\text{-}C_7H_7)]$. After stirring for 2 h the solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–hexane and subsequently, acetone–hexane to give the product as a red to purple solid. Details of colours and yields are presented in Table 1.

4.7. Preparation of $[Mo(NCO)(CO)_2(dmpe)(\eta^3\text{-}C_7H_7)]$ (**14**)

A stirred solution of $[Mo(NCO)(CO)_2(\eta\text{-}C_7H_7)]$ (0.175 g, 0.61 mmol) in CH_2Cl_2 (20 cm^3) was cooled to -78 °C and then treated with dmpe (0.100 g, 0.66 mmol). The reaction mixture was allowed to warm slowly to r.t. and reaction to give a red solution of the product commenced at -40 °C. After stirring at r.t. for 30 min the reaction mixture was evaporated to dryness and the residue dried in vacuo, for 2 h. The crude product was then recrystallised from CH_2Cl_2–hexane to give **14** as a deep purple solid; yield 0.080 g (30%).

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