Mono(η-cyclopentadienyl)molybdenum Chemistry: Acetylene, Tertiary Phosphine, and Related Derivatives

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Displacement of chloride in $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Cl]$ gives $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)L][PF_6]$, [L = PPh_3, PMe_2Ph, CO, C_2H_4, C_2H_2, or $C_2(CO_2Me)_2$] or $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)X]$ (X = H or Me). Loss of benzene gives rise to $[Mo(\eta\text{-}C_5H_5)(dppe)_2][PF_6]$, $[Mo(\eta\text{-}C_5H_5)Cl(O)_2]$, $[Mo(\eta\text{-}C_5H_5)Cl_2O]$, and $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)][PF_6]$. Replacement of dppe in $[Mo(\eta\text{-}C_5H_5)(dppe)_2][PF_6]$ (or $[BF_4]$) leads to the salts $[Mo(\eta\text{-}C_5H_5)(dppe)L_2][PF_6]$, [$L_2$ = (CO)(NCMe), $(CO)_2$, $\eta^4\text{-}C_6H_8$, C_4H_6, C_2Me_2, or C_2Ph_2]. Oxidation of $[Mo(\eta\text{-}C_5H_5)(dppe)_2][BF_4]$ by iodine gives paramagnetic $[Mo(\eta\text{-}C_5H_5)(dppe)_2][PF_6]_2$. The compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)][PF_6]$ reacts with L = CO or PPh_3 giving $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)L][PF_6]$ and with $Ph_2P[CH_2]_2PPh_2$ (dppe) giving $[Mo(\eta\text{-}C_5H_5)(\eta^4\text{-}C_8H_8)(dppe)][PF_6]$. The compound $[Mo(\eta\text{-}C_5H_5)(\eta^4\text{-}C_4H_6)(dppe)][PF_6]$ exists in solutions as a mixture of isomers. These react with $Na[AlH_2(OCH_2CH_2OMe)_2]$ giving a separable mixture of the η^3-3-methylallyl compounds $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}MeCHCHCH_2)(dppe)]$ where the allylic group is oriented 'up' or 'down' relative to the $\eta\text{-}C_5H_5$ ring.

THERE is an extensive chemistry of mono(η-cyclopentadienyl)molybdenum carbonyl derivatives.[1] It is derived from molybdenum hexacarbonyl as the starting material and with few exceptions it is not possible to completely remove all the carbonyl groups from the compounds prepared in this manner.

Our interest in highly electron-rich molybdenum compounds and their unusual reactivity led us to explore routes to carbonyl-free mono(η-cyclopentadienyl)molybdenum compounds. The compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Cl]$ has been found to act as a precursor for many new mono(cyclopentadienyl)molybdenum derivatives, as briefly described in preliminary communications.[2,3]

RESULTS AND DISCUSSION

The compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Cl]$ (1) has been previously described.[4] We have also prepared the

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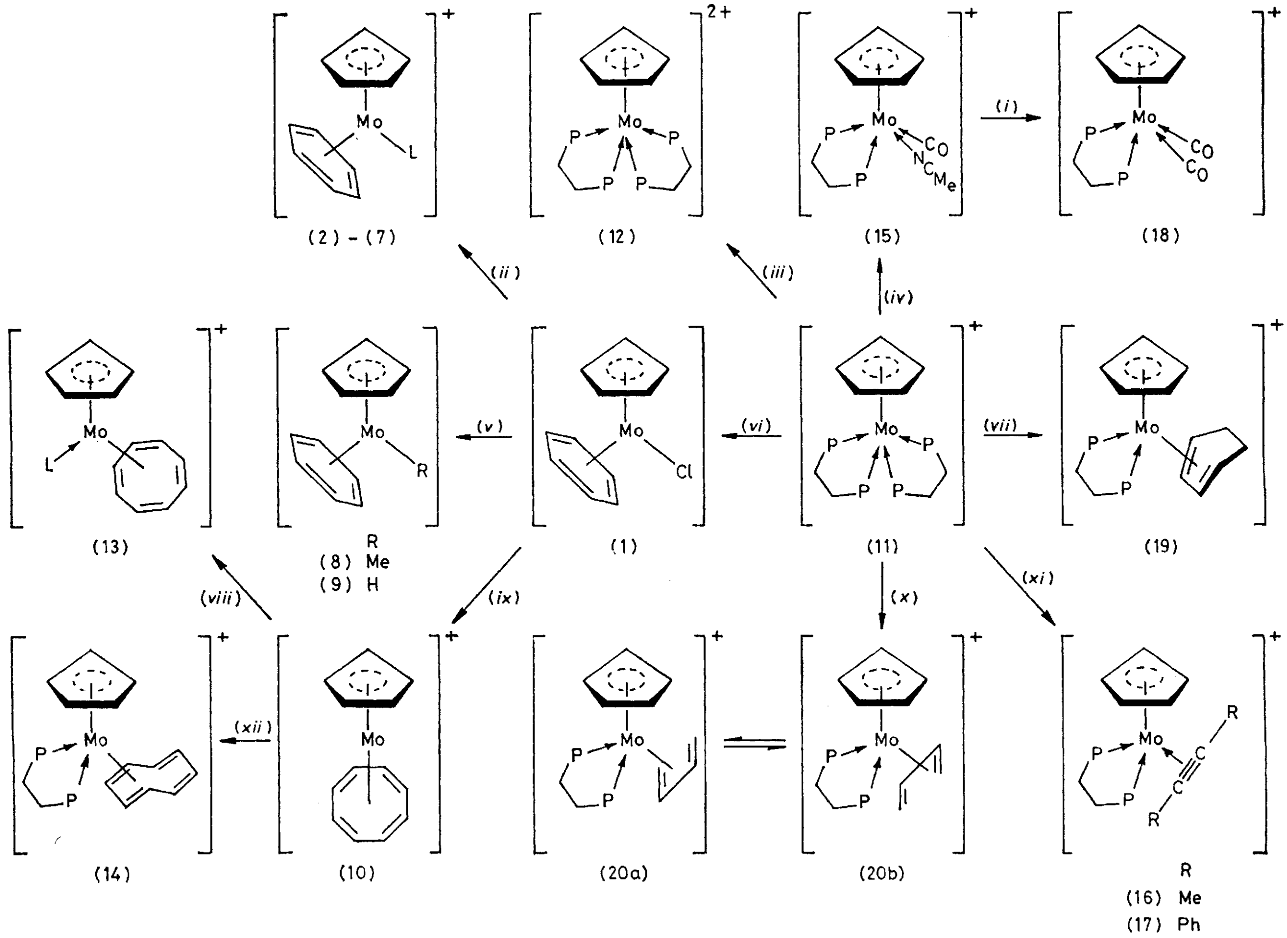
[1] M. L. H. Green, *Pure Appl. Chem.*, 1972, **30**, 373 and refs. therein.

