An Improved Synthesis and Some Reactions of a Hydrido-bridged Ruthenium–Manganese Complex†

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An improved synthesis of the heterodimetallic complex $[RuMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_5]$ **1** is described and the reactions of this complex with alkynes RC≡CR (R = Ph, H or CO_2Me) and with tertiary phosphines have been studied. Complexes containing μ-alkenyl ligands are obtained from the reaction of **1** with alkynes and the crystal structure of one of these, $[RuMn\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4]$ has been determined by X-ray analysis; the alkenyl ligand is σ bonded to Ru and π bonded to Mn, while the PPh_2 group asymmetrically bridges the Ru–Mn bond [2.729(2) Å]. Tertiary phosphines react with **1** to give complexes which are monosubstituted at the manganese atom.

The reactions of phosphido-bridged heterodimetallic complexes with phosphines[1,2] and alkynes[3] show a surprising diversity, although there have been relatively few studies on the corresponding reactions of complexes of this type which also contain a μ-hydrido ligand.[4] We previously reported the reactions of the molybdenum–manganese complex, $[MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_6]$, with phosphines[4d] and alkynes[4b,c] and have recently synthesised a related ruthenium–manganese complex $[RuMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_5]$ **1**, as a low-yield (*ca.* 7%) and not easily separable product of the photolytic reaction of $[RuMn(\eta^5\text{-}C_5H_5)(CO)_7]$ with PPh_2H.[5]

In order to be able to compare the reactivity of **1** with that of the molybdenum–manganese complex above we have now developed a more convenient and higher-yield synthesis of **1** which we report in this paper together with some of its reactions.

Results and Discussion

(*a*) *Synthesis of* $[RuMn(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_5]$ **1**.—The new complex $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_2H)Cl]$ **2** was prepared *in situ* by a similar method to that used for $[Ru(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Cl]$.[6] Reaction of crude **2** with $Na[Mn(CO)_5]$ in tetrahydrofuran (thf) at 328 K gave **1** in 31% yield based on $[Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl]$. The reaction presumably proceeds *via* nucleophilic attack of $[Mn(CO)_5]^-$ on **2** to give $[(HPh_2P)(OC)(\eta^5\text{-}C_5H_5)RuMn(CO)_5]$ although no intermediate species of this formula could be isolated from the reaction mixture. It seems likely that the dissociation of a carbonyl group from manganese and oxidative addition of a P–H bond is too rapid to allow this.

(*b*) *Reaction of Complex* **1** *with Alkynes*.—Reaction of complex **1** with PhC≡CPh under UV irradiation and RC≡CR (R = H or CO_2Me) under thermolysis gave the μ-alkenyl complexes $[RuMn\{\mu\text{-}\sigma{:}\eta^2\text{-}C(R){=}CHR\}(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4]$ (R = Ph **3a**, H **3b** or CO_2Me **3c** in yields of *ca.* 20–50%. Complexes **3** have been characterised spectroscopically (see Experimental section) and, in addition, the solid state structure of **3a** has been determined by a single-crystal X-ray diffraction study. Suitable crystals of **3a** were grown by slow evaporation of a dichloromethane–hexane solution.

The molecular structure of complex **3a** is shown in Fig. 1 and Table 1 lists selected bond lengths and angles. The two metal atoms are bridged by a phosphido and an alkenyl ligand. The ruthenium atom is additionally ligated by a cyclopentadienyl and a carbonyl ligand, while the manganese is ligated by three carbonyls.

