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# PREPARATION AND CHARACTERISATION OF SOME 4,4-DIMETHYLBUTA-1,3-DIENONE-TRANSITION METAL CARBONYLS

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## Summary

(4,4-Dimethylbuta-1,3-dienone)iron tricarbonyl (IIa) is obtained in 70% yield from 3,3-dimethylcyclopropene (I) and nonacarbonyldiiron and in 17% yield from I and pentacarbonyliron. Analogously (4,4-dimethylbuta-1,3-dienone)-($\eta^5$-cyclopentadienyl)manganese carbonyl (V) is formed from I and ($\eta^5$-cyclopentadienyl)(tetrahydrofuran)manganese dicarbonyl. Complexes IIa and V have been characterised by physical and chemical methods. Triphenylphosphine displaces one CO ligand from IIa to yield the corresponding triphenylphosphine-iron complex. The structure of IIa has been determined by X-ray diffraction.

## Introduction

Recently we described a new and effective synthesis of a σ-trishomotropone derivative which was formed by cotetramerisation of 3,3-dimethylcyclopropene (I) with carbon monoxide in the presence of phosphine-modified palladium(0) catalysts [1]. Later we found that tetracarbonylnickel is a good catalyst for the cotrimerisation of I with carbon monoxide [2]. Because of this a systematic study of the reaction of I with transition metal carbonyls was undertaken. The first results of this work are described below. Two dimethylvinylketeneiron complexes, IIa and IId, and a dimethylketenemanganese complex, V, have been obtained,

## Results

When nonacarbonyldiiron is treated with an excess of 3,3-dimethylcyclopropene (I) at 30—35°C in acetone, (4,4-dimethylbuta-1,3-dienone)iron tricarbonyl (IIa) is formed in 70% yield as a yellow, crystalline air-stable compound.

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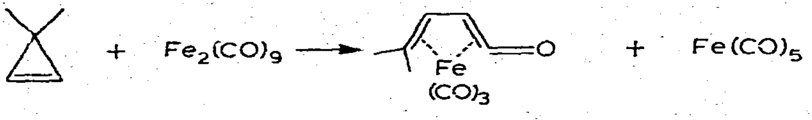
* X-ray structure analysis.

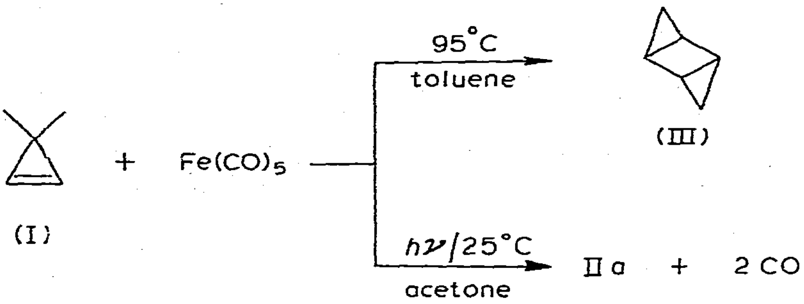
The choice of the solvent is important, since lower yields are obtained in other media. Thus, in diethyl ether or benzene the yield is less than 5% despite the fact that IIa is more easily separated from these solvents.



(1)

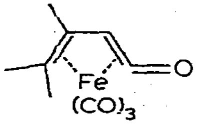
(I) (IIa)

Attempts were also made to prepare IIa from pentacarbonyliron and I. No reaction occurs at room temperature, and upon heating to 95°C the pentacarbonyl iron acts as a catalyst for the cyclodimerisation of I to 3,3,6,6-tetramethyl-*trans*-tricyclo[3.1.0.$0^{2,4}$]hexane (III). IIa is not formed under these conditions. The reaction can be brought about, however, by UV-irradiation of I and pentacarbonyliron at room temperature. The solvent is important, as in the preparation of IIa described above. In acetone IIa is obtained in a maximum yield of 17%, whereas in pentane CO is evolved but no IIa is formed.

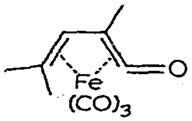


(2)

IIa is not the first vinylketeneