The synthesis of Ru(diene)$_2$P(OMe)$_3$ complexes and the formation of η^3:η^3-octadienediyl or η^4-octatriene ligands upon phosphite addition to M(dimethylbutadiene)$_2$CO (M = Fe, Ru)

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Abstract

Low temperature addition of P(OMe)$_3$ to Ru/2,3-dimethylbutadiene and Ru/1,3-cyclohexadiene cocondensates yields Ru(diene)$_2$P(OMe)$_3$ complexes. The reactions of the bis(dimethylbutadiene) complexes M(C$_6$H$_{10}$)$_2$CO (M = Fe, Ru) with P(OMe)$_3$ give new complexes containing either η^3:η^3-octadienediyl or η^4-octatriene ligands.

Introduction

It is generally accepted that transition metal catalysed dimerisations of 1,3-dienes involve a multistep mechanism [1,2]. Coordination of two diene monomers to the metal atom is thought to precede formation of an octadienediyl ligand; subsequent transformation to the stable organic dimerisation product and release from the metal centre then complete the cycle. A complete series of representative intermediates has never been isolated, although octadienediyl complexes have been observed in certain active systems [3,4].

We now report that the stoichiometric reactions of M(dimethylbutadiene)$_2$CO (M = Fe, Ru) with trimethylphosphite provide a model for the formation of 1,3,6-octatrienes via the multistep mechanism outlined above. Some new complexes produced from the reaction of trimethylphosphite with Ru/diene cocondensates are also presented.

Results and discussion

Syntheses of Ru(diene)$_2$P(OMe)$_3$ complexes

The use of metal vapours is now established as a route for the synthesis of certain classes of organometallic compounds of the refractory transition elements [5]. We have previously prepared Ru/diene cocondensates on a satisfactory scale (ca. 1 g
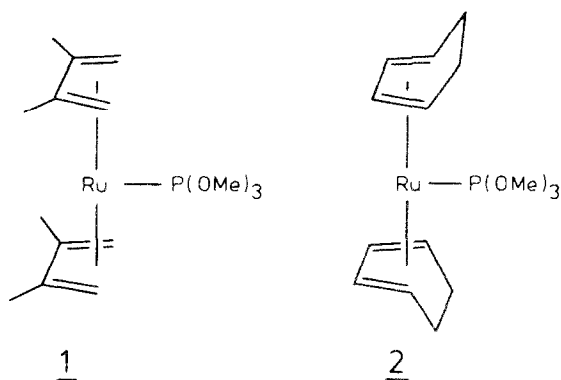
Ru/30 ml diene) using positive hearth electron beam vaporisation. and have studied their low temperature carbonylation [6,7].

The preparations of Ru/2.3-dimethylbutadiene and Ru/1,3-cyclohexadiene cocondensates have now been repeated, and $P(OMe)_3$ has been condensed on to the matrices at $-196°C$. Upon work-up (see Experimental) the stable complexes $Ru(C_6H_{10})_2P(OMe)_3$ (1) and $Ru(C_6H_8)_2P(OMe)_3$ (2) have been isolated as crystalline solids in yields of 26 and 22%, respectively.

Spectral analyses of the crude organometallic products (^1H, ^{31}P NMR) indicated that only the Ru/1.3-cyclohexadiene reaction had produced significant quantities of a further phosphite complex. Isolation of this minor product was not attempted, but it was spectroscopically identified as $Ru(\eta^4-C_6H_8)[P(OMe)_3]_3$, formed in a 1/4 molar ratio with respect to 2.

In the low temperature carbonylation of Ru/cyclohexadiene cocondensates, $Ru(\eta^5-C_6H_7)(\eta^3-C_6H_9)CO$ was isolated as the initial kinetic product; subsequent transformation to the symmetrical bis(diene) species was observed at room temperature and above [7]. In the reaction giving 2, however, we found no evidence for an analogous (cyclohexadienyl)(cyclohexenyl)phosphite intermediate. despite rapid manipulations (< 2 h between extraction from reactor and NMR) at low temperature (≤ $-20°C$).

