η^3- and η^7-Cycloheptatrienyltungsten Chemistry: Synthesis of $[W(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(PMe_3)_2]$ and $[W(\eta\text{-}C_7H_7)(\eta^3\text{-}C_7H_{11})(PMe_3)]$

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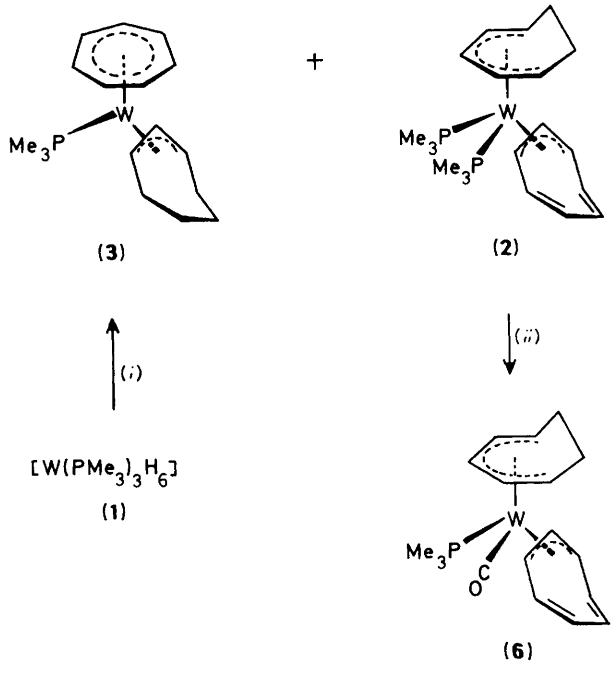
The reaction of $[W(PMe_3)_3H_6]$ with cycloheptatriene at 80 °C gives the compounds $[W(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(PMe_3)_2]$ and $[W(\eta\text{-}C_7H_7)(\eta^3\text{-}C_7H_{11})(PMe_3)]$ in moderate yields. $[W(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(PMe_3)_2]$ reacts with carbon monoxide giving $[W(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(PMe_3)(CO)]$, both of which have been characterised using two-dimensional n.m.r. spectroscopy.

Although the chemistry of η-cycloheptatrienyl-chromium and -molybdenum compounds is well developed,[1] the chemistry of η-cycloheptatrienyltungsten compounds is relatively unexplored.[2] We have shown that the readily available tungsten polyhydride complex $[W(PMe_3)_3H_6]$ (**1**) reacts with dienes to give compounds of the general formula $[W(\eta\text{-diene})(PMe_3)_3H_2]$.[3] Here we describe a study of the reaction of (**1**) with cycloheptatriene as a synthetic route to η-cycloheptatrienyltungsten complexes.



Scheme. (*i*) Cycloheptatriene in light petroleum (b.p. 100—120 °C) at 80 °C for 9 d, (*ii*) carbon monoxide (202 650 Pa) in light petroleum (b.p. 40—60 °C) at 50 °C for 4 d

Results and Discussion

Treatment of $[W(PMe_3)_3H_6]$ (**1**) with cycloheptatriene at 80 °C for 9 d gave, after crystallisation from pentane, a yellow crystalline solid. The ^1H n.m.r. spectrum of this product showed the presence of three compounds. Extraction of this mixture with cold pentane (*ca.* −20 °C) selected the more soluble product, $[W(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(PMe_3)_2]$ (**2**), which was isolated as yellow crystals in 20% yield. The less soluble residues were recrystallised from pentane to give $[W(\eta\text{-}C_7H_7)(\eta^3\text{-}C_7H_{11})(PMe_3)]$ (**3**) as yellow crystals in 18% yield. The third product, (**4**), was not isolated as a pure compound. The structures proposed for (**2**) and (**3**) are shown in the Scheme and characterising data are summarised in the Table.

The ^1H n.m.r. spectrum of (**3**) shows doublets due to the η-C_7H_7 [δ 4.65, *J*(P–H) 2 Hz] and the PMe_3 ligands [δ 0.55, *J*(P–H) 8 Hz]. The methylene hydrogens of the η^3-C_7H_{11} ligand are observed as four 2 H multiplets at δ 3.45, 2.22, 1.40, and 1.30. This is clearly consistent with the presence of a plane of symmetry in the molecule in solution, as shown in the Scheme.