[2] M. L. H. Green, J. Knight, and J. A. Segal, *J.C.S. Chem. Comm.*, 1975, 283.

[3] J. A. Segal, M. L. H. Green, J.-C. Daran, and K. Prout, *J.C.S. Chem. Comm.*, 1976, 766.

[4] M. L. H. Green and J. Knight, *J.C.S. Dalton*, 1976, 213.

analogues $[Mo(\eta-C_5H_5)(\eta-C_6H_6)X]$ (X = Br or I). However, (1) was found to be satisfactory for the reactions described below.



Anions of salts are omitted. (*i*) CO in EtOH at 80 °C; (*ii*) $Tl[PF_6]$ in Me_2CO, then L at r.t. where L = C_2H_4 (2), C_2H_2 (3), $C_2(CO_2Me)_2$ (4), CO (5), PPh_3 (6), or PMe_2Ph (7); (*iii*) I_2 in CH_2Cl_2 at r.t.; (*iv*) CO in MeCN at 80 °C; (*v*) MgXMe in diethyl ether [R = Me (8)] or $Na[BH_4]$ in thf [R = H (9)]; (*vi*) dppe in MeOH at 65 °C; (*vii*) cyclohexa-1,3-diene in MeCN at 80 °C; (*viii*) L = CO or PPh_3 in acetone at r.t.; (*ix*) $Tl[PF_6]$ in Me_2CO, then C_8H_8 at 80 °C; (*x*) butadiene in MeCN at 80 °C; (*xi*) RC≡CR (R = Me or Ph) in MeCN at 80 °C; (*xii*) dppe in Me_2CO at r.t.

Treatment of (1) in acetone with thallium(I) hexafluorophosphate gives a turquoise-green solution which behaves as though it were a compound such as $[Mo(\eta-C_5H_5)(\eta-C_6H_6)(OCMe_2)][PF_6]$. Thus, the solution reacts with a variety of ligands L giving the compounds $[Mo(\eta-C_5H_5)(\eta-C_6H_6)L][PF_6]$ [L = C_2H_4 (2), C_2H_2 (3), $C_2(CO_2Me)_2$ (4), CO (5), PPh_3 (6), or PMe_2Ph (7)]. Compounds (2)—(7) are red crystalline solids soluble in acetone and most of them are steadily oxidised in air; (5) has been previously described.[5] The ^1H n.m.r. spectrum of the ethylene compound (2) at room temperature shows a singlet resonance assignable to the C_2H_4 hydrogens. It is presumed that the ethylene ligand rotates around the metal–ligand axis.

Treatment of (1) in benzene with methylmagnesium bromide gives red highly air-sensitive crystals of $[Mo(\eta-C_5H_5)(\eta-C_6H_6)Me]$ (8). Attempts to prepare the corresponding hydride $[Mo(\eta-C_5H_5)(\eta-C_6H_6)H]$ (9) by reaction of (1) with sodium tetrahydroborate or $Na[AlH_2(OCH_2CH_2OMe)_2]$ gave a thermally unstable red compound. The ^1H n.m.r. spectrum showed a band at τ 11.77 assignable to the expected Mo–H hydrogen. This may be compared with the band due to W–H at τ 12.2 found for the analogue $[W(\eta-C_5H_5)(\eta-C_6H_6)H]$.[6] The ^1H n.m.r. spectrum of (9), however, broadens very rapidly at room temperature. The mass spectrum of the red crystals isolated from the preparations gave only the spectrum of the paramagnetic compound $[Mo(\eta-C_5H_5)(\eta-C_6H_6)]$. We conclude that it is highly likely that (9) exists but is thermally unstable at room temperature.

Compound (1) is very sensitive to oxidation by oxygen both in solutions and in the solid state. A study of the oxidation products in chloroform showed that $[Mo(\eta-C_5H_5)Cl(O)_2]$ was formed in good yields. Perhaps

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[5] E. O. Fischer and F. J. Köhl, *Chem. Ber.*, 1965, **98**, 2134.

[6] E. M. van Dam, W. N. Brent, M. P. Silvon, and P. S. Skell, *J. Amer. Chem. Soc.*, 1975, **97**, 465.

surprisingly, examination of the oxidation of solid (1) showed the major product to be $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Cl_2O}]$.

When the turquoise solution described above is treated with cyclo-octatetraene under reflux then it becomes light green, giving the mixed sandwich compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_8H_8})][\mathrm{PF_6}]$ (10).

Treatment of (1) in hot methanol with 1,2-bis(diphenylphosphino)ethane (dppe) causes displacement of both benzene and chloride to give the compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})_2][\mathrm{A}]$ (11; A = $\mathrm{PF_6}$ or $\mathrm{BF_4}$). This compound is unexpectedly labile and undergoes reactions with weak donor solvents such as acetone, tetrahydrofuran, or acetonitrile. It may, however, be recrystallised from methanol. Treatment of (11; A = $\mathrm{PF_6}$) with iodine causes oxidation giving the paramagnetic salt $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})_2][\mathrm{PF_6}]_2$ (12). The e.s.r. spectrum of (12) is given in Figure 1 and it shows a well resolved quintet of sextets which we interpret as arising from coupling of the main molybdenum isotope with the four equivalent ^{31}P nuclei and the five hydrogens of the η-$\mathrm{C_5H_5}$ ring. The structure expected from the other molybdenum isotopes is not resolved.

