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A study of η^3-allyl(η^5-cyclopentadienyl)-dicarbonylmanganese salts

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Abstract

New substituted η^3-allyl(η^5-cyclopentadienyl)dicarbonylmanganese cations have been prepared as their tetrafluoroborates. They readily add a wide range of nucleophiles yielding η^2-alkene(η^5-cyclopentadienyl)dicarbonylmanganese complexes. Of the latter, in general only those involving terminal alkenes are sufficiently stable to permit ready isolation; otherwise metal-free alkenes are obtained. Regioselectivity in these additions depends on the nucleophile.

Introduction

Transition metals form numerous stable cationic complexes with hydrocarbon ligands, and the synthetic potential of nucleophilic addition to such species has been widely appreciated and studied. Tsuji [1], Trost [2] and others have demonstrated the great synthetic value of nucleophilic additions to both neutral and cationic η^3-allylpalladium systems, but the only other allyl complexes which have received significant attention are the η^3-allyl(η^5-cyclopentadienyl)carbonylnitrosylmolybdenum salts [3]. The closely related η^3-allyl(η^5-cyclopentadienyl)dicarbonylmanganese salts have been largely neglected, although Krivykh et al. [4] have shown their accessibility in one step from tricarbonylcyclopentadienylmanganese as well as their ability to react with simple nucleophiles.

We have reexamined these manganese complexes and although we can confirm their ready accessibility, our results lead to the conclusion that any synthetic utility is severely limited by the low stability of the corresponding neutral alkene complexes. We therefore only record here the preparation of a few new complexes and the regioselectivity of their addition reactions.

Discussion

The preparation of the parent allyl complex **1a** by direct reaction involving irradiation of tricarbonylcyclopentadienylmanganese, allyl alcohol, and tetrafluoro-

Table 1

Yields, IR data (ν(CO) in KCl) and analyses of the salts **1**

Complex	Yield (%)	IR (cm^{-1})	m.p. (°C)	C (found)	C (calc.)	H (found)	H (calc.)
1a	60	2020, 1990	180				
1b	40	2030, 1985	dec. 155	41.2	41.0	3.75	3.8
1c	63 [a]	2015, 1990	dec. 155	49.5	50.0	3.5	3.7
1d	62 [a,b]	2020, 1985	175–176	55.5	56.9	5.4	5.6
1e	26 [a]	2015, 1985	dec, 170				
1f	36 [a]	2010, 1970	dec. 165–166				
1g	59 [a]	2020, 1973	196–198	56.3	56.0	5.6	5.4
1h	49 [a]	2020, 1980	199–200	55.1	55.2	5.0	5.7

[a] Photolysis time 20 h. [b] Yield from 1-phenylbut-1-en-3-ol; the same product (42%) was obtained from 1-phenylbut-2-en-1-ol.

boric acid, described by the Russian authors [4], was readily duplicated and extended both to the methyl- and pentamethyl-cyclopentadienyl analogues and to substituted allyl alcohols to yield the complexes listed in Table 1. All of these cationic complexes readily add nucleophiles yielding neutral or cationic alkene complexes **2**. This had previously been demonstrated [4] for the parent complex **1a** and hydroxide, hydride, or triethylamine as nucleophiles. As further examples we report the addition of methyl (preferably as lithium dimethylcuprate), phenyl, methoxy, malonate, cyanide and iodide anions to yield the neutral complexes **2a–2f**. All of these reactions proceed smoothly and some, notably with carbanions, in high yield. But the resulting alkene complexes proved to be of only moderate stability and although all were fully characterised spectroscopically, the difficulty of