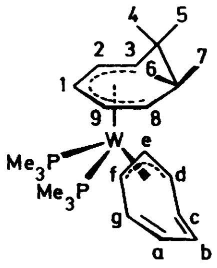
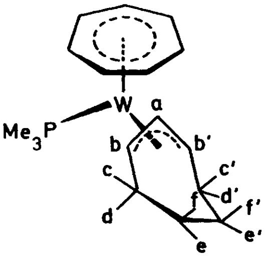
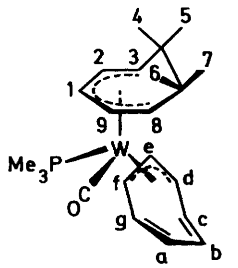
The room-temperature ^1H n.m.r. spectrum of (**2**) showed the molecule to be fluxional. The slow exchange limit spectrum, which was observed at −45 °C, showed that the molecule is asymmetric. The low-temperature spectrum was assigned by means of a [^1H–^1H]-COSY two-dimensional n.m.r. spectrum which is shown in Figure 1. The presence of an η^3-C_7H_7 ligand was inferred from the four 1 H resonances assigned to H^a, H^b, H^c, and H^g in the region normally observed for unco-ordinated olefinic hydrogens. The ^1H–^1H connectivities were deduced by noting the scalar coupling between H^g and H^f, and between H^c and H^d. The resonances due to the η^5-C_7H_9 ligand were assigned by assuming that the strongest couplings are between the methylene hydrogens H^4, H^5, H^6, and H^7, and that the *endo* hydrogens would occur in the higher field region. The asymmetry of compound (**2**) on the n.m.r. time-scale most likely arises from the presence of a high barrier to rotation of the η^5-cycloheptadienyl ligand giving a ground-state structure which does not have a plane of symmetry. High barriers to the rotation of η^5-dienyl ligands have been observed in the compounds $[M(\eta^5\text{-}C_6H_7)(dmpe)(\eta\text{-}C_3H_5)]$,[4] $[Mo(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(dmpe)]$,[5] and $[Mo(\eta^5\text{-}C_6H_7)(dmpe)(PMe_3)(\eta\text{-}C_2H_4)]PF_6$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[6] We therefore propose the structure for (**2**) shown in the Scheme.

The resonances due to the η^3-C_7H_7 ligand in the ^1H n.m.r. spectrum of (**2**) broaden as the temperature is increased from −45 °C and disappear into the baseline at 85 °C. However, the fast exchange limit spectrum was not attained. The resonances due to the η^5-C_7H_9 and PMe_3 ligands did not change significantly with temperature. The ^{31}P-{^1H} n.m.r. spectrum of (**2**) at room temperature shows two doublets with *J*(P–P) 18 Hz.

The ^1H and ^{31}P-{^1H} n.m.r. spectra of the third product (**4**) suggest that the molecule contains the '$W(PMe_3)H$' moiety, while the ^{13}C–^1H DEPT n.m.r. spectrum shows the presence of nine methine and five methylene carbons. However, assignment of the ^1H n.m.r. spectrum was not possible even with the help of a 500 MHz [^1H–^1H]-COSY two-dimensional n.m.r. spectrum because of extensive overlap of resonances in the region δ 2.5—1, and the presence of small amounts of (**2**) and (**3**).

The reaction between (**1**) and cycloheptatriene was monitored by ^1H n.m.r. spectroscopy. After one day at 80 °C, the ^1H

Table. Analytical and n.m.r. data[a]