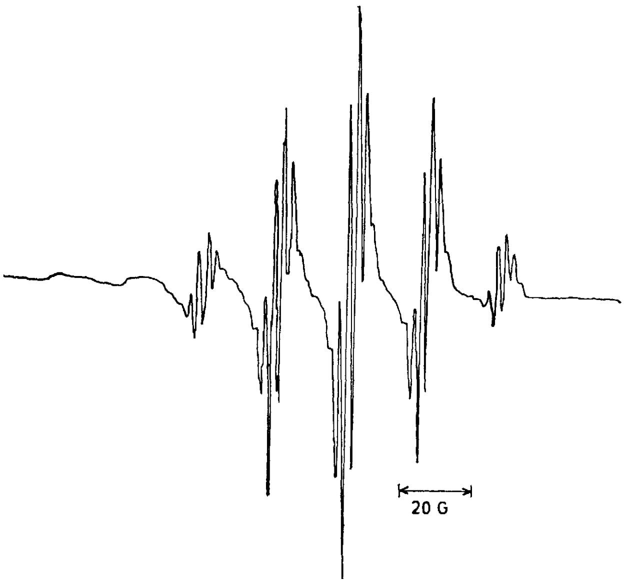

FIGURE 1 E.s.r. spectrum of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})_2][\mathrm{PF_6}]_2$

We were interested to explore the lability of the η-$\mathrm{C_8H_8}$ ligand in (10). Treatment of (10) with carbon monoxide or triphenylphosphine gives the η^6-$\mathrm{C_8H_8}$ derivatives $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_8H_8})\mathrm{L}][\mathrm{PF_6}]$ (13; L = CO or $\mathrm{PPh_3}$). However, (10) reacts with dppe giving the η^4-$\mathrm{C_8H_8}$ compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\eta^4\text{-}\mathrm{C_8H_8})(\mathrm{dppe})][\mathrm{PF_6}]$ (14). In contrast to (13), the ^{1}H n.m.r. spectrum of (14) shows the η^4-$\mathrm{C_8H_8}$ ring to be fluxional since it gives rise to a single resonance, even at −90 °C.

As mentioned above, cation (11) reacts with acetonitrile although it was not possible to characterise the species present in the resulting red solutions. However, treatment of this with carbon monoxide gives the yellow compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\mathrm{NCMe})(\mathrm{CO})][\mathrm{PF_6}]$ (15). The ^{1}H n.m.r. spectrum shows only a doublet for the η-$\mathrm{C_5H_5}$ hydrogens, and we assume that the different effects of the MeCN and CO ligands causes the coupling of one of the ^{31}P nuclei to the ring hydrogens to be too small to be resolved. Prolonged heating of (15) in ethanol under an atmosphere of CO gives the known dicarbonyl $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\mathrm{CO})_2][\mathrm{PF_6}]$. Clearly the MeCN ligand in (15) is not readily displaced.

Treatment of the red acetonitrile solutions of (11; A = $\mathrm{BF_4}$) with dimethyl- or diphenyl-acetylene at 80 °C gives emerald-green compounds $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\mathrm{C_2Me_2})][\mathrm{BF_4}]$ (16) and $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\mathrm{C_2Ph_2})][\mathrm{BF_4}]$ (17) respectively. These are formally 16-electron compounds. The ^{1}H n.m.r. spectrum of (16) at room temperature shows no bands assignable to the $\mathrm{CH_3}$ hydrogens. However, at lower temperatures (*ca.* −50 °C) two resonances appear at τ 6.93 and 8.75. These coalesce to a sharp singlet at 110 °C. The data indicate an energy barrier $\Delta G^\ddagger$ *ca.* 14.3 ± 0.6 kcal mol^{-1} for rotation about the metal–ligand axis.* Similar observations of rotation of acetylene ligands have been recently noted for some chromium and osmium compounds.[7]

Compound (16) reacts only slowly with CO giving the dicarbonyl $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\mathrm{CO})_2][\mathrm{PF_6}]$ (18).

Diolefins also react with the acetonitrile solutions of (11; A = $\mathrm{BF_4}$). Cyclohexa-1,3-diene gives the compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\eta^4\text{-}\mathrm{C_6H_8})][\mathrm{BF_4}]$ (19), the crystal structure [3] of which, as an $\mathrm{SO_2}$ adduct, shows the $\mathrm{C_6H_8}$ ring to be orientated in the manner indicated in the Scheme. Butadiene and (11; A = $\mathrm{BF_4}$) give a compound of stoicheiometry $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\mathrm{C_4H_6})][\mathrm{BF_4}]$ (20). The ^{1}H and ^{13}C n.m.r. spectra show that (20) exists in solution as a mixture of isomers and the ratio of isomers is solvent dependent, varying from *ca.* 1 : 1 in dimethyl sulphoxide solutions to *ca.* 1 : 1.6 in liquid sulphur dioxide solutions. We propose that the isomers arise from an ' up ' or ' down ' orientation of the butadiene ligand (see the Scheme). Related isomers of $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\{\mathrm{C_4(CF_3)_4CO}\}\mathrm{Cl}]$ have recently been described.[8]

Treatment of (20) with $\mathrm{Na[AlH_2(OCH_2CH_2OMe)_2]}$ gives two isomers of stoicheiometry $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{dppe})(\eta^3\text{-}\mathrm{MeCHCHCH_2})]$ (21) which could be separated by fractional crystallisation. Detailed study of the ^{1}H n.m.r. spectra (270 MHz) does not allow clear assignment of the stereochemistry about the 1-carbon of the 1-methylallyl ligand. However, for the more-soluble isomer all the H–H coupling constants may be determined by decoupling experiments. This leads us to propose a tentative structural assignment, based on the magnitudes of the vicinal coupling constants, as the *anti* configuration (Figure 2). The data are given in the

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* Throughout this paper: 1 cal = 4.184 J; 1 atm = 101 325 Pa; 1 G = 10^{-4} T.