The related reaction of Fe/cyclohexadiene cocondensates and $P(OMe)_3$ under similar conditions has been reported by Ittel et al. [8]. Interestingly, an iron analogue of 2 is not produced in this reaction, although an iron complex corresponding to 1 has been prepared from Fe/2.3-dimethylbutadiene cocondensates.

Ligand addition to M(dimethylbutadiene)$_2$L

The first reports of the reactions of M(diene)$_2$L complexes (M = Fe, Ru) with two-electron ligands were limited to simple diene displacements; for example. reaction of Fe(butadiene)$_2$CO or Ru(butadiene)$_2$PPh$_3$ with $P(OMe)_3$ in toluene was reported to yield the corresponding $M(\eta^4-C_4H_6)L[P(OMe)_3]_2$ complexes [9]. More recently, we have shown that the formation of stable $\eta^3 : \eta^3$-octadienediyl metal complexes might be a possible alternative to diene displacement for reactions of this type. Thus $M(\eta^3 : \eta^3-C_{12}H_{20})(CO)_2$ was isolated after carbonylation of M(dimethylbutadiene)$_2$CO (M = Fe, Ru) [10].
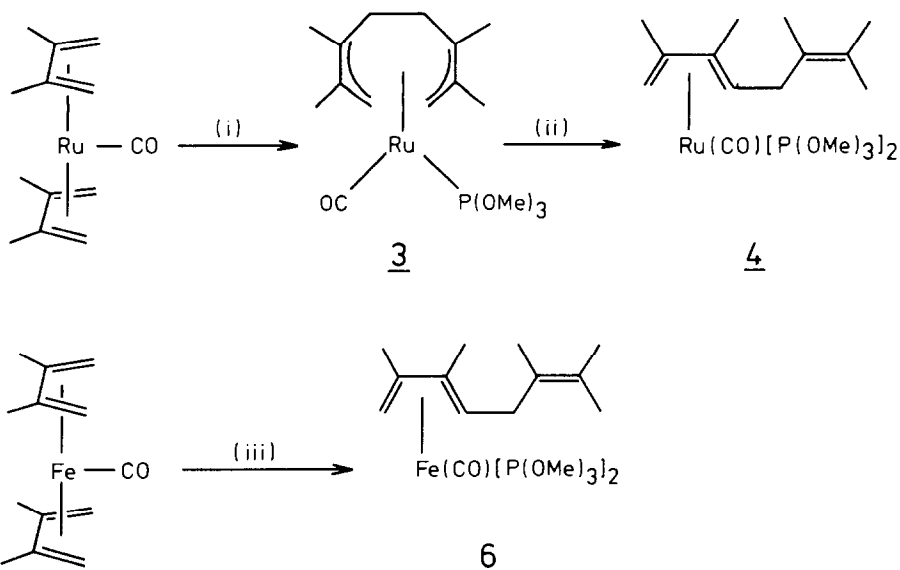
Scheme 1. (i) P(OMe)$_3$ excess, refluxing THF, 90 min, yield 72%. (ii) P(OMe)$_3$ excess, refluxing toluene, 40 h, yield 85%. (iii) P(OMe)$_3$ excess, refluxing THF, 15 h, yield 87%.

The reactions of M(dimethylbutadiene)$_2$CO complexes with P(OMe)$_3$ have been found to differ somewhat from the carbonylation reactions, and our results are summarised in Scheme 1.