Compound, colour, and analysis (%)	^{1}H	^{31}P and ^{13}C
(2) $[W(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(PMe_3)_2]$ yellow C, 49.0 (49.1); H, 6.8 (6.9) *m/e* 489 $[M^+]$  	-45 °C: 6.45 (m, 1 H, H^g), 6.28 (m, 1 H, H^c), 5.75 (m, 2 H, H^a and H^b), 2.90 (m, 1 H, H^f), 2.36 (m, obscured, 1 H, H^f), 0.78 (m, 1 H, H^d), 5.40 [t, 1 H, $J(H^1\text{–}H^2) = J(H^1\text{–}H^9)$ 9, H^1], 4.33 [apparent q, 1 H, $J(H^2\text{–}H^1) = J(H^2\text{–}H^3)$ 9, H^2], 3.21 [m, 1 H, $J_d(H^8\text{–}H^9)$ 9, H^8], 2.36 [br m, 2 H, H^5 and H^7], 1.98 [apparent q, 1 H, $J_d(H^3\text{–}H^2)$ 9, H^3], 1.67 (m, 1 H, H^4), 1.49 (m, 1 H, H^6), 1.21 [t, 1 H, $J(H^9\text{–}H^1) = J(H^9\text{–}H^8)$ 9, H^9]	^{31}P-{^{1}H}: 46.65 [d, 1 P, J(P–P) 18, $J(^{183}W\text{–}P)$ 230], 34.8 [d, 1 P, J(P–P) 18, $J(^{183}W\text{–}P)$ 203] ^{13}C (-50 °C):[b] 117.2 (d, η-CH of $\eta^5\text{-}C_7H_9$), 101.6 (d, η-CH of $\eta^5\text{-}C_7H_9$), 84.9 (d, η-CH of $\eta^5\text{-}C_7H_9$), 65.6 [dt, J_t(P–C) 8, η-CH of $\eta^5\text{-}C_7H_9$], 56.4 [dt, J_t(P–C) 34, η-CH of $\eta^5\text{-}C_7H_9$], 32.7 [dt, J_d(P–C) 4, CH_2 of $\eta^5\text{-}C_7H_9$], 32.5 (t, CH_2 of $\eta^5\text{-}C_7H_9$), 140.5 (d, unco-ordinated CH of C_7H_7), 138.5 (d, unco-ordinated CH of C_7H_7), 113.0 (d, unco-ordinated CH of C_7H_7), 111.8 (d, unco-ordinated CH of C_7H_7), 46.5 (d, η-CH of C_7H_7), 41.6 (d, η-CH of C_7H_7), 32.8 (d, η-CH of C_7H_7), 19.3 [d, J(P–C) 23, PMe_3], 17.5 [d, J(P–C) 23, PMe_3]
(3) $[W(\eta\text{-}C_7H_7)(\eta^3\text{-}C_7H_{11})(PMe_3)]$ yellow C, 45.8 (45.7); H, 6.0 (6.1) *m/e* 446 $[M^+]$  	[$^2H_6$]benzene: 4.65 [d, 7 H, J(P–H) 2, $J(^{183}W\text{–}H)$ *ca.* 4, $\eta^7\text{-}C_7H_7$], 3.45 (m, 2 H, $H^{c,c'}$ or $H^{d,d'}$), 2.38 (m, ABB′ spin system, 3 H, H^a, H^b and $H^{b'}$), 2.22 (m, 2 H, $H^{d,d'}$ or $H^{c,c'}$), 1.40 (m, 2 H, $H^{e,e'}$ or $H^{f,f'}$), 1.30 (m, 2 H, $H^{f,f'}$ or $H^{e,e'}$), 0.55 [d, 9 H, J(P–H) 8, PMe_3]	^{31}P-{^{1}H} n.m.r. ([$^2H_6$]benzene): 30.5 (s, PMe_3)
(6) $[W(\eta^5\text{-}C_7H_9)(\eta^3\text{-}C_7H_7)(PMe_3)(CO)]$ yellow C, 49.6 (49.5); H, 5.6 (5.6)[c]  	500 MHz, -20 °C: 5.99 [dd, 1 H, $J(H^c\text{–}H^b)$ 11, $J(H^c\text{–}H^d)$ 8, H^c], 5.89 [dd, 1 H, $J(H^g\text{–}H^a)$ 11, $J(H^g\text{–}H^f)$ 8, H^g], 5.66 [dd, 1 H, $J(H^b\text{–}H^c)$ 11, $J(H^b\text{–}H^a)$ 7.5, H^b], 5.35 [dd, 1 H, $J(H^a\text{–}H^b)$ 7.5, $J(H^a\text{–}H^g)$ 11, H^a], 3.30 [ddd, 1 H, $J(H^d\text{–}H^f)$ 3, $J(H^d\text{–}H^c)$ 8, $J(H^d\text{–}H^e)$ 8.7, H^d], 2.72 [dddd, 1 H, $J(H^f\text{–}H^g)$ 8, $J(H^f\text{–}H^e)$ 8.7, $J(H^f\text{–}H^d)$ 3, $J(H^f\text{–}P)$ 3.2, H^f], 1.36 [dt, 1 H, $J(H^e\text{–}P)$ 3.3, $J(H^e\text{–}H^d) = J(H^e\text{–}H^f)$ 8.7, H^e], 5.41 [tt, 1 H, $J(H^1\text{–}H^2) = J(H^1\text{–}H^9)$ 13, $J(H^1\text{–}H^8) = 1.70$, $J(H^1\text{–}H^3)$ 1.7, H^1], 4.84 [dd, 1 H, $J(H^2\text{–}H^3)$ 6.5, $J(H^2\text{–}H^1)$ 13, H^2], 3.65 [m, 1 H, $J(H^8\text{–}H^9)$ 13, H^8], 2.85 [m, 1 H, $J(H^3\text{–}H^2)$ 6.5, H^3], 2.03 (m, 2 H, H^5, H^7), 1.86 [tm, 1 H, $J(H^9\text{–}H^1) = J(H^9\text{–}H^8)$ 13, H^9], 1.60 (m, 1 H, H^6), 1.4 (m, 1 H, H^4)	