[7] M. Herberhold, H. Alt, and C. G. Kreiter, *J. Organometallic Chem.*, 1977, **42**, 413; J. A. Segal and B. F. G. Johnson, *J.C.S. Dalton*, 1975, 1990.

[8] J. L. Davison, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 739.

Analytical and spectroscopic data

Compound	Colour	Analysis (%) [a]		^{1}H N.m.r. data [b]
		C	H	
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Br]$	Red–black	41.0 (41.4)	3.7 (3.5)	
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)I]$	Purple–black	35.8 (36.1)	3.5 (3.0)	4.82, **5**, **s**, C_5H_5; 5.17, **6**, **s**, C_6H_6 [c]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)(C_2H_4)][PF_6]$ (2)	Orange–red	37.9 (37.9)	3.4 (3.7)	4.42, **6**, **s**, C_6H_6; 4.80, **5**, **s**, C_5H_5; 7.00, **4**, **s**, C_2H_4 [d]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)(C_2H_2)][PF_6]$ (3)	Orange–red	38.4 (38.1)	3.2 (3.2)	2.17, **2**, **s**, C_2H_2; 4.15, **6**, **s**, C_6H_6; 4.78, **5**, **s**, C_5H_5 [d,e]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)\{C_2(CO_2Me)_2\}][PF_6]$ (4)	Orange	38.6 (38.8)	3.2 (3.3)	3.70, **6**, **s**, C_6H_6; 4.39, **5**, **s**, C_5H_5; 6.09, **6**, **s**, 2Me [d,f]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)(PPh_3)][PF_6]$ (6)	Red	53.5 (53.9)	4.2 (4.1)	2.28, **15**, **c**, 3Ph; 5.03, **5**, **d** (2), C_5H_5; 5.13, **6**, **d** (1), C_6H_6 [d]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)(PMe_2Ph)][PF_6]$ (7)	Orange	44.0 (43.8)	4.3 (4.3)	2.26, **5**, **c**, Ph; 4.75, **5**, **d** (5.4), C_5H_5; 5.02, **6**, **d**, (6.6), C_6H_6; 7.96, **6**, **d** (10.2), 2Me [d]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Me]$ (8)	Deep red	*g*		5.5, **5**, **s**, C_5H_5; 6.05, **6**, **s**, C_6H_6; 9.55, **3**, **s**, Me [h,i]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)H]$ (9)	Deep red	*g*		5.35, **5**, **s**, C_5H_5; 5.85, **6**, **s**, C_6H_6; 11.7, **1**, **s**, MoH [h]
$[Mo(\eta\text{-}C_5H_5)(dppe)_2][PF_6]$ (11)	Orange–red	61.9 (62.1)	4.7 (4.8)	2.4, **40**, **c**, 8Ph; 5.46, **5**, **q** (2), C_5H_5 [d]
$[Mo(\eta\text{-}C_5H_5)(dppe)_2][PF_6]_2$ (12) [j]	Yellow	54.9 (54.9)	4.4 (4.3)	
$[Mo(\eta\text{-}C_5H_5)(dppe)(NCMe)(CO)][PF_6]\cdot CH_2Cl_2$ (15)	Yellow	49.2 (49.0)	4.3 (4.0)	2.4, **20**, **c**, 4Ph; 4.65, **2**, **s**, CH_2Cl_2; 4.80, **5**, **d** (2.0), C_5H_5; 7.15, **4**, **c**, $(CH_2)_2$; 7.95, **3**, **d** (2.5), Me [k]
$[Mo(\eta\text{-}C_5H_5)(dppe)(C_4H_6)][BF_4]$ (20)	Yellow	60.1 (60.0)	5.1 (5.0)	Isomer (a): 2.42, **20**, **c**, 4Ph; 4.83, **5**, **t** (2.8), C_5H_5; 5.37 **2**, **c**, C_4H_6; 6.76, **4**, **c**, $(CH_2)_2$; 8.11, **2**, **c**, C_4H_6; 8.34, **2**, **c**, C_4H_6 [c] Isomer (b): 2.42, **20**, **c**, 4Ph; 4.78, **c**, **2**, C_4H_6; 5.22, **5**, **t** (2.8), C_5H_5; 6.76, **4**, **c**, $(CH_2)_2$; 9.17, **2**, **m**, C_4H_6; 11.38, **2**, **c**, C_4H_6 [c,l]
$[Mo(\eta\text{-}C_5H_5)(dppe)(\eta^4\text{-}C_6H_8)][BF_4]\cdot CH_2Cl_2$ (19)	Yellow	56.3 (56.3)	4.7 (4.9)	2.6, **20**, **c**, 4Ph; 4.65, **2**, **s**, CH_2Cl_2; 5.13, **5**, **t** (1.4), C_5H_5; 5.43, **2**, **c**, C_6H_4 (C^2,C^3); 6.68, **2**, **c**, C_6H_8 (C^1, C^4); 6.95, **4**, **c**, $(CH_2)_2$; 8.28, **4**, **c**, C_6H_8 (C^5,C^6) [k,m]
$[Mo(\eta\text{-}C_5H_5)(dppe)(C_2Me_2)][BF_4]$ (16)	Green	60.3 (60.0)	5.3 (5.0)	At −50 °C: 2.6, **20**, **c**, 4Ph; 4.65, **5**, **t** (2.4), C_5H_5; 6.5, **4**, **c**, $(CH_2)_2$; 6.93, **6**, **s**, Me; 8.75, **6**, **s**, Me.[d] At 110 °C: Me resonances coalesce at 7.36, **6**, **s**, 2Me (60 MHz) [d,n]
$[Mo(\eta\text{-}C_5H_5)(dppe)(C_2Ph_2)][BF_4]$ (17)	Green	65.5 (65.6)	4.7 (4.8)	
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)][PF_6]$ (10)	Silver–green	38.2 (38.4)	3.3 (3.0)	2.60, **8**, **s**, C_8H_8; 4.49, **5**, **s**, C_5H_5 [d]
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)(PPh_3)][PF_6]$ (13)	Red	55.5 (55.4)	4.7 (4.2)	2.32, **15**, **c**, 3Ph; 3.33, **2**, **c**, C_8H_8; 4.05, **2**, **c**, C_8H_8; 4.95, **5**, **d**, (4.5) C_5H_5; 5.35, **2**, **c**, C_8H_8; 5.67, **2**, **c**, C_8H_8 [d]
$[Mo(\eta\text{-}C_5H_5)(\eta^6\text{-}C_8H_8)(CO)][PF_6]$ (13)	Red	38.6 (38.4)	3.3 (3.0)	3.58, **4**, **c**, C_8H_8; 4.18, **5**, **s**, C_5H_5; 4.57, **2**, **c**, C_8H_8; 5.20, **2**, **c**, C_8H_8 [d,o]
$[Mo(\eta\text{-}C_5H_5)(\eta^4\text{-}C_8H_8)(dppe)][PF_6]$ (14)	Red	58.2 (57.9)	4.8 (4.6)	2.34, **20**, **c**, 4Ph; 5.00, **8**, **t** (2.0), C_8H_8; 5.40, **5**, **t** (1.1), C_5H_5; 6.94, **4**, **c**, $(CH_2)_2$ [d]
$[Mo(\eta\text{-}C_5H_5)(dppe)(\eta^3\text{-}MeCHCHCH_2)]$ (21)	Orange	68.2 (68.4)	6.1 (5.9)	More-soluble isomer: 2.70, **20**, **m**, 4Ph; 5.86, **1**, **c**, C_4H_7; 6.06, **5**, **t** (0.7), C_5H_5; 7.19 **1**, **c**, C_4H_7; 7.49, **1**, **c**, C_4H_7;[h,p] 8.0, **4**, **c**, $(CH_2)_2$; 8.14, **3**, **d**, (6.4) Me; 8.38 **1**, **c**, C_4H_7 Less-soluble isomer: 2.74, **20**, **c**, 4Ph; 5.64, **5**, **t** (0.7), C_5H_5; 6.79, **1**, **c**, C_4H_7; 7.34, **1**, **c**, C_4H_7; 8.00, **4**, **c**, $(CH_2)_2$; 8.50, **3**, **d** (6.4), Me [h]