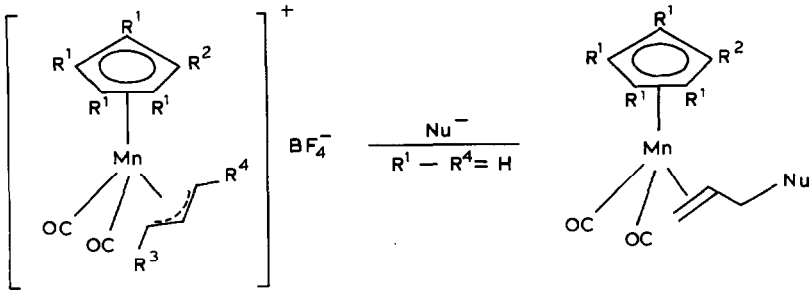
Table 2

^{1}H NMR spectra of the salts **1** (δ in CD_3COCD_3)

Salt no.	C_5 Ring		Allylic ligand					
	ring-H	CH_3	H-1 *anti*	H-2	H-3 *syn*	H-3 *anti*	CH_3	C_6H_5
1a	5.83 (s)		2.41 (d) [a] J = 11.3 Hz	5.90 (m)				
1b	5.80 (s)						2.18 (d) [b] 1.18 (d)	
1c	5.66 (s)		4.32 (d) J = 12.6 Hz	5.66 (m)	4.60 (d) J = 6.8 Hz	2.49 (d) J = 10.6 Hz		6.5, 7.82 (m)
1d	5.23 (s)		3.73 (d) J = 11.3 Hz	6.25 (t) J = 11.3 Hz		3.10 (m)	2.17 (d) J = 5.8 Hz	7.50–7.65 (m)
1e	5.36 (m)	1.93 (s)	3.04 (m)	5.36 (m)	3.87 (d) J = 6.8 Hz	*c*	2.03 (d) J = 6.6 Hz	
1f	5.22 (m)	1.78 (s)	3.98 (d) J = 12.3 Hz	6.10 (m)	4.14 (d) J = 7.2 Hz	2.21 J = 11.0 Hz		7.48–7.68 (m)
1g		1.84 (s)	3.60 (d) J = 10.5 Hz	5.34 (m)	4.60 (d) J = 12.4 Hz	2.54 (d) J = 10.6 Hz		7.33–8.00 (m)
1h		1.98 (s)	3.60 (d) J = 12.0 Hz	5.30 (m)		3.05 (m)	2.28 (d) J = 6.2 Hz	7.46–7.77 (m)

[a] H-1 *syn* at 4.49 (d), J = 6.94 Hz. [b] These peaks are in the ratio 2.5:1 and show that the product is a mixture of *syn*- and *anti*-methyl isomers in that ratio; the other peaks could not be assigned. [c] Signal obscured by water peak from solvent.

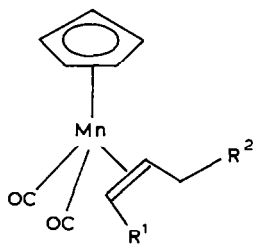
avoiding slight decomposition during attempted purification led us to forgo micro-analytical confirmation. By contrast, the phosphonium, **2g**, and pyridinium salts, **2h**, although isolated in only modest yield, could readily be obtained analytically pure.

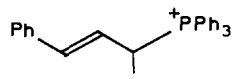


(**1a** $R^1 = R^2 = R^3 = R^4 = H$
1b: $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$
1c: $R^1 = R^2 = R^3 = H$, $R^4 = Ph$
1d: $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = CH_3$
1e: $R^1 = R^3 = H$, $R^2 = R^4 = CH_3$
1f: $R^1 = R^3 = H$, $R^2 = CH_3$, $R^4 = Ph$
1g: $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = Ph$
1h: $R^1 = R^2 = R^3 = CH_3$, $R^4 = Ph$)

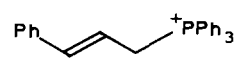
(**2a**: Nu = CH_3
2b: Nu = Ph
2c: Nu = OMe
2d: Nu = $CH(COOMe)_2$
2e: Nu = CN
2f: Nu = I
2g: Nu = PPh_3^+
2h: Nu = $NC_5H_5^+$)

When we attempted similar nucleophilic addition to complexes with substituted η^3-allylic ligands, the products proved to be even less stable and in most cases only the metal-free alkenes resulting from their decomposition could readily be characterised. One complex which could be isolated and identified was the allylbenzene complex **2b**, obtained by the action of sodium borohydride on the phenylallyl complex, **1c**, and resulting from addition at the substituted end of the η^3-allylic group. Hydride addition to the η^3-1-phenylbut-1-en-3-yl complex **1d** also yielded an isolable product which was shown by NMR to be a 2.75:1 mixture of the complexes **3a** and **3b**. Addition of triphenylphosphine to the same complex **1d** yielded only the metal-free phosphonium cation **4** [5], characterised by independent synthesis from 1-phenylbut-1-en-3-ol.