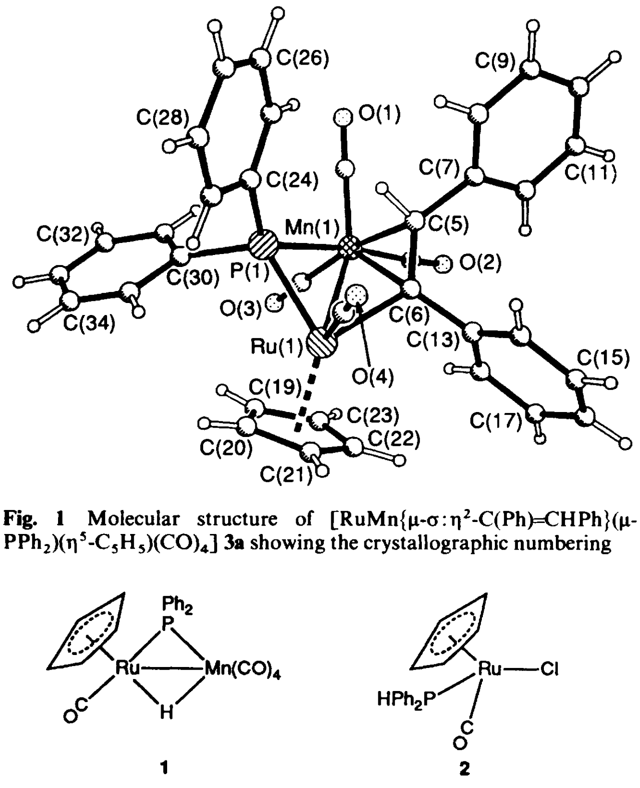
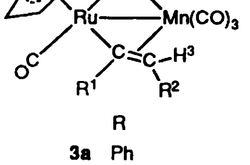
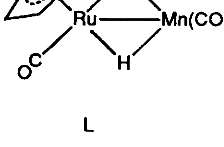


Fig. 1 Molecular structure of $[RuMn\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(\eta^5\text{-}C_5H_5)(CO)_4]$ **3a** showing the crystallographic numbering



1



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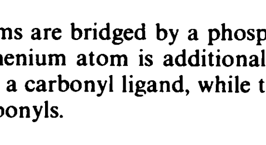
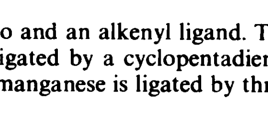


	R
3a	Ph
3b	H
3c	CO_2Me



	L
4a	$P(C_6H_4Me\text{-}4)_3$
4b	$P(OMe)_3$
4c	$PPh_2C{\equiv}CPh$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Selected bond lengths (Å) and angles (°) for complex **3a**

Ru–Mn	2.729(2)	Ru–P	2.310(3)
Ru–C(4)	1.858(16)	Ru–C(6)	2.107(12)
Ru–C(19)	2.212(12)	Ru–C(20)	2.227(12)
Ru–C(21)	2.252(15)	Ru–C(22)	2.250(14)
Ru–C(23)	2.254(14)	Mn–P	2.251(3)
Mn–C(1)	1.763(17)	Mn–C(2)	2.804(14)
Mn–C(3)	1.754(18)	Mn–C(5)	2.202(12)
Mn–C(6)	2.049(12)	C(5)–C(6)	1.395(16)
C(5)–C(7)	1.493(16)	C(16)–C(13)	1.512(16)
P–Ru–Mn	52.3(1)	C(6)–Ru–Mn	48.0(3)
C(6)–Ru–P	88.1(3)	P–Mn–Ru	54.3(1)
C(5)–Mn–Ru	75.2(3)	C(5)–Mn–P	87.0(3)
C(6)–Mn–Ru	49.9(3)	C(6)–Mn–P	91.2(3)
Mn–P–Ru	73.5(1)	C(6)–C(5)–Mn	65.0(7)
C(7)–C(5)–Mn	123.7(8)	C(7)–C(5)–C(6)	128.3(11)
Mn–C(6)–Ru	82.1(4)	C(5)–C(6)–Ru	118.9(9)
C(5)–C(6)–Mn	76.9(7)	C(13)–C(6)–Ru	114.6(8)
C(13)–C(6)–Mn	132.9(9)	C(13)–C(6)–C(5)	121.7(10)

The alkenyl group is σ-bonded to Ru *via* C(6) [2.107(12) Å] and asymmetrically π-bonded to Mn with Mn–C(6) and Mn–C(5) bond lengths of 2.049(12) and 2.202(12) Å, respectively. The C(5)–C(6) bond length of 1.395(16) Å is typical for such double bonds in dinuclear bridging alkenyl complexes.[7] The phenyl substituents of the alkenyl ligand adopt a pseudo-*cis* orientation as in [Mn$_2${μ-σ:η^2-C(Ph)=CHPh}(μ-PPh$_2$)(CO)$_6$(CNBu^t)].[7a] The Ru–Mn bond length in **3a** of 2.729(2) Å is *ca.* 0.2 Å shorter than that found in [RuMn(μ-H)(μ-PPh$_2$)(η^5-C$_5$H$_5$)(CO)$_5$].[5] A similar shortening in the metal–metal bond lengths was noted on going from [Mn$_2$(μ-H)(μ-PPh$_2$)(CO)$_8$] to [Mn$_2$(μ-σ:η^2-CH=CH$_2$)(μ-PPh$_2$)(CO)$_7$][7b] and this may be correlated in both cases with the lengthening effect on metal–metal bonds of bridging hydride ligands.[8] Although **3a** obeys the effective atomic number rule overall, each metal atom obeys the 18-electron rule individually only if the phosphido group is considered to donate two electrons to the manganese atom and one to the ruthenium atom. This electron imbalance is reflected in the Mn–P distance which is *ca.* 0.06 Å shorter than the Ru–P distance whereas in [RuMn(μ-H)(μ-PPh$_2$)(η^5-C$_5$H$_5$)(CO)$_5$][5] the Mn–P and Ru–P bond distances are virtually identical.

The ^{1}H and ^{31}P NMR and IR spectra of the complexes **3a**–**3c** suggest that they possess similar structures in solution to that observed for **3a** in the solid state. In heterodimetallic complexes containing bridging alkenyl ligands there is generally a strong preference as to which metal is σ- and which is π-bonded to the alkenyl ligand[7d,9] and there was no evidence in the case of the complexes **3** for the presence of more than one isomer in solution.

The formation of μ-alkenyl complexes in the reaction of **1** with alkynes parallels the reaction of the homodimetallic dimanganese complex [Mn$_2$(μ-H)(μ-PPh$_2$)(CO)$_8$] with alkynes[7b] but the heterodimetallic complex [MoMn(μ-H)(μ-PPh$_2$)(η^5-C$_5$H$_5$)(CO)$_6$] does not react at all with PhC≡CPh[10] nor does it give simple μ-alkenyl complexes with other alkynes.[4b–d]

The μ-alkenyl ligands in the dimanganese complexes [Mn$_2${μ-σ:η^2-C(R)=CHR}(μ-PPh$_2$)(CO)$_7$] react with nucleophilic reagents such as CO, PPhMe$_2$, Bu^{t}NC or NaBH$_4$ to give a wide range of products,[7a] but **3a** is unreactive under similar conditions towards these reagents and towards LiAlH$_4$ (see Experimental section). This lower reactivity of **3a** relative to the μ-alkenyl dimanganese complexes may be steric in origin. Alternatively it may reflect a lower lability of the CO groups in the ruthenium–manganese complex which would inhibit nucleophilic attack at the metal centres, this being the initial mode of reaction of the dimanganese complexes.[7a]

(*c*) *Reaction of Complex* **1** *with Phosphines*.—The reaction of complex **1** with tertiary phosphines in toluene at 373 K gave the monosubstitution products [RuMn(μ-H)(μ-PPh$_2$)(η^5-C$_5$H$_5$)(CO)$_4$L] [L = P(C$_6$H$_4$Me-4)$_3$ **4a**, P(OMe)$_3$ **4b** or PPh$_2$C≡CPh **4c**]. This formulation is supported by the observation of molecular ion peaks in the mass spectra together with fragmentation peaks showing up to four carbonyl losses. The ^{1}H NMR spectra of **4** reveal in each case that a single isomer is present in solution, with the bridging hydride resonances showing coupling in the range 23–29 Hz to each of the phosphorus nuclei. Of the two resonances observed in the ^{31}P-{^{1}H} NMR spectrum of **4a** a sharp low-field signal at δ 32.2 is assigned to the μ-PPh$_2$ ligand, while a broader high-field signal at δ −77.2 is assigned to the phosphorus of the P(C$_6$H$_4$Me-4)$_3$ group. The breadth of the latter resonance is presumably due to coupling to the quadrupolar ^{55}Mn nucleus and suggests strongly that the P(C$_6$H$_4$Me-4)$_3$ ligand is attached to the manganese rather than the ruthenium atom. In contrast the ruthenium-co-ordinated PPh$_2$H ligand in [RuMn$_2$(μ-H)(μ-PPh$_2$)$_2$(η^5-C$_5$H$_5$)(CO)$_8$(PPh$_2$H)] gives rise to a sharp ^{31}P-{^{1}H} NMR signal.[5]

It was of course possible that PPh$_2$C≡CPh could have reacted with complex **1** *via* the alkyne function either in addition to[11,12] or instead of[12] the phosphine function. Phosphorus–carbon bond-cleavage reactions have also been reported with this ligand.[13,14] However the similarity of the spectroscopic properties of **4c** to those of **4a** and **4b** suggest that all three complexes have analogous structures.

Experimental

All reactions were carried out under a nitrogen atmosphere in N$_2$-saturated solvents distilled from the appropriate drying agent and stored over 4 Å molecular sieves. Ultraviolet irradiation was carried out in a glass photolysis vessel using a Hanovia 4 W low-pressure immersion lamp in a water-cooled quartz inner tube. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.25 mm layer of silica.

The instrumentation used to obtain spectroscopic data has been described previously.[5] Phosphorus-31 NMR chemical shifts are given relative to P(OMe)$_3$ with upfield shifts negative. All NMR spectra were recorded at 293 K. The complexes [Ru(η^5-C$_5$H$_5$)(CO)$_2$Cl][15] and Na[Mn(CO)$_5$][16] were prepared by the literature methods.

Preparation of [RuMn(μ-H)(μ-PPh$_2$)(η^5-C$_5$H$_5$)(CO)$_5$] **1**.—The complex [Ru(η^5-C$_5$H$_5$)(CO)$_2$Cl] (1.17 g, 4.5 mmol) was dissolved in heptane (100 cm^3) and PPh$_2$H (0.80 cm^3, 4.6 mmol) was added. The solution was refluxed for 16 h and then allowed to cool slowly before being placed in a freezer at −30 °C for 1 d. The supernatant liquor was then slowly decanted off to leave an orange precipitate which was washed with cold pentane and dried under vacuum to yield crude [Ru(η^5-C$_5$H$_5$)(CO)(PPh$_2$H)Cl] **2** [ν_{max}/cm^{-1}(CO)(CH$_2$Cl$_2$) at 1967s]. Complex **2** was used without further purification. A solution of Na[Mn(CO)$_5$] (1.70 g, 4.9 mmol) in thf (50 cm^3) was added to a solution of **2** in thf (50 cm^3). The mixture was heated at 328 K for 16 h. The solvent was removed on a rotary evaporator and the residue, after being dissolved in the minimum quantity of CH$_2$Cl$_2$, was adsorbed onto silica. The silica was pumped dry and added to the top of a 3 cm × 30 cm chromatography column (Kieselgel 60, 70–230 mesh). Elution with hexane–CH$_2$Cl$_2$ (3:1) gave orange crystalline complex **1** {0.76 g, 31% based on [Ru(η^5-C$_5$H$_5$)(CO)$_2$Cl]}.

Reactions of Complex **1** *with Alkynes*.—(*i*) PhC≡CPh. A solution of PhC≡CPh (0.078 g, 0.44 mmol) and complex **1** (0.040 g, 0.073 mmol) in toluene (60 cm^3) was irradiated with UV light for 15 h. After this time the colour of the solution had changed from orange to red. The solvent was removed on a rotary evaporator and the residue, after being dissolved in the minimum of CH$_2$Cl$_2$, was applied to the base of TLC plates. Elution with hexane–CH$_2$Cl$_2$ (3:1) gave purple [RuMn{μ-σ:η^2-C(Ph)=CHPh}(μ-PPh$_2$)(η^5-C$_5$H$_5$)(CO)$_4$] **3a** (0.017 g,

Table 2 Crystal data, data collection and processing parameters for complex **3a**

Formula	$C_{35}H_{26}MnO_4PRu$
M	697.54
Crystal system	Monoclinic
Space group	$P2_1/n$
Colour, habit	Red wedge-shaped block
Dimensions/mm	0.32 × 0.38 × 0.45
a/Å	9.865(4)
b/Å	10.734(6)
c/Å	29.848(26)
β/°	95.30(6)
U/Å^3	3147(4)
D_c/g cm^{-3}	1.472
Z	4
Diffractometer	Siemens R3m/V
Radiation	Mo-Kα (λ = 0.710 73 Å)
2θ range/°	5.0–45.0
F(000)	1408
T/K	290
Scan type	2θ–θ
Scan speed/° min^{-1}	Variable, 2.50–29.30 in ω
Scan range (ω)/°	0.90 plus Kα separation
Index ranges	$-10 \leqslant h \leqslant 10, 0 \leqslant k \leqslant 11, 0 \leqslant l \leqslant 32$
Reflections collected	4600
Independent reflections	4113 (R_{int} = 0.80%)
Observed reflections	3071 [$F > 5.0\sigma(F)$]
Absorption correction	Semiempirical
Transmission factors (maximum, minimum)	0.690, 0.558
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0020F^2$
R, R' (observed data)	0.070, 0.0770
Data to parameters ratio	8.0:1
Goodness of fit	1.84
Largest and mean Δ/σ	0.100, 0.024
Largest difference peak/e Å^{-3}	0.63
Largest difference hole/e Å^{-3}	−1.39