[a] Calculated analyses values given in parentheses. N.m.r. data given as: chemical shift (δ/p.p.m.), multiplicity, relative intensity, J in Hz, assignment; all spectra were obtained in [$^2H_8$]toluene and at room temperature, ^{1}H at 300 MHz, ^{31}P at 101.26 MHz, and ^{13}C at 62.89 MHz, unless otherwise stated. [b] The multiplicities were determined by a ^{13}C–^{1}H DEPT experiment. No coupling constants were obtained. [c] ν(C–O) at 1 996 cm^{-1} (Nujol mull).

n.m.r. spectrum of the reaction mixture revealed the absence of starting material and, in addition to the compounds (2), (3), and (4), a tungsten phosphine hydride complex, (5), was also present. The hydride ligands due to (5), which was not isolated, were observed as broad resonances at δ −1.70 and −5.00. As the reaction proceeded, the concentration of (5) decreased while those of (2), (3), and (4) increased but their relative concentrations remained constant. After 9 d (5) was not detected. Compound (5) is therefore a kinetic product of the reaction and reacts further to form the observed products.

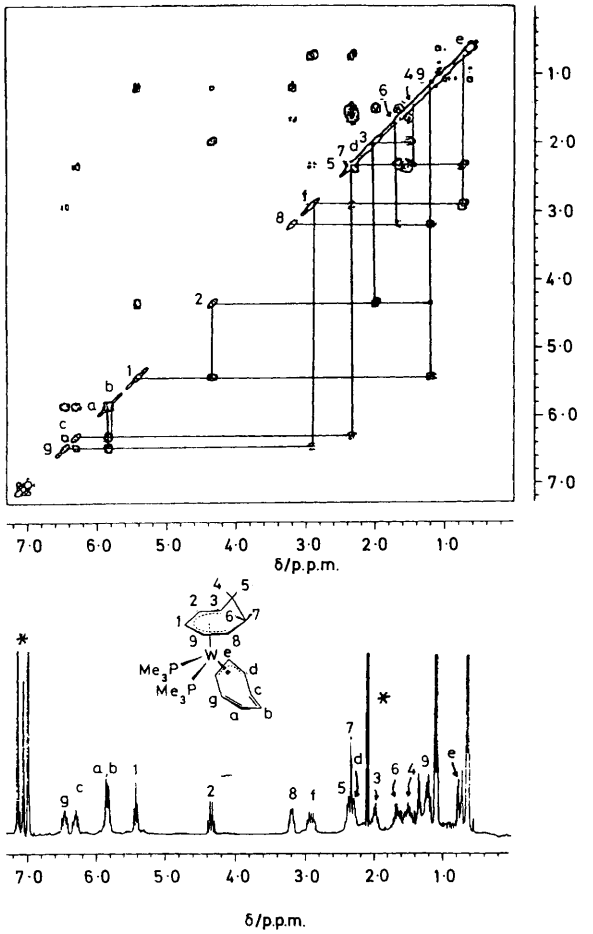


Figure 1. 250-MHz [^{1}H-^{1}H]-COSY-45 two-dimensional n.m.r. spectrum of (**2**) in [^{2}H$_8$]toluene at −45 °C. Asterisks denote the solvent resonances