(a) M = Ruthenium.   The high yield formation of the η^3: η^3-octadienediyl complex Ru(η^3: η^3-C$_{12}$H$_{20}$)(CO)P(OMe)$_3$ (3) from Ru(η^4-C$_6$H$_{10}$)$_2$CO and P(OMe)$_3$ requires only 90 min in refluxing THF. A structure for 3 may be proposed by analogy with the crystallographically determined structure of the related dicarbonyl species Ru(η^3: η^3-C$_{12}$H$_{20}$)(CO)$_2$ [10]. It is shown schematically in Fig. 1, and features an octadienediyl ligand with an approximately gauche-locked methylene chain, anti-substitution of both allyl groups, and a trans-arrangement of the terminal carbon atoms. NMR data for 3 (Table 1) are consistent with this structure; in particular, the four methyl groups are chemically inequivalent and a large value of J(P–C) (43 Hz) is observed for the coupling between the trans related P and C(3) atoms.
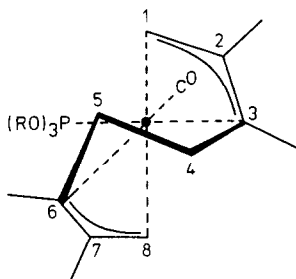

Fig. 1. Proposed structure for the η^3: η^3-octadienediyl species M(η^3: η^3-C$_{12}$H$_{20}$)(CO)P(OR)$_3$ 3, 5 and 7.

The rate law for the formation of **3** was determined in octane solutions at 45 °C, using IR spectroscopy. The absorbances (A) of the bands due to **3** ($\nu(CO)$ 1930 cm^{-1}) and to Ru(η^4-C$_6$H$_{10}$)$_2$CO ($\nu(CO)$ 1993 cm^{-1}) were monitored, as a function of time, in solutions of different P(OMe)$_3$ concentration (0.1–0.4 M; 20–80 molar equivalents P(OMe)$_3$). Plots of $\ln(A_\infty - A_t)$ vs. t and $\ln(A_t)$ vs. t for the product and reactant bands, respectively, were linear, confirming first order behaviour in Ru(η^4-C$_6$H$_{10}$)$_2$CO. The resulting pseudo-first order rate constants were plotted against the absolute phosphite concentrations to yield the following rate equation:

$$\text{Rate of formation of } \mathbf{3} = k \left[\text{Ru}(\eta^4\text{-C}_6\text{H}_{10})_2\text{CO} \right] \left[\text{P(OMe)}_3 \right]$$

$$k = (79 \pm 6) \times 10^{-5} \ M^{-1} \ \text{s}^{-1} \ (\text{octane, } 45°C)$$

This result provides the first kinetic data for formation of an octadienediyl complex from a bis(diene) complex, but unfortunately, no detailed mechanistic conclusions can be drawn.

An alternative synthesis of **3** by carbonylation of Ru(η^4-C$_6$H$_{10}$)$_2$P(OMe)$_3$ (**1**) was attempted, but proved unsuccessful. Interestingly, extremely forcing conditions were necessary to carbonylate **1**, and Ru(η^4-C$_6$H$_{10}$)(CO)$_2$P(OMe)$_3$ was the only tractable product (21% yield).

Further reaction of **3** with P(OMe)$_3$ does not occur in refluxing THF. The use of more severe conditions, however, was found to give a new complex (85% yield) with a mass spectrum indicative of additional P(OMe)$_3$ uptake. On the basis of NMR data (Table 2), the complex was characterised as the η^4-octatriene species Ru(η^4-C$_{12}$H$_{20}$)(CO)[P(OMe)$_3$]$_2$ (**4**). The conversion of **3** into **4** requires a hydrogen transfer from either C(4) to C(8) or C(5) to C(1) (Fig. 1) and uptake of P(OMe)$_3$.

In an attempt to destabilise an η^3 : η^3-octadienediylruthenium species, and possibly parallel the behaviour observed for the reaction of Fe(η^4-C$_6$H$_{10}$)$_2$CO and P(OMe)$_3$ (vide infra), the reaction of Ru(η^4-C$_6$H$_{10}$)$_2$CO and P(OPh)$_3$ was studied. Despite the slightly larger phosphite (cone angles [11]: P(OPh)$_3$ 128°; P(OMe)$_3$ 107°) the η^3 : η^3-octadienediyl complex still proved isolable (74% yield), and NMR data (Table 1) for Ru(η^3 : η^3-C$_{12}$H$_{20}$)(CO)P(OPh)$_3$ (**5**) are consistent with the proposed structure (Fig. 1).