(**4**)



(**5**)

(**3a**: $R^1 = CH_3$, $R^2 = Ph$
3b: $R^1 = Ph$, $R^2 = CH_3$)

Addition of triphenylphosphine to either the methyl-, **1f**, or the pentamethylcyclopentadienyl(phenylallyl) complex, **1g**, yielded the cinnamyltriphenylphosphonium cation, **5**, showing that the bulky phosphine, in contrast to hydride, attacks the unsubstituted end of the phenylallyl group. Triethylamine behaved similarly, converting complex **1f** to the cinnamyltriethylammonium ion. Analogous behaviour

was shown by the butenyl complex **1e**, which yielded but-2-enyltriphenylphosphonium and but-2-enyltriethylammonium ions with the same nucleophiles.

Experimental

All reactions involving organometallic compounds were conducted under nitrogen. Column chromatography was carried out on neutral alumina prepared from Spence's grade 'H' by storage under ethyl acetate (7 d) followed by washing with ethanol and water, and drying at 120 °C. Light petroleum refers to the fraction of b.p. 40–60 °C unless otherwise stated. Yields of incomplete reactions are based on unrecovered starting material. Pentamethylcyclopentadiene was prepared as described by Kohl and Jutzi [6].

Cyclopentadienyl- and methylcyclopentadienyl-tricarbonylmanganese and decacarbonyldimanganese were obtained from the Ethyl Corp.

Tricarbonyl(pentamethylcyclopentadienyl)manganese [7]

Replacing n-decane by the higher-boiling decalin in the literature method [7] significantly improved the yield: Decacarbonyldimanganese (10.34 g, 26.5 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene [6] (5.02 g, 37 mmol) were heated under reflux in decalin (95 ml) for 12 h. The cooled solution was filtered to remove a pyrophoric residue, diluted with an equal volume of light petroleum and chromatographed on active alumina (not neutralised). Light petroleum eluted decalin and diethyl ether eluted the complex (4.57 g, 45%), m.p. 76 °C (lit. [7]: 78 °C), ν(CO)(CH_2Cl_2) 2020, 1930 cm^{-1}, δ ($CDCl_3$) 1.89.

The cationic complexes 1

Although we also used the 2-step procedure of Rosan [8] for the preparation of the salts **1a–1d**, the yields in each case were much inferior to those obtained by the direct method of Krivykh, Gusev and Rybinskaya [4], to which the yields in Table 1 refer and which is here exemplified for the parent complex **1a**.

Tricarbonylcyclopentadienylmanganese (5.06 g, 24.8 mmol) and allyl alcohol (5 ml, 4.27 g, 74 mmol) were dissolved in diethyl ether (250 ml). Aqueous fluoboric acid (6 ml, 40%) was added and the mixture was irradiated through a quartz tube with a Hanovia broad spectrum medium pressure 480 watt mercury arc for 5 h. The precipitated yellow crystalline product (**1a**) (4.48 g, 60%) was collected by filtration, washed with diethyl ether (2 × 50 ml) and dried *in vacuo*.