33%) (Found: C, 60.2; H, 3.60; P, 4.15. $C_{35}H_{26}MnO_4PRu$ requires C, 60.2; H, 3.70; P, 4.45%). Fast atom bombardment (FAB) mass spectrum: m/z 698 (M^+) and $M^+ - n$CO (n = 1–4): ν_{max}/cm^{-1}(CO)(hexane) at 2002m, 1983s, 1934m and 1918. NMR: ^{1}H (CD_2Cl_2), δ 8.0–6.5 (m, 20 H, Ph), 5.00 (s, 5 H, C_5H_5) and 3.31 [d, 1 H, ^3J(PH) 12.6 Hz, CPh=C*H*Ph]; ^{31}P ($CDCl_3$, ^{1}H-gated decoupled), δ 48.4 (s, μ-PPh_2).

(*ii*) HC≡CH. (*a*) A solution of complex **1** (0.040 g, 0.07 mmol) in toluene–hexane (1:1) (50 cm^3) was purged with HC≡CH and irradiated with UV light. After 12 h, spot TLC and IR spectroscopy showed only the presence of decomposition material together with traces of **1**.

(*b*) Complex **1** (0.040 g, 0.07 mmol) was dissolved in toluene (50 cm^3). The solution was heated to 353 K and HC≡CH slowly bubbled through for 15 h. Infrared spectral monitoring at this stage indicated that no new products were present. The solution was then refluxed for 3.5 h, after which IR spectroscopy showed that no starting material remained. The solvent was removed on a rotary evaporator and the product isolated by TLC using hexane–CH_2Cl_2 (3:1) as eluent, to give orange crystalline complex **3b** (0.008 g, 20%). FAB mass spectrum: m/z 546 (M^+) and $M^+ - n$CO (n = 1–4): ν_{max}/cm^{-1}(CO)(hexane) at 2006m, 1988s, 1946w and 1924s. NMR: ^{1}H ($CDCl_3$), δ 10.19 [ddd, 1 H, ^3J(H^{1}H^3) 12.8, ^3JH^{1}H^2) 7.7, ^3J(PH^1) 2.9, H^1], 7.9–7.3 (m, 10 H, Ph), 5.28 (s, 5 H, C_5H_5), 3.24 [dd, 1 H, ^3J(PH^2) 7.6, H^2] and 2.87 [dd, 1 H, ^3J(PH^3) 9.7 Hz, H^3]; ^{31}P ($CDCl_3$, ^{1}H-gated decoupled), δ 45.9 (s, μ-PPh_2).

(*iii*) $C_2(CO_2Me)_2$. Complex **1** (0.060 g, 0.11 mmol) and an excess of $C_2(CO_2Me)_2$ (0.2 cm^3) were refluxed in hexane (50 cm^3) for 3 d. The solvent was removed on a rotary evaporator and the product isolated by TLC using CH_2Cl_2–acetone (25:1) as eluent, to give blood red complex **3c** (0.035 g, 48%) (Found: C, 48.9; H, 3.25. $C_{27}H_{22}MnO_8PRu$ requires C, 48.9; H, 3.30%). FAB mass spectrum: m/z 662 (M^+) and $M^+ - n$CO (n = 1–4); ν_{max}/cm^{-1}(CO)(hexane) at 2026m, 2003s, 1963m, 1932m and 1733w. NMR: ^{1}H (CD_2Cl_2), δ 7.9–7.3 (m, 10 H, Ph), 5.25 (s, 5 H, C_5H_5), 3.77 (s, 3 H, Me), 3.55 (s, 3 H, Me) and 2.31 [d, 1 H, ^3J(PH) 11.6 Hz, C(CO_2Me)=C*H*CO_2Me]; ^{31}P ($CDCl_3$, ^{1}H-gated decoupled), δ 57.6 (s, μ-PPh_2).