(b) M = Iron. Complete reaction of Fe(η^4-C$_6$H$_{10}$)$_2$CO and P(OMe)$_3$ requires 15 h in refluxing THF. The product, isolated in 87% yield, was characterised as the η^4-octatriene complex Fe(η^4-C$_{12}$H$_{20}$)(CO)[P(OMe)$_3$]$_2$ (**6**), and NMR data are listed in Table 2.

The formation of an intermediate η^3 : η^3-octadienediyl complex Fe(η^3 : η^3-C$_{12}$H$_{20}$)(CO)P(OMe)$_3$ (**7**) could not be detected in this reaction. Spectral analysis (IR, NMR) of the mixture when the reaction was interrupted in mid-course, or carried out with a molar equivalent of P(OMe)$_3$, revealed the presence of only the starting complex and **6**.

A probable mechanism, involving a near-zero concentration of **7** throughout the reaction, consists of rate-determining formation of **7** followed by rapid C(4) to C(8) or C(5) to C(1) hydrogen transfer and P(OMe)$_3$ uptake. The high reactivity of **7** (probable structure shown in Fig. 1) can be ascribed to a facilitation of the hydrogen transfer by steric effects. As already mentioned, the less crowded dicarbonyl analogue Fe(η^3 : η^3-C$_{12}$H$_{20}$)(CO)$_2$ has been isolated.

For the octatriene complexes **4** and **6**, the proposed *trans*-substitution of the C(3)–C(4) double bond is based on analysis of their ^{1}H NMR spectra. In particular,

Table 1

NMR data for octadienediyl complexes Ru(η^3: η^3-C$_{12}$H$_{20}$)(CO)P(OR)$_3$ [a]

	3, R = Me	5, R = Ph
¹H [b]		
H(1), H(1'), H(8), H(8') [c]	3.02 (d, 4.6); 2.93	3.06; 3.06;
	2.78; 2.61	2.86; 2.47
H(4), H(4'), H(5), H(5') [d]	1.75 (m); 1.50 (m)	1.75 (m); 1.45 (m)
Methyls on C(2),	2.11; 2.05 (d, 3.0);	2.35 (d, 2.9); 1.56;
C(3), C(6) and C(7)	1.62 (d, 7.7); 1.43	1.55 (d, 9.6); 1.34
P(OR)$_3$	3.43 (d, 11.5)	7.2(m)
¹³C [e]		
C(1), C(8) [f]	38.4; 37.2	39.3; 37.5
C(2), C(7)	114.6; 110.5	116.1; 111.9
C(3) [g]	81.6 (d, 43)	81.4 (d, 51)
C(4) [g,h]	43.0 (d, 10)	42.9 (d, 13)
C(5) [h]	42.6	43.4
C(6)	85.8	88.3
Methyls on C(2),	23.3; 22.3 (d, 9);	22.7 (d, 7); 22.2;
C(3), C(6) and C(7) [i]	22.2; 20.8	21.4; 20.8
CO	209.5	209.9
P(OR)$_3$	50.9 [j]	151.9; 129.4; 124.1; 121.7 [k]
³¹P{¹H}		
	167.2	146.4

[a] In CDCl$_3$ (298 K), δ (ppm). Figures in parentheses refer to the J values (Hz) for coupling with phosphorus. Signals are singlets unless otherwise stated. [b] Proton integrations are all consistent with their assignment. [c] $^2J(syn - anti)$ not observed. [d] Complexity of signals is consistent with four inequivalent protons. [e] J(C–H) multiplicities are all consistent with their assignment. [f] t, J(C–H) ~ 155 Hz. [g] Assigned on the basis of large J(P–C). [h] t, J(C–H) ~ 125 Hz. [i] q, J(C–H) ~ 126 Hz. [j] q, J(C–H) ~ 145 Hz. [k] 151.9 (J(P–C) 11 Hz), others d, J(C–H) ~ 160 Hz.

the chemical shift of the H(4) proton (4: δ 0.47, 6: δ 0.02 ppm) is in the range characteristic of the terminal *endo*-protons for M(diene)L$_3$ complexes of iron and ruthenium. Furthermore, the downfield shift of H(4) relative to H(1(*endo*)) (0.83 ppm in 4; 0.75 ppm in 6) has been noted as a general feature in the ¹H NMR spectra of Fe(diene) complexes bearing an *exo*-substituent on C(4) [12].
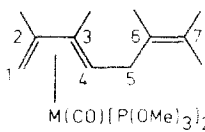
More detailed structural information on the η^4-octatriene complexes 4 and 6 cannot be derived with certainty from the NMR data. The most stable conformation about the metal atom in 4 and 6, however, may be inferred from the results of a ¹⁹F NMR study of Fe(diene)(CO)(PF$_3$)$_2$ complexes by Busch and Clark [13], and is shown below. The unequal J(P–H) values between the individual octatriene protons
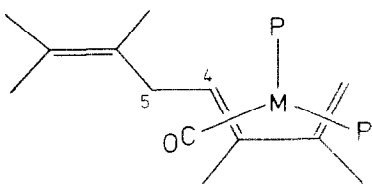
and the two phosphorus atoms are consistent with a static square pyramidal coordination, but since even complete diene rotation does not render the phosphites equivalent, the absence of fluxionality is unproven. Similarly, restricted rotation about the C(4)–C(5) bond of the octatriene ligand, although unconfirmed, is

Table 2

NMR data for 1,3,6-octatriene complexes $M(\eta^4\text{-}C_{12}H_{20})(CO)[P(OMe)_3]_2$ [a]

	4. M = Ru	6. M = Fe
^1H [b,c]		
H(1(exo))	1.34 (d, 8.5)	1.21 (d, 11.0)
H(1(endo))	−0.36 (dd, 14.5, 9.5)	−0.73 (dd, 16.7, 9.9)
H(4)	0.47 (ddd, ~18)	0.02 (ddd, ~11, ~5)
H(5)	2.79 (ddd, ~6)	2.66 (d)
H(5′)	2.57 (ddd, ~4)	2.40 (dd)
Methyls on C(2), C(3)	2.20 (d, 3.9);	2.06 (d, 2.7),
	2.10 (dd, 4.4, 4.3)	2.00 (d, 2.7)
Methyls on C(6), C(7)	1.71; 1.68;	1.69; 1.64;
	1.62	1.59
$P(OMe)_3$	3.57 (d, 11.9);	3.61 (d, 10.8);
	3.46 (d, 11.8)	3.49 (d, 10.8)
^{13}C [d]		
C(1) [e]	34.3	39.4
C(2), C(3)	97.4; 94.9	94.2; 91.9
C(4) [f]	53.3 (d, 40)	58.0 (d, 12)
C(5) [g]	36.7	35.5
C(6), C(7)	129.9; 122.6	129.2; 123.0
Methyls on	20.6; 20.3; 20.3;	20.6; 20.3; 19.9;
C(2), C(3), C(6), C(7) [h]	17.7; 15.8	18.0; 15.5
CO	204.9	216.8
$P(OMe)_3$ [i]	50.7; 50.5	50.9; 50.7
$^{31}P\{^1H\}$ [j]		
	178.7; 164.6	195.8; 183.3

[a] In $CDCl_3$ (298 K), δ (ppm). Figures in parentheses refer to the J values (Hz) for coupling with the inequivalent phosphorus nuclei. [b] Proton integrations are all consistent with assignment. [c] $J(H–H)$ values for the octatriene ligand: 4. $^3J(4–5)$ ~4, $^3J(4–5')$ ~9, $^2J(5–5')$ ~15 Hz. 6. $^3J(4–5)$ not observed; $^3J(4–5')$ ~9, $^2J(5–5')$ ~14 Hz. [d] $J(C–H)$ multiplicities are all consistent with their assignment. [e] t, $J(C–H)$ ~153 Hz. [f] d, $J(C–H)$ ~153 Hz. [g] t, $J(C–H)$ ~125 Hz. [h] q, $J(C–H)$ ~126 Hz. [i] q, $J(C–H)$ ~145 Hz. [j] $J(P–P)$ 15 Hz (4); 10 Hz (6). There was no coalescence up to 90°C.

suggested by the unequal ^3J(H–H) values between the inequivalent protons on C(5) and the *endo*-proton on C(4).