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (τ), **relative intensity, multiplicity** (*J* in Hz), assignment, *etc.* [c] In $S(CD_3)_2O$. [d] In $(CD_3)_2CO$. [e] $\nu(C\equiv C)$ at 1 689 cm^{-1} (mull). [f] $\nu(C\equiv C)$ at 1 836 cm^{-1}, $\nu(C=O)$ at 1 692 cm^{-1} (mull). [g] Decomposes at r.t. [h] In C_6D_6. [i] Mass spectrum, *m/e* 256 for ^{98}Mo. [j] Quintet of sextets in e.s.r., $\langle g \rangle = 1.988$, $\langle a \rangle_{iso}$ (P) = 20.4 G, $\langle a \rangle$ (H) = 2.1 G. [k] In SO_2. Phosphorus-31 n.m.r. 69.0 and 79.5 p.p.m. relative to $P(OMe)_3$, *J*(PP) 40 Hz. $\nu(C\equiv O)$ at 1 871 cm^{-1} (mull). N, 1.4 (1.6%). [l] Carbon-13 n.m.r. for C_4H_6 ligand: isomer (a) 102.3 (CH), 48.1 p.p.m. (CH_2); (b), 77.2 (CH), 44.0 p.p.m. (CH_2). [m] In SO_2. [n] Coalescence temperature = 2 °C. [o] $\nu(C\equiv O)$ at 2 002 cm^{-1}. [p] *J*(AB) 5.4, *J*(AC) 8.9, *J*(AD) 7.3, *J*(BD) *ca.* 0.0, *J*(CMe) 6.4, *J*(B,^{31}P) 11.3 Hz; for key see Figure 2.

Table. We are not able to distinguish which isomer of (21) has the ' up ' or the ' down ' configuration, but we propose that the isomers are of this type by analogy with similar observations of Faller *et al.*[9]

EXPERIMENTAL

All the reactions and manipulations were carried out under nitrogen or *in vacuo*. All the solvents were dried and distilled. (η-Benzene)chloro(η-cyclopentadienyl)-molybdenum was prepared as described.[4] Hydrogen-1 n.m.r. spectra were determined using a Brucker (90 MHz), JEOL (60 MHz), or a 270-MHz instrument available at Oxford. E.s.r. spectra were obtained on a JEOL JES-PE spectrometer. Microanalyses were by A. Bernhardt or by the microanalytical department of this laboratory. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film.