Additions to the unsubstituted cation 1a

(i) Addition of lithium dimethylcuprate:

Methyllithium (6.8 ml of a 1.5 M solution in hexane, 10.1 mmol) was added dropwise by syringe to an ice-cooled suspension of copper(I) bromide (0.72 g, 5.05 mmol) in ether (50 ml) and stirred until all the copper(I) bromide had dissolved (ca. 30 min). The complex **1a** (0.608 g, 2.02 mmol) dissolved in acetonitrile (6 ml) was then added by syringe and the mixture stirred for 10 min, then poured into water (50 ml). The ether phase was separated and the aqueous phase extracted with more ether (2 × 30 ml). The combined, dried ($MgSO_4$) extracts were evaporated and the residue chromatographed. The only visible band was eluted with ether to give the somewhat unstable 1-butene complex **2a** (0.412 g, 89%). The

same product was obtained in 60% yield when methylmagnesium iodide was used in place of the cuprate. Complex **2a** is an amber oil, ν(CO)(CH_2Cl_2) 1945, 1880 cm^{-1}, δ (CD_3COCD_3) 4.63 (5H, s, C_5H_5), 3.45 (3H, m, H-2 and CH_2), 2.64 (1H, d, J = 8.2 Hz, H-1 *syn* *), 1.85 (1H, d, J = 12.2 Hz, H-1 *anti*), 1.09 (3H, t, J = 7.1 Hz, CH_3).

(ii) Addition of phenyllithium

To a solution of complex **1a** (0.278 g, 0.92 mmol) in ether (25 ml), cooled with solid CO_2, phenyllithium (0.6 ml of 1.6 *M* solution, 0.96 mmol) was added dropwise by syringe and the mixture stirred with continued cooling for 3 h. The solution was then filtered, evaporated, and the residue chromatographed. Ether eluted (η^2-allylbenzene)dicarbonyl(η^5-cyclopentadienyl)manganese, **2b** (0.149 g, 55%), a yellow oil, ν(CO)(CH_2Cl_2) 1950, 1885 cm^{-1}, δ (CD_3COCD_3) 7.28 (5H, m, C_6H_5), 4.69 (5H, s, C_5H_5), 2.71 (1H, d, J = 8.0 Hz, H-1 *syn*), 2.02 (1H, d, H-1 *anti*); peaks due to H-2 and CH_2 overlap with the br H_2O peak near 3.3. The above properties were identical with those of a sample obtained in low yield by irradiation (90 min) of tricarbonylcyclopentadienylmanganese and excess of allylbenzene in light petroleum.

(iii) Addition of methoxide

To a solid CO_2 cooled solution of sodium methoxide prepared by dissolving sodium (0.12 g, 5 g atom) in methanol (3 ml) the allyl complex **1a** (0.281 g, 0.93 mmol) was added and the mixture stirred for 1 h. The resultant solution was rapidly filtered and evaporated *in vacuo*. The residue was chromatographed, ether eluting the unstable allyl methyl ether complex **2c** (0.163 g, 70%), as an amber oil, ν(CO)(CH_2Cl_2) 1955, 1890 cm^{-1}, δ (CD_3COCD_3) 4.71 (5H, s, C_5H_5), 4.04 (2H, d, H-3), 3.40 (1H, m, H-2), 2.89 (3H, s, CH_3), 2.76 (1H, d, J = 12.1 Hz, H-1 *anti*), 1.91 (1H, d, J = 7.9 Hz, H-1 *syn*).

(iv) Addition of dimethyl lithiomalonate

n-Butyllithium (1.01 ml of a 2.6 M solution, 2.6 mmol) was added by syringe to a solid CO_2 cooled solution of dimethyl malonate (0.35 g, 0.3 ml, 2.6 mmol) in a mixture of acetonitrile (5 ml) and tetrahydrofuran (5 ml) and the mixture stirred for 30 min. The allyl complex **1a** (0.272 g, 90 mmol) in acetonitrile (3 ml) was added by syringe and stirring continued for 3 h during which the mixture was allowed to come to room temperature. The filtered solution was evaporated and the residue chromatographed. Ether eluted the yellow allyl malonate complex **2d** (0.286 g, 85%) which solidified on ice-cooling, m.p. 63–67 °C, ν(CO)(CH_2Cl_2) 1953, 1890 cm^{-1}, δ (C_6D_6) 3.85 (5H, s, C_5H_5), 3.36 (1H, t, H-2, superimposed on 6H, s, CH_3), 2.08–3.06 (3H, m, H-3 and H-4), 2.32 (1H, d, J = 8.2 Hz, H-5 *syn*), 1.88 (1H, d, J = 12.3 Hz, H-5 *anti*).

The same product was synthesised in low yield by photolysis (1 h) of tricarbonylcyclopentadienylmanganese in light petroleum with an equimolar quantity of methyl (2-methoxycarbonyl)pent-4-enoate [9]. The latter ester prepared essentially by the literature method [9], had b.p. 65–71 °C/3 Torr (lit. [10]: b.p. 206.5–

* *syn* and *anti* are used to denote relation to H-2 of allyl.

207.5/771 Torr), δ (CD_3COCD_3) 5.72 (1H, m, H-4), 5.07 (2H, m, H-5), 3.60 (6H, s, CH_3), 3.50 (1H, t, H-2), and 2.60 (2H, dd, H-3).

(v) Addition of cyanide

A solution of the allyl complex **1a** (0.305 g, 1.01 mmol) in water (50 ml) was covered with light petroleum (b.p. 30–40 °C, 50 ml). On addition of sodium cyanide (63 mg, 1.26 mmol) the aqueous phase turned bright red. The mixture was stirred for 1.5 h; then the layers were separated and the aqueous layer extracted with ether (3 × 30 ml). The combined petroleum and ether solutions were dried ($MgSO_4$) and evaporated and the residue chromatographed. The first band eluted with ether yielded the allyl cyanide complex **2e** (0.203 g, 82%), yellow crystals, m.p. 25 °C, ν(CO)(CH_2Cl_2) 1963, 1895 cm^{-1}, δ (C_6D_6) 3.71 (7H, s, C_5H_5 and CH_2), 2.48 (1H, m, H-3), 2.02 (1H, dd, H-4 *syn*), 1.45 (1H, dd, H-4 *anti*). A second band eluted with acetone yielded the allyl alcohol complex **2** (Nu = OH) (11 mg, 5%), identified by TLC comparison with an authentic sample [4].

(vi) Addition of iodide

A solution of the allyl complex **1a** (0.30 g, 1.0 mmol) and potassium iodide (1.4 g, 14 mmol) in water (50 ml) was stirred for 7 h, then extracted with ether (2 × 50 ml). The combined extracts were dried ($MgSO_4$) and evaporated and the residue chromatographed. Ether eluted the allyl iodide complex **2f** (0.12 g, 35%), an air-stable yellow solid, m.p. 110 °C (decomp.), ν(CO)(CH_2Cl_2) 1960, 1890 cm^{-1}, δ (C_6D_6) 3.85 (5H, s, C_5H_5), 3.80 (2H, d, J = 6.2 Hz, H-3), 3.20 (1H, m, H-2), 2.40 (1H, d, J = 8.2 Hz, H-1 *syn*) and 1.96 (1H, d, J = 12.1 Hz, H-1 *anti*). Acetone then eluted the allyl alcohol complex **2** (Nu = OH) (70 mg, 30%) (cf. preceding experiment).

The same complex **2f** was also prepared as follows: Tricarbonylcyclopentadienylmanganese (2.98 g, 14.5 mmol) was photolysed in tetrahydrofuran (150 ml) for 6 h. The resultant solution was filtered, allyl iodide (7.72 g, 4.2 ml, 45 mmol) was added and the mixture stirred for 30 min, then filtered and evaporated. On chromatography, light petroleum eluted unreacted $C_5H_5Mn(CO)_3$ (2.13 g) and ether then eluted the product **2f** (0.39 g, 41%).

(vii) Addition of triphenylphosphine

The complex **1a** (0.33 g, 1.1 mmol) and triphenylphosphine (0.32 g, 1.22 mmol) were dissolved in dimethylsulphoxide (2 ml) and stirred for 15 min. The solution was then diluted with a small volume of nitromethane and the product precipitated with ether. The pure tetrafluoroborate salt of cation **2g** (0.24 g, 38%) was obtained after repeated reprecipitation from nitromethane with ether; yellow crystals, m.p. 137 °C, ν(CO) (KBr) 1945, 1870 cm^{-1}, δ (CD_3CN) 7.80 (15H, m, C_6H_5), 4.68 (5H, s, C_5H_5), 4.38 (2H, t, J = 12.3 Hz, H-1), 3.07 (1H, m, H-2), 2.49 (1H, d, J = 8.2 Hz, H-3 *syn*), and 1.58 (1H, d, J = 11.5 Hz, H-3 *anti*). Anal. Found: C, 58.7; H, 4.2. $C_{28}H_{25}BF_4MnO_2P$ calc.: C, 59.0; H, 4.4%.

(viii) Addition of pyridine

A solution of the complex **1a** (0.308 g, 1.02 mmol) and pyridine (2.93 g, 3 ml, 37 mmol) in acetone (50 ml) was stirred for 5 h, then filtered and evaporated. Crystallisation of the residue from acetone/ether gave the yellow tetrafluoroborate of the cation **2h** (0.18 g, 47%), m.p. 128–132 °C, ν(CO)(KCl) 1960, 1890 cm^{-1},

δ (CD_3COCD_3) 9.28 (2H, d, J = 5.66 Hz, H-2,6 of py), 8.71 (1H, t, J = 7.49, H-4 of py), 8.26 (2H, m, H-3,5 of py), 4.87 (5H, s, C_5H_5), 3.82 (1H, m, H-2), 2.79 (1H, d, J = 7.6 Hz, H-3 *syn*), and 2.28 (1H, d, J = 12.2 Hz, H-3 *anti*). Anal. Found: C, 46.65; H, 3.8; N, 3.5. $C_{15}H_{15}BF_4MnNO_2$ calc.: C, 47.0; H, 3.95; N, 3.7%.

Additions to the substituted cations ***1b–1h***

(i) Additions of hydride (as $NaBH_4$)

(a) Excess of sodium borohydride (0.18 g, 4.6 mmol) was added to the butenyl complex **1b** (0.294 g, 0.933 mmol) in water (100 ml) and the solution was stirred for 30 min, then extracted with ether (2 × 50 ml). The dried ($MgSO_4$) extracts were evaporated and the residue chromatographed giving the 1-butene complex **2a** (95 mg, 43%) identical (IR, NMR) with the sample described above.

(b) By the same procedure complex **1c** (0.25 g, 0.663 mmol) yielded the allylbenzene complex **2b** (0.12 g, 60%) identical (IR, NMR) with the sample described above.

(c) Under the same conditions complex **1d** (0.288 g, 0.737 mmol) gave a neutral product (58 mg, 25%), ν(CO)(CH_2Cl_2) 1947, 1880 cm^{-1}, shown by the cyclopentadienyl resonances in the NMR (s at δ 4.71 and 4.56) to be a 2.75 : 1 mixture of two components and by the methyl signals (d at δ 1.60 and t at δ 1.16) to be the isomers **3a** and **3b**, respectively.

(ii) Addition of methyllithium to complex ***1c***

Methyllithium (0.6 ml of a 1.6 *M* solution, 0.96 mmol) was added to a solution of the phenylallyl complex **1c** (0.30 g, 0.8 mmol) in acetonitrile (10 ml). The mixture was stirred for 30 min, filtered, and evaporated; the residue was chromatographed to yield an unstable amber oil (0.13 g, 52%) probably containing the 3-phenylbut-1-ene complex isomeric with compounds **3**.