Attempted Reactions of Complex **3a** *with Nucleophiles*.—(*i*) CO. A solution of complex **3a** (0.012 g, 0.02 mmol) in nonane (20 cm^3) was refluxed for 2 d with a CO purge. Infrared spectroscopy indicated the presence of **3a** only.

(*ii*) PMe_2Ph, Bu^{t}NC *or* $LiAlH_4$. Complex **3a** (0.021 g, 0.03 mmol) was dissolved in heptane (25 cm^3) and PMe_2Ph (0.005 cm^3, 0.03 mmol) was added. After refluxing the solution for 1 d, IR spectroscopy indicated that no reaction had taken place and **3a** was recovered quantitatively. The compounds Bu^{t}NC and $LiAlH_4$ also did not react under the same conditions.

Substitution Reactions of Complex **1**.—(*i*) *With* $P(C_6H_4Me$-$4)_3$. A solution of complex **1** (0.523 g, 0.96 mmol) and $P(C_6H_4Me$-$4)_3$ (0.295 g, 0.97 mmol) in toluene (50 cm^3) was heated at 373 K for 16 h. The solvent was removed on a rotary evaporator and the product was isolated by TLC. Elution with hexane–CH_2Cl_2 (1:1) afforded orange [RuMn(μ-H)(μ-PPh_2)(η^5-C_5H_5)(CO)$_4${$P(C_6H_4Me$-$4)_3$}] **4a** (0.090 g, 12%) (Found: C, 60.6; H, 4.50; P, 7.30. $C_{42}H_{39}MnO_4P_2Ru\cdot 0.1CH_2Cl_2$ requires C, 60.7; H, 4.70; P, 7.45%). FAB mass spectrum: m/z 824 (M^+) and $M^+ - n$CO (n = 3): ν_{max}/cm^{-1}(CO)(CH_2Cl_2) at 2017w, 1940s and 1898m. NMR: ^{1}H (CD_2Cl_2), δ 8.0–7.2 (m, 22 H, Ph), 4.63 (s, 5 H, C_5H_5), 2.39 (s, 9 H, Me) and −15.76 [dd, 1 H, ^2J(PH) 24.5, ^2J(P′H) 24.5 Hz, Ru(μ-H)Mn]; ^{31}P ($CDCl_3$, ^{1}H-gated decoupled), δ 32.2 (s, μ-PPh_2) and −77.2 [s, br, $P(C_6H_4Me$-$4)_3$].

(*ii*) *With* $P(OMe)_3$. In a procedure analogous to (*i*) above

Table 3 Atomic coordinates (× 10^4) for complex **3a**

Atom	x	y	z	Atom	x	y	z
Ru	8 087(1)	4 321(1)	1 065(1)	C(15)	5 642(17)	6 694(16)	2 190(6)
Mn	5 768(2)	2 968(2)	863(1)	C(16)	4 934(19)	7 534(19)	1 939(8)
P	7 910(3)	2 246(3)	863(1)	C(17)	4 627(16)	7 301(14)	1 467(8)
C(1)	4 964(16)	1 501(16)	855(5)	C(18)	5 048(14)	6 134(14)	1 289(6)
O(1)	4 448(16)	535(13)	865(7)	C(19)	8 593(18)	5 052(14)	407(4)
C(2)	4 124(15)	3 716(14)	819(4)	C(20)	9 740(14)	5 185(13)	710(5)
O(2)	3 031(10)	4 089(13)	746(4)	C(21)	9 405(18)	6 029(15)	1 041(6)
C(3)	5 752(14)	3 258(15)	284(6)	C(22)	8 053(19)	6 384(13)	931(7)
O(3)	5 625(12)	3 460(13)	−101(4)	C(23)	7 535(15)	5 801(14)	544(6)
C(4)	8 889(13)	3 871(13)	1 629(6)	C(24)	8 664(12)	1 065(10)	1 260(4)
O(4)	9 421(9)	3 640(10)	1 968(4)	C(25)	7 886(14)	99(12)	1 401(4)
C(5)	6 092(12)	2 944(11)	1 603(4)	C(26)	8 446(20)	−812(14)	1 694(6)
C(6)	6 323(12)	4 091(11)	1 404(4)	C(27)	9 759(21)	−805(14)	1 832(5)
C(7)	5 013(10)	2 607(11)	1 901(4)	C(28)	10 594(17)	139(16)	1 686(5)
C(8)	5 213(13)	1 576(13)	2 186(4)	C(29)	10 053(13)	1 098(13)	1 389(4)
C(9)	4 288(17)	1 185(16)	2 470(6)	C(30)	8 648(13)	1 830(11)	346(4)
C(10)	3 070(16)	1 835(16)	2 458(6)	C(31)	7 888(15)	1 276(13)	−9(5)
C(11)	2 853(13)	2 840(16)	2 192(5)	C(32)	8 413(19)	969(15)	−424(5)
C(12)	3 793(12)	3 253(14)	1 912(5)	C(33)	9 752(20)	1 230(15)	−450(5)
C(13)	5 743(12)	5 287(10)	1 573(5)	C(34)	10 581(16)	1 790(13)	−87(5)
C(14)	6 007(15)	5 579(14)	2 018(5)	C(35)	10 035(14)	2 083(13)	292(5)