(η-Benzene)bromo(η-cyclopentadienyl)molybdenum.—The dimer $[\{Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_3H_5)Cl\}_2]$ (2.0 g), prepared as described,[4] was treated with $(AlEtCl_2)_2$ in toluene (9 cm^3, 230 mg cm^{-3}) at 0 °C. The mixture was shaken for 5 min giving an intense blue-violet solution. This was cooled (−50 °C) and freshly distilled cyclopentene (2.5 cm^3) was added dropwise. The stirred solution was allowed to

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[9] J. W. Faller, C.-C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organometallic Chem.*, 1973, **52**, 361.

warm to room temperature (r.t.); at *ca.* 0 °C an oily red-brown lower layer appeared leaving a pale upper layer. The mixture was left for 2 h at r.t. and the upper layer was then discarded. The lower layer was washed with light petroleum (50 cm^3, b.p. 30—40 °C) and the residue was placed under reduced pressure until it became a tarry solid. This was cooled to −50 °C and cool lithium bromide (6 g) in pure methanol (30 cm^3) was added. The mixture was shaken vigorously and allowed to warm to r.t. At *ca.* −10 °C vigorous effervescence was observed and a red-black precipitate separated. After 15 min the solvent was removed under reduced pressure and the residue was immediately extracted with benzene (200 cm^3) and water (30 cm^3). The benzene layer was collected and dried. A second benzene (100 cm^3) extraction of the aqueous suspension was made and the extracts were combined and the solvent was removed under reduced pressure. The dry residue was extracted with dry benzene and the extract was filtered through Keiselguhr, concentrated to *ca.* 40 cm^3, treated with light petroleum (80 cm^3, b.p. 100—120 °C), and then the solvent was removed under reduced pressure. Red-black crystals separated and were collected, washed with light petroleum, and dried (1.5 g, 60%).

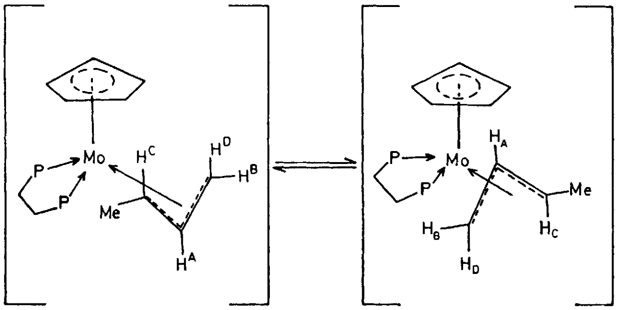

FIGURE 2 Proposed structures for the isomers (21)

(η-Benzene)(η-cyclopentadienyl)iodomolybdenum.—Pure $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]$ (3.0 g) in benzene (60 cm^3) was treated with iodine (1.7 g) in light petroleum (150 cm^3, b.p. 100—120 °C). The initially deep yellow solution gave a dark precipitate and purple solution. After concentration to *ca.* 100 cm^3 under reduced pressure, the precipitate was collected and recrystallised from acetone–ethanol, giving purple-black crystals which were dried *in vacuo* (2.3 g, *ca.* 50%).

(η-Benzene)(η-cyclopentadienyl)(ethylene)molybdenum Hexafluorophosphate (2).—Pure $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Cl]$ (1) (0.35 g) in acetone (20 cm^3) was treated with thallium(I) hexafluorophosphate (0.5 g) and the mixture was shaken for 30 min and then filtered. The dark green filtrate was treated with ethylene and it gradually became dark yellow. After filtration under an ethylene atmosphere the filtrate was treated with ethanol (30 cm^3) and then concentrated under reduced pressure to give orange-red crystals. These were recrystallised from ethylene-saturated acetone–ethanol, separated, washed with ethanol and then diethyl ether, and dried *in vacuo* (0.2 g, 38%).

(Acetylene)(η-benzene)(η-cyclopentadienyl)molybdenum hexafluorophosphate (3) was obtained as a very air-sensitive compound in a manner entirely analogous to the preparation of (2) using acetylene instead of ethylene, *ca.* 40%.

(η-Benzene)(η-cyclopentadienyl)(dimethyl acetylenedicarboxylate)molybdenum Hexafluorophosphate (4).—Pure (1) (0.21 g) and $Tl[PF_6]$ (0.30 g) in acetone (20 cm^3) were shaken for 30 min. The solution was filtered so that the filtrate passed directly into dimethyl acetylenedicarboxylate (0.2 g) in acetone (10 cm^3), giving a deep yellow solution. After filtration, the filtrate was treated with ethanol (40 cm^3) and concentrated under reduced pressure, giving orange crystals. Recrystallisation was from acetone–ethanol, the pure crystals being washed with ethanol then diethyl ether and dried *in vacuo* (*ca.* 50%).

(η-Benzene)carbonyl(η-cyclopentadienyl)molybdenum Hexafluorophosphate (5).—A suspension of pure (1) (0.05 g) and $Tl[PF_6]$ (0.2 g) in acetone (15 cm^3) was shaken for 1 h. After filtration, the filtrate was treated with carbon monoxide (1 atm) for 5 min giving a red solution. Ethanol (30 cm^3) was added and the solution was concentrated giving red crystals. These were washed and dried as before (0.04 g, 54%). The product was identified by comparison of the i.r. spectrum with that of an authentic sample.[5]

(η-Benzene)(η-cyclopentadienyl)(triphenylphosphine)molybdenum Hexafluorophosphate (6).—Compound (1) (0.05 g) in acetone (20 cm^3) and $Tl[PF_6]$ (0.1 g) were shaken for 30 min and filtered into triphenylphosphine (0.1 g) in acetone (10 cm^3). After filtration, ethanol (30 cm^3) was added to the filtrate and on concentration under reduced pressure bright red crystals separated. Recrystallisation was from acetone–ethanol and the pure compound was washed and dried as before (0.08 g, 68%).

(η-Benzene)(η-cyclopentadienyl)(dimethylphenylphosphine)-molybdenum Hexafluorophosphate (7).—Pure (1) (0.1 g) and dimethylphenylphosphine (0.2 cm^3) in methanol (20 cm^3) were heated under reflux for 20 min. After cooling the resulting red solution, $[NH_4][PF_6]$ (0.15 g) was added and then excess of diethyl ether. The orange precipitate was collected, washed with water, and dried. Recrystallisation was from acetone–ethanol and the pure product was washed and dried as before (0.13 g, 68%).