Experimental

Solvents were dried, distilled, and deoxygenated prior to use, and all organometallic manipulations were routinely carried out under nitrogen. Commercial reagents were used, and the free dienes and P(OMe)$_3$ were purified by distillation.

Fe(η^4-C$_6$H$_{10}$)$_2$CO and Ru(η^4-C$_6$H$_{10}$)$_2$CO were prepared by published procedures [14,6], and a vapour synthesis plant (Planar, VSP 500), fitted with a positive hearth electron beam furnace, was used to produce Ru/diene cocondensates. Mass spectra (electron impact, 70 eV) were recorded with a Finnigan 1020 GC-MS spectrometer. NMR spectra were recorded on Bruker WH-360 (^{1}H, 360 MHz; ^{13}C, 90.55 MHz) and CXP-200 (^{31}P, 81.01 MHz) FT spectrometers. Phosphorus chemical shifts are reported in ppm downfield from 85% H$_3$PO$_4$. Infrared spectra were recorded on a Perkin–Elmer 577 spectrophotometer. Elemental analyses were performed by Ilse Beetz Mikroanalytische Laboratorium, Kronach, West Germany.

Vapour syntheses

Ru(2,3-dimethylbutadiene)$_2$P(OMe)$_3$ (1). In the apparatus previously described [6], Ru vapour (950 mg, 9.4 mmol) and an excess of 2,3-dimethylbutadiene (40 ml) were cocondensed over a period of 2 h at $-196°$C. P(OMe)$_3$ (5 ml) was then rapidly condensed on to the mixture, the reaction chamber filled with nitrogen gas, and the temperature allowed to rise under constant pressure (1 atm). Extraction with THF (200 ml) at $-20°$C, filtration through dry Florisil and solvent evaporation gave an oil, which was taken up in pentane (150 ml). Treatment with activated carbon (2 g), stirring for 5 min, filtration and solvent evaporation gave an orange oil, which was sublimed (50°C; 10^{-4} mbar; 72 h) on to a cold finger kept at $-30°$C. The sublimate was recrystallised from pentane to yield **1** as pale yellow plates (950 mg, 26%): m.p. 104°C; MS, *m/e* for ^{102}Ru (relative intensity) 390 [M^+] (55), 359 (8), 308 (26), 278 (69), 266 (100); ^{1}H NMR (CDCl$_3$) δ 3.62 (d, 9H, J(P–H) 11.4 Hz, OMe), 1.68 (d, 12H, J(P–H) 2.4 Hz; Me), 1.59 (s, 4H, H(*exo*)), -0.37 (d, 4H, J(P–H) 17.8 Hz, H(*endo*)); ^{13}C NMR (CDCl$_3$) δ 89.2 (s), 50.6 (q, J(C–H) 145 Hz, OMe), 35.9 (t, J(C–H) 154 Hz), 18.2 (q, J(C–H) 126 Hz); ^{31}P{^{1}H}NMR (CD$_2$Cl$_2$) δ 190.1 (s). Anal. Found: C, 46.41; H, 7.49; P, 8.03. C$_{15}$H$_{29}$O$_3$PRu calc: C, 46.26; H, 7.51; P, 7.95%.