(iii) Additions of triphenylphosphine

(a) Triphenylphosphine (0.65 g, 2.5 mmol) in acetone (5 ml) was added to the 1-phenylbutenyl complex **1d** (0.25 g, 0.70 mmol) in acetone (10 ml) and stirred for 15 min, then filtered and the product precipitated as very pale yellow crystals by addition of diethyl ether (50 ml). Filtration and washing with ether left a product (0.32 g, 83%) which initially still showed carbonyl stretching peaks in the infrared (1950, 1875 cm^{-1} (in KCl)) attributable to the intermediate alkene complex, but after dissolution in CD_3CN, its NMR spectrum showed only signals of the metal-free cation **4**: δ 7.65 (15H, m, C_6H_5P), 7.28 (5H, s, C_6H_5C), 6.53 (1H, dd, H-3), 6.05 (1H, m, H-2), 4.55 (1H, m, H-1) and 1.53 (3H, dd, CH_3); this spectrum was indistinguishable from that of an authentic sample of the cation **4** (as the chloride [5]) prepared from 4-phenylbut-3-en-2-ol [11] by successive treatment with thionyl chloride and triphenylphosphine.

(b) Analogous reaction of complex **1e** gave a 20% yield of the tetrafluoroborate salt of the *E*-crotyltriphenylphosphonium cation, identified by NMR comparison with an authentic commercial sample of the corresponding chloride, δ (CD_3CN) 7.75 (15H, m, C_6H_5), 5.82 (1H, m, H-3), 5.41 (1H, m, H-2), 4.03 (2H, dd, H-1) and 3.58 (3H, d, J = 8.2 Hz, H-4).

(c) The mixture obtained similarly from triphenylphosphine and complex **1f** was allowed to stand for 2 d to complete decomposition of the intermediate alkene

complex. Filtration, evaporation and addition of ether then gave the tetrafluoroborate of the cinnamyltriphenylphosphonium cation **5**, identified by NMR comparison with an authentic commercial sample of the corresponding chloride, δ (CD_3CN) 7.79 (15H, m, C_6H_5P), 7.18 (5H, s, C_6H_5C), 6.58 (1H, dd, H-3), 6.07 (1H, m, H-2) and 4.25 (2H, m, H-1).

(d) Complex **1g** similarly yielded a product (0.18 g, 61%) which contained a complex with ν(CO)(KCl) 1945, 1880 cm^{-1} and (chiefly) the tetrafluoroborate of the cation **5**, identical with the sample from the preceding experiment.

(e) Complex **1h** yielded an analogous mixture (0.14 g, 54%) containing a complex with ν(CO)(KCl) 1935, 1870 cm^{-1}, but chiefly the salt of the cation **5**.

(iv) Additions of triethylamine

(a) Following the procedure of the preceding experiments, except by replacing triphenylphosphine by an equivalent amount of triethylamine, complex **1e** yielded crotyltriethylammonium tetrafluoroborate (17%); the NMR spectrum of this salt was indistinguishable from that of an authentic sample of the same cation [12] prepared as the chloride by refluxing crotyl chloride with 1.2 molar equivalents of triethylamine in acetonitrile for 2 h. Ether precipitated the salt (76%) as colourless crystals from the cooled solution, δ (CD_3CN) 6.05 (1H, m, =C*H*CH_3), 5.50 (1H, m, =C*H*CH_2), 4.16 (2H, d, J = 7.5 Hz, CH_2C=), 3.62 (3H, d, J = 7.9 Hz, CH_3C=), 3.12 (6H, m, C*H*$_2CH_3$) and 1.22 (9H, t, J = 7.3 Hz, C*H*$_3CH_2$).

(b) Similarly complex **1f** yielded cinnamyltriethylammonium tetrafluoroborate (25%), identified by comparison of its NMR spectrum with that of an authentic sample of the corresponding chloride, prepared by the above procedure from cinnamyl chloride (2.12 g, 13.9 mmol) and triethylamine (1.82 g, 18 mmol) in acetonitrile (10 ml) and precipitated with ether (100 ml) as colourless crystals (3.39 g, 86%), δ (CD_3CN) 7.48 (5H, m, C_6H_5), 6.95 (1H, d, C*H*Ph), 6.25 (1H, m, C*H*CH_2), 3.88 (2H, d, CH_2C=), 3.22 (6H, q, C*H*$_2CH_3$), and 1.28 (9H, t, CH_3).

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