(η-Benzene)(η-cyclopentadienyl)methylmolybdenum (8).—Pure (1) (0.4 g) in dry benzene (30 cm^3) was treated with MgBrMe in diethyl ether (1 mol dm^{-3}, 2.5 cm^3) and the mixture was shaken vigorously for 30 min. An orange-red solution formed which was cooled to 5 °C and water (1 cm^3) was added slowly. The mixture was warmed to r.t. and the solvent was removed under reduced pressure. The residue was extracted with light petroleum (30 cm^3), the extract was filtered, and the filtrate was concentrated under reduced pressure and cooled to −20 °C giving deep red needles. These were separated, washed with cold light petroleum, and dried *in vacuo* (0.2 g, 55%).

Reaction of (1) *with Sodium Tetrahydroborate.*—Pure (1) (0.3 g) and $Na[BH_4]$ (0.1 g) in dry tetrahydrofuran (thf) (50 cm^3) were stirred at 20 °C for 2.5 h under an argon atmosphere. The solvent was removed from the yellow solution under reduced pressure and the residue was extracted with light petroleum (100 cm^3). After filtration the filtrate was concentrated (to 20 cm^3) and cooled to −78 °C giving deep red crystals, which were separated, washed with light petroleum, and dried *in vacuo* (*ca.* 50%). A similar reaction occurred when $Na[BH_4]$ and thf were replaced by $Na[AlH_2(OCH_2CH_2OMe)_2]$ and benzene.

Bis[1,2-bis(diphenylphosphino)ethane](η-cyclopentadienyl)-molybdenum Hexafluorophosphate (11).—Pure (1) (1.5 g) and 1,2-bis(diphenylphosphino)ethane (5.0 g) in pure methanol (250 cm^3) were heated under reflux for 2 h. The resulting red solution was cooled, then treated with excess of aqueous ammonium hexafluorophosphate. Concentration under reduced pressure followed by addition of water (500 cm^3) gave an orange precipitate which was collected, washed with water and toluene, recrystallised from methanol, and dried *in vacuo* (4.3 g, 72%). The analogue [Mo(η-C_5H_5)(dppe)$_2$][BF_4] was similarly prepared by using sodium tetrafluoroborate instead of [NH_4][PF_6]. The tetrafluoroborate salt is the more soluble and therefore more convenient as a starting material.

Bis[1,2-*bis(diphenylphosphino)ethane*](*η-cyclopentadienyl*)-*molybdenum Bis(hexafluorophosphate)* (12).—Compound (11; A = PF_6) (0.1 g) was added with stirring to dichloromethane (20 cm^3) containing iodine (0.02 g). The solvent was removed from the resulting yellow solution under reduced pressure. The residue was extracted with acetone (15 cm^3) and treated with excess of aqueous [NH_4][PF_6] and then with distilled water. The yellow precipitate was collected, washed with water, and recrystallised from methanol–ethanol as yellow needles. These were washed with ethanol and dried *in vacuo* (*ca.* 60%).

Chloro(*η-cyclopentadienyl*)*dioxomolybdenum*.—Pure (1) (0.1 g) in chloroform (40 cm^3) gave a red solution which was then saturated with dry oxygen. The mixture was warmed to 65 °C and after a few min the solution became deep yellow. The solvent was removed under reduced pressure and the residue was extracted with carefully dried diethyl ether (100 cm^3). The extract was filtered, concentrated under reduced pressure to 10 cm^3, and then treated with light petroleum (2—3 cm^3). Slow evaporation of the solvent under reduced pressure gave pale yellow crystals which were collected and dried *in vacuo* (0.04 g, 48%). The compound was identified by comparison of the i.r. spectrum with that of an authentic sample.[10] The mass spectrum gave a parent-ion peak at *m*/*e* 230.

Dichloro(*η-cyclopentadienyl*)*oxomolybdenum*.—Pure (1) (0.2 g) was exposed to air for 2 d and then extracted with dry benzene. The filtered extract was concentrated giving dark brown crystals. These were collected, washed with light petroleum, and dried *in vacuo* (*ca.* 30%). The compound was identified by comparison of the i.r. and e.s.r. spectra with those of an authentic sample.[10]

(*Acetonitrile*)[1,2-*bis(diphenylphosphino)ethane*]*carbonyl*-(*η-cyclopentadienyl*)*molybdenum Hexafluorophosphate–Dichloromethane* (1/1) (15).—Compound (11; A = PF_6) (0.6 g) in acetonitrile (150 cm^3) at 80 °C was treated with carbon monoxide (1 atm). The solution rapidly turned from red to yellow and after 15 min it was cooled and the solvent was removed under reduced pressure. The residue was washed with toluene (30 cm^3) and diethyl ether (100 cm^3) and recrystallised from acetone–diethyl ether and then from dichloromethane giving yellow crystals (0.3 g, 60%)

[1,2-*Bis(diphenylphosphino)ethane*]*dicarbonyl*(*η-cyclopentadienyl*)*molybdenum Hexafluorophosphate* (18).—Compound (15) (0.05 g) in ethanol (30 cm^3) was maintained at 80 °C under carbon monoxide (1 atm) for 12 h. The solution was cooled giving yellow crystals which were collected, washed, and dried *in vacuo* (80%). The product was identified by comparison of the i.r. spectrum with that of an authentic sample.

[1,2-*Bis(diphenylphosphino)ethane*](*η-butadiene*)(*η-cyclopentadienyl*)*molybdenum Tetrafluoroborate* (20).—Compound (11; A = BF_4) (1.4 g) in acetonitrile (200 cm^3) was saturated with butadiene and heated to 80 °C. After 30 min the initial red solution became yellow and the solution was then cooled and the solvent was removed under reduced pressure. The residue was extracted with dichloromethane (200 cm^3) and the extract was concentrated, then placed on an alumina column made up in toluene. The column was washed with toluene then elution with acetone gave a yellow band which was collected. Excess of aqueous Na[BF_4] was added to the eluate and the solution was concentrated under reduced pressure giving a yellow solid. This was collected, washed twice with water, dried, and then extracted with dichloromethane (300 cm^3). Slow concentration of the filtered extract gave yellow crystals which were collected, washed, and dried *in vacuo* (0.7 g, 75%).