complex **1** (0.045 g, 0.08 mmol) and $P(OMe)_3$ (0.01 cm^3, 0.10 mmol) were used. Preparative TLC gave yellow complex **4b** (0.038 g, 72%). Trace amounts of a second orange product eluting after **4b** were noted. Complex **4b**: mass spectrum, m/z 644 (M^+) and $M^+ - n$CO (n = 1–4); ν_{max}/cm^{-1}(CO)(hexane) at 2030w, 1957s and 1922m; ^{1}H NMR (CD_2Cl_2), δ 8.0–7.2 (m, 10 H, Ph), 4.94 (s, 5 H, C_5H_5), 3.83 [d, 9 H, ^3J(PH) 11, Me] and −15.92 [dd, 1 H, ^2J(PH) 29, ^2J(P′H) 23 Hz, Ru(μ-H)Mn].

(*iii*) *With* $PPh_2C{\equiv}CPh$. Complex **1** (0.042 g, 0.077 mmol) was dissolved in toluene (50 cm^3) and $PPh_2C{\equiv}CPh$ (0.025 g, 0.088 mmol) was added. The mixture was irradiated with UV light for 17 h. Separation of the residue by TLC, eluting with hexane–CH_2Cl_2 (2:5) gave yellow-orange crystalline complex **4c** (0.041 g, 66%). Mass spectrum: m/z 806 (M^+) and $M^+ - n$CO (n = 1–4): ν_{max}/cm^{-1}(CO)(hexane) at 2027w, 1952s and 1913m. ^{1}H NMR (CD_2Cl_2): δ 8.1–7.2 (m, 25 H, Ph), 4.72 (s, 5 H, C_5H_5) and −15.53 [dd, 1 H, ^2J(PH) 27, ^2J(P′H) 24 Hz, Ru(μ-H)Mn].

Crystal Structure Determination and Refinements.—A suitable crystal of complex **3a** was mounted on a glass fibre with epoxy resin. Details of crystal data, data collection and refinement parameters are given in Table 2.

The Ru atom was located from a Patterson synthesis and the remaining non-hydrogen atoms from subsequent Fourier difference syntheses. The phenyl hydrogen atoms were placed in idealised positions (C–H 1.08 Å) and allowed to ride on the relevant carbon atom; each type of hydrogen was assigned a common isotropic thermal parameter. The alkenyl hydrogen atom was allowed to refine freely. The structure was refined to convergence by full-matrix least squares with all non-hydrogen atoms assigned anisotropic thermal parameters. A weighting scheme was applied and analysis of the variation of the sum of $w\Delta^2$ ($\Delta = F_o - |F_c|$) according to $|F_o|$ and sin θ indicated that it was appropriate. The final positional coordinates for all the non-hydrogen atoms are listed in Table 3. All atoms were assigned complex neutral-atom scattering factors taken from ref. 17. Calculations were performed on the University of Cambridge IBM 3084Q mainframe computer using SHELX 76.[18] Structural diagrams were drawn using the SHELXTL PLUS package.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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