Ru(1,3-cyclohexadiene)$_2$P(OMe)$_3$ (2). As above, P(OMe)$_3$ (5 ml) was added to a Ru vapour (620 mg, 6.1 mmol)/1,3-cyclohexadiene (30 ml) cocondensate held at $-196°$C. Work-up was as for **1**, except that before sublimation crude **2** was obtained as a brown powder on decantation from a concentrated pentane solution ($-78°$C). Complex **2** was obtained as cream coloured plates (525 mg, 22%): m.p. 109°C (dec); MS, *m/e* (relative intensity) 386 [M^+] (14), 355 (6), 304 (100), 289 (85); ^{1}H NMR (CDCl$_3$) δ 4.38 (m, 4H, J(P–H) 2.9 Hz, H(2) and H(3)), 3.74 (d, 9H, J(P–H) 11.8 Hz, OMe), 3.00 (m, 4H, H(1) and H(4)), 1.59 (m, 4H, *J(gem)* 10 Hz), 1.16 (m, 4H, J(P–H) 3.7 Hz); ^{13}C NMR (CDCl$_3$) δ 75.4 (d, J(C–H) 166 Hz), 53.8 (d, J(C–H) 153 Hz), 49.6 (q, J(C–H) 145 Hz, OMe), 24.0 (td, J(C–H) 130, J(P–C) 10 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 188.7 (s). Anal. Found: C, 46.81; H, 6.62; P, 7.95. C$_{15}$H$_{25}$O$_3$PRu calc: C, 46.75; H, 6.54; P, 8.04%. The minor product

Ru(η^4-C$_6$H$_8$)[P(OMe)$_3$]$_3$, formed in a 1/4 molar ratio with **2**, was identified spectroscopically in the crude product prior to purification: ^{1}H NMR (CDCl$_3$) δ 4.96 (m, 2H), 3.53 (d, 27H, J(P–H) 10.8 Hz), 2.66 (m, 2H), CH$_2$ ~ 1.6–1.2 (masked); ^{31}P{^{1}H}NMR (CDCl$_3$, 253 K) δ 181.9 (apical P atom), 162.6 (2 basal P atoms).

Octadienediyl complexes

Ru(η^3:η^3-C$_{12}$H$_{20}$)(CO)P(OMe)$_3$ (3).   A solution of Ru(η^4-C$_6$H$_{10}$)$_2$CO (410 mg, 1.4 mmol) and P(OMe)$_3$ (360 mg, 2.9 mmol) in THF (80 ml) was refluxed for 90 min and the solvent then evaporated under reduced pressure. Pentane extraction (2 × 50 ml) gave a turbid solution, which was clarified by addition of activated carbon (0.5 g) and filtration. Chromatography (SiO$_2$, pentane/ether) followed by sublimation (50°C; 10^{-4} mbar; 48 h) gave **3** as a straw coloured oil (422 mg, 72%): IR (pentane), ν(CO) 1930 cm^{-1}; MS, m/e (relative intensity) 418 [M$^+$] (42), 390 (48), 308 (27), 278 (40), 266 (100). Anal. Found: C, 46.58; H, 7.10; P, 8.04. C$_{16}$H$_{29}$O$_4$PRu calc: C, 46.03; H, 7.00; P, 7.42%.

Kinetics: For each run, 25 ml of an octane solution of known P(OMe)$_3$ concentration (0.1–0.4 M) was transferred to a Schlenk tube fitted with a subaseal cap and magnetic stirrer, and this was placed in a constant temperature bath at 45°C. Ru(η^4-C$_6$H$_{10}$)$_2$CO (40 mg) was added (initial concentration ~ 5 × 10^{-3} M). Aliquots were removed at 5 min intervals for immediate IR spectral analysis (2000–1900 cm^{-1}). The absorbances (A) due to Ru(η^4-C$_6$H$_{10}$)$_2$CO (1993 cm^{-1}) and **3** (1930 cm^{-1}) were measured, and from the gradients of the linear plots of ln(A_t) vs. t and ln($A_\infty - A_t$) vs. t, respectively, the following pseudo-first order rate constants (k_{obs}) were derived: [P(OMe)$_3$] (M)/k_{obs} (s^{-1}): 0/0; 0.112/1.03 × 10^{-4}; 0.220/1.88 × 10^{-4}; 0.274/2.30 × 10^{-4}; 0.326/2.67 × 10^{-4}; 0.430/3.42 × 10^{-4}. A least-squares fit of k_{obs} vs. [P(OMe)$_3$] gave the rate equation reported in the text.

Ru(η^3:η^3-C$_{12}$H$_{20}$)(CO)P(OPh)$_3$ (5).   Similar treatment of Ru(η^4-C$_6$H$_{10}$)$_2$CO (320 mg, 1.1 mmol) and P(OPh)$_3$ (710 mg, 2.30 mmol), but without the sublimation, gave, after two recrystallisations from pentane, pale yellow crystals of **5** (490 mg, 74%): m.p. 114°C; IR (pentane), ν(CO) 1942 cm^{-1}; MS, m/e (relative intensity) 604 [M$^+$] (3), 576 (6), 494 (10), 412 (10), 310 (5), 266 (12), 217 (100). Anal. Found: C, 62.20; H, 5.96; P, 5.15. C$_{31}$H$_{35}$O$_4$PRu calc: C, 61.68; H, 5.84; P, 5.13%.

Octatriene complexes

Ru(η^4-C$_{12}$H$_{20}$)(CO)[P(OMe)$_3$]$_2$ (4).   A solution of complex **3** (235 mg, 0.6 mmol) and P(OMe)$_3$ (1.45 g, 11.7 mmol) in toluene (60 ml) was refluxed for 40 h. Work-up as for **3** gave **4** as a straw coloured oil (260 mg, 85%): IR (pentane), ν(CO) 1923 cm^{-1}; MS, m/e (relative intensity) 542 [M$^+$](42), 514 (13), 511 (22), 390 (72), 350 (100). Anal. Found: C, 43.31; H, 7.29; P, 10.98. C$_{19}$H$_{38}$O$_7$P$_2$Ru calc: C, 42.14; H, 7.07; P, 11.44%.

Fe(η^4-C$_{12}$H$_{20}$)(CO)[P(OMe)$_3$]$_2$ (6).   A solution of Fe(η^4-C$_6$H$_{10}$)$_2$CO (570 mg, 2.3 mmol) and P(OMe)$_3$ (630 mg, 5.1 mmol) in THF (100 ml) was refluxed for 15 h. Work-up as for **3** gave **6** as a yellow oil (990 mg, 87%): IR (pentane), ν(CO) 1902 cm^{-1}; MS, m/e for ^{56}Fe (relative intensity) 496 [M$^+$] (16), 468 (2), 465 (4), 437 (3), 344 (41), 304 (100), 220 (14). Anal. Found: C, 46.45; H, 7.68. C$_{19}$H$_{38}$O$_7$P$_2$Fe calc: C, 45.98; H, 7.72%.

Carbonylation of 1. Complex **1** (250 mg) was heated at 120 °C in toluene (20 ml) for 72 h under CO (150 atm). Work-up as for **3** gave Ru(2,3-dimethyl-butadiene)(CO)$_2$P(OMe)$_3$ as an orange oil (49 mg, 21%): IR (pentane), ν(CO) 2005, 1945 cm^{-1}; MS, *m/e* (relative intensity) 364 [M^+] (41), 336 (87), 308 (100), 278 (81); ^{1}H NMR (CDCl$_3$) δ 3.61 (d, 9H, *J*(P–H) 13.4 Hz, OMe), 2.25 (d, 6H, *J*(P–H) ~ 3 Hz, Me), 1.62 (d, 2H, *J*(H–H) ~ 2 Hz, H(*exo*)), −0.07 (dd, 2H, *J*(P–H) ~ 10 Hz, H(*endo*)); ^{13}C NMR (CDCl$_3$) δ 200.3 (CO), 100.4 (s), 51.2 (q, *J*(C–H) 146 Hz), 35.4 (t, *J*(C–H) 154 Hz), 20.8 (q, *J*(C–H) 127 Hz).

Acknowledgment

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