[1,2-*Bis(diphenylphosphino)ethane*](*η-cyclohexa*-1,3-*diene*)-(*η-cyclopentadienyl*)*molybdenum tetrafluoroborate–dichloromethane*(1/1) (19) was obtained (*ca.* 75%) in an essentially similar manner to that used for (20) but using cyclohexa-1,3-diene (2 cm^3) instead of butadiene. The compound could be recrystallised from liquid sulphur dioxide giving the SO_2 adduct.

[1,2-*Bis(diphenylphosphino)ethane*](*but*-2-*yne*)(*η-cyclopentadienyl*)*molybdenum Tetrafluoroborate* (16).—Compound (11; A = BF_4) (0.7 g) and but-2-yne (1.3 cm^3) in acetonitrile (100 cm^3) were warmed to 80 °C. The initially red solution became green after 1 h. The mixture was cooled and the solvent was removed under reduced pressure. The residue was extracted in dichloromethane and the extract was placed on an alumina column made up in toluene. The column was washed with toluene and then elution with acetonitrile gave a green band which was collected. The solvent was removed from the eluate and the residue was extracted with acetone (150 cm^3). Excess of aqueous Na[BF_4] was added to the extract followed by water (50 cm^3). The resulting green precipitate was collected, washed with water, then dried. Recrystallisation from acetone–ethanol gave green crystals (0.3 g, 64%).

[1,2-*Bis(diphenylphosphino)ethane*](*η-cyclopentadienyl*)(*diphenylacetylene*)*molybdenum tetrafluoroborate* (17) was prepared (*ca.* 60%) in the same manner as (16) using diphenylacetylene instead of but-2-yne.

(*η-Cyclo-octatetraene*)(*η-cyclopentadienyl*)*molybdenum Hexafluorophosphate* (10).—Pure (1) (1.6 g) and Tl[PF_6] (5 g) in acetone (200 cm^3) were shaken for 2 h. After filtration, cyclo-octatetraene (3.0 cm^3) was added and the mixture was warmed to 80 °C. After 1 h the light green solution was cooled, filtered, and concentrated under reduced pressure to 50 cm^3. Ethanol (100 cm^3) was added and the mixture was concentrated further to *ca.* 30 cm^3. Crystals separated which were collected, washed, and recrystallised (1.4 g, 60%) from acetone–ethanol in the presence of cyclo-octatetraene (1 cm^3).

(1—6-*η-Cyclo-octatetraene*)(*η-cyclopentadienyl*)(*triphenylphosphine*)*molybdenum Hexafluorophosphate* (13).—Compound (10) (0.23 g) and triphenylphosphine (0.15 g) in acetone (40 cm^3) were warmed to reflux during which time the solution became orange. The solution was cooled and concentrated to 10 cm^3 and toluene (30 cm^3) was added. Orange-red crystals separated slowly (2 h) and further concentration of the mother liquor gave more orange-red crystals. The crystals were collected, washed with toluene, recrystallised from acetone–ethanol, and washed and dried as before (0.17 g, 45%).

Carbonyl(1—6-*η-cyclo-octatetraene*)(*η-cyclopentadienyl*)-*molybdenum Hexafluorophosphate* (13).—Compound (10) (0.2 g) in acetone (25 cm^3) was treated with carbon monoxide

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[10] M. Cousins and M. L. H. Green, *J. Chem. Soc.* (*A*), 1969, 16.

at 1 atm for a few minutes. The initially green solution rapidly became orange. Ethanol was added (50 cm^3) and the solution was filtered and concentrated giving orange crystals which were collected and dried as before (*ca.* 60%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*](1—4-η-*cyclo-octatetraene*)(η-*cyclopentadienyl*)*molybdenum Hexafluorophosphate* (14).—Compound (10) (0.20 g) and dppe (0.2 g) in acetone (70 cm^3) were heated under reflux for 20 min. The solvent was removed from the resulting wine-red solution under reduced pressure and the residue was extracted in the minimum of dichloromethane. The extract was placed on an alumina column made up in toluene. The column was washed with toluene and then a red band was eluted using acetone–diethyl ether (1 : 3). The red eluate was collected and the solvent was removed under reduced pressure. The residue was dissolved in acetone (10 cm^3) and then ethanol (30 cm^3) was added. After concentration, red crystals slowly separated (10 h). These were collected, washed with diethyl ether, and dried *in vacuo* (0.31 g, 79%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*](η-*cyclopentadienyl*)(η-3-*methylallyl*)*molybdenum* (21) (*Two Isomers*).—A suspension of the compound [Mo(η-C_5H_5)(dppe)(C_4H_6)][PF_6] (0.5 g) in thf (50 cm^3) was treated with Na[$AlH_2(OCH_2CH_2OMe)_2$] (70% in benzene, 0.5 cm^3) and the mixture was stirred at 50 °C. The yellow starting product dissolved giving a red solution. This was cooled to 0 °C and water (2 cm^3) was added slowly. The solution became orange. The solvent was removed under reduced pressure and the residue was washed with water and then extracted with benzene (3 × 20 cm^3). The benzene extract was washed with water and then the benzene was removed under reduced pressure. The dry residue was redissolved in benzene (20 cm^3), the extract was filtered, and light petroleum (50 cm^3, b.p. 100—120 °C) was added. Slow concentration under reduced pressure gave a cloudy solution which was left overnight. Orange crystals separated which were collected and dried *in vacuo*. The compound recrystallised from benzene–light petroleum giving the less-soluble isomer. The mother liquor was removed from the initial crystallisation and the residue was extracted with hexane. Careful fractional crystallisation by concentration of the solution gave the more-soluble isomer in an almost pure state (^{1}H n.m.r.).

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