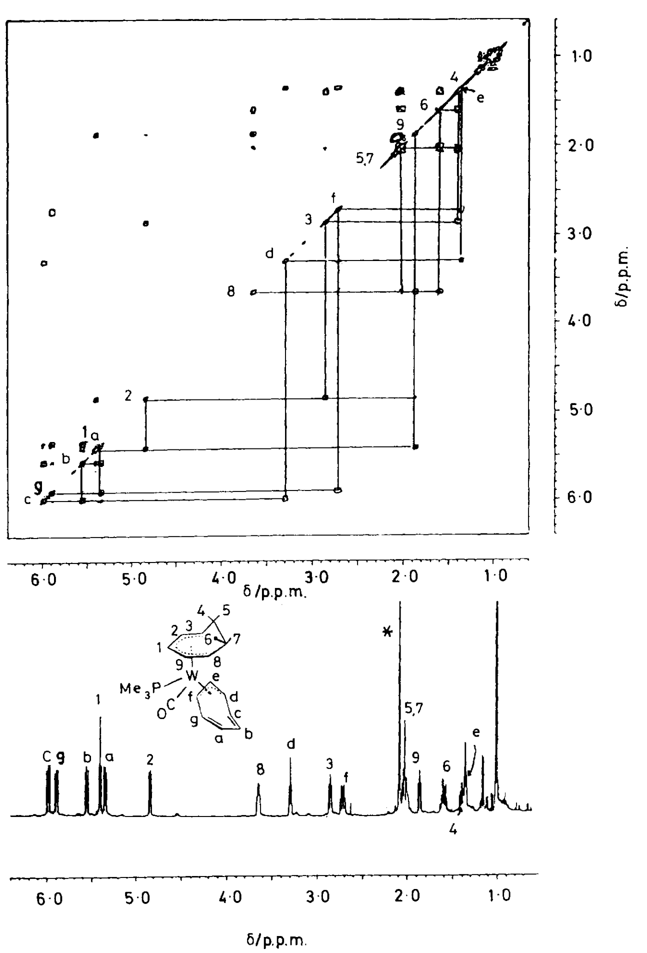


Figure 2. 500-MHz [^{1}H-^{1}H]-COSY-45 two-dimensional n.m.r. spectrum of (**6**) in [^{2}H$_8$]toluene at −20 °C. Asterisk denotes the solvent resonance

Treatment of (**2**) with carbon monoxide results in displacement of a PMe$_3$ ligand rather than the C$_7$ ligands to give yellow crystals of the new compound [W(η^5-C$_7$H$_9$)(η^3-C$_7$H$_7$)(PMe$_3$)(CO)], (**6**). The ν(C–O) stretching mode is observed at 1 996 cm^{-1}. Compound (**6**) is fluxional and the ^{1}H n.m.r. spectrum at −20 °C is complex. However, complete assignment of the resonances was possible using a [^{1}H–^{1}H]-COSY two-dimensional n.m.r. spectrum which is shown in Figure 2. The assignment is straightforward and follows the arguments used for (**2**).

Experimental

General Techniques.—All preparations, manipulations, and reactions were carried out under an inert atmosphere of dinitrogen (< 10 p.p.m. oxygen, <20 p.p.m. water) using standard Schlenk-tube and vacuum line techniques, or in a dry box. Dinitrogen was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Solvents were pre-dried over activated molecular sieves and then distilled from sodium (light petroleum, b.p. 100—120 °C) or sodium–potassium alloy (pentane), under an inert atmosphere of dinitrogen before use. Deuteriated solvents for n.m.r. samples were stored in ampoules over activated molecular sieves and transferred by vacuum distillation. Celite 545 filtration aid (Koch-Light) was pre-dried in an oven at 80 °C before use. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 1510 FT interferometer. Hydrogen-1 n.m.r. spectra were determined at 300 or 500 MHz using Bruker WH-300 or AM-500 spectrometers. Carbon-13 and ^{31}P n.m.r. spectra were determined at 62.89 and 101.26 MHz, respectively, using a Bruker AM-250 spectrometer. Two-dimensional n.m.r. spectra were determined at 250 or 500 MHz using Bruker AM250 or AM500 spectrometers and processed with standard Bruker software. Spectra were referenced internally using the residual solvent (^{1}H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ = 0 p.p.m.), or externally using P(O)(OMe)$_3$ in D$_2$O (^{31}P). All chemical shifts are quoted in δ (p.p.m.) and coupling constants are in Hz.

Reaction of [W(PMe$_3$)$_3$H$_6$] *with Cycloheptatriene*.—The compound [W(PMe$_3$)$_3$H$_6$] (**1**) was synthesised as previously described.[7] [W(PMe$_3$)$_3$H$_6$] (1.0 g, 2.39 mmol) in light petroleum (b.p. 100—120 °C, 40 cm^3) in a thick-walled glass ampoule equipped with a Teflon stopcock was treated with freshly distilled cycloheptatriene (2 cm^3) and the mixture stirred at 80 °C for 9 d. The mixture was filtered and the volatile components removed from the filtrate under reduced pressure at room temperature (r.t.), giving a brown oil. Volatile organic residues were sublimed [r.t., 10^{-4} mbar (10^{-2} Pa)] onto a liquid-nitrogen cooled probe for 8 h and discarded. The brown residue, still oily, was extracted into pentane (20 cm^3) and filtered through a Celite bed. The yellow filtrate was concentrated to *ca.* 8 cm^3 giving a viscous solution which was cooled to −80 °C. Yellow crystals formed over 1 d. The crystals were separated by filtration and shown to consist of a *ca.* 1:1 mixture of [W(η^5-C_7H_9)(η^3-C_7H_7)(PMe_3)$_2$] (**2**), [W(η-C_7H_7)(η^3-C_7H_{11})(PMe_3)] (**3**), and traces of the third, uncharacterised product (**4**) by their ^{1}H n.m.r. spectrum ([$^2H_6$]benzene). Total yield, *ca.* 0.9 g.

Separation of Compounds (**2**) *and* (**3**).—The mixture of (**2**), (**3**), and (**4**) was cooled to −20 °C and extracted with cold pentane (*ca.* −20 °C), and filtered. The filtrate was concentrated to *ca.* 5 cm^3 and cooled to −80 °C, whereupon yellow crystals formed over 1 d. Recrystallisation of these crystals gave pure [W(η^5-C_7H_9)(η^3-C_7H_7)(PMe_3)$_2$] (**2**), yield 0.40 g (20%). The crystals, insoluble in cold pentane, were extracted into pentane (r.t., 20 cm^3), and filtered. The yellow filtrate was concentrated to *ca.* 5 cm^3 and cooled to −80 °C. Yellow crystals formed over 1 d. These crystals were isolated and recrystallised giving pure [W(η-C_7H_7)(η^3-C_7H_{11})(PMe_3)] (**3**), yield 0.36 g (18%).

Reaction of [W(η^5-C_7H_9)(η^3-C_7H_7)(PMe_3)$_2$] (**2**) *with Carbon Monoxide.*—The compound [W(η^5-C_7H_9)(η^3-C_7H_7)(PMe_3)$_2$] (0.2 g, 0.4 mmol) in light petroleum (b.p. 40—60 °C, 20 cm^3) in a thick-walled glass ampoule equipped with a Teflon stopcock was treated with carbon monoxide (202 650 Pa) and stirred at 50 °C for 4 d. The solution was filtered and volatile components removed from the filtrate under reduced pressure at r.t. giving an orange oil. The oil was extracted into pentane (15 cm^3) and filtered. The yellow filtrate was concentrated to *ca.* 8 cm^3 and cooled to −80 °C. Yellow crystals formed over 3 d. The crystals were separated by filtration and washed with cold pentane at −78 °C. Yield: 130 mg, 72%.

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References

1 J. R. Blackborrow and D. Y. Young, 'Metal Vapour Synthesis in Organometallic Chemistry,' Springer-Verlag, Berlin, 1979; F. G. N. Cloke, J. C. Green, M. L. H. Green, and C. P. Morley, *J. Chem. Soc., Chem. Commun.*, 1985, 945; M. L. H. Green and P. A. Newman, *ibid.*, 1984, 816; R. C. Tovey, D. Phil. Thesis, University of Oxford, 1987; E. F. Isaacs and W. A. G. Graham, *J. Organomet. Chem.*, 1976, **120**, 407; E. F. Ashworth, J. C. Green, M. L. H. Green, J. Knight, R. B. A. Pardy, and N. J. Wainwright, *J. Chem. Soc., Dalton Trans.*, 1977, 1693.

2 R. Breeze, S. Endud, and M. W. Whiteley, *J. Organomet. Chem.*, 1986, **302**, 371; R. Breeze, A. Ricalton, and M. W. Whiteley, *ibid.*, 1987, **327**, C29.

3 M. L. H. Green and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1985, 771.

4 M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 2177.

5 M. L. H. Green and P. A. Newman, unpublished work.

6 H. E. Bunting, M. L. H. Green, and P. A. Newman, *J. Chem. Soc., Dalton Trans.*, 1988, 557.

7 D. Lyons and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1985, 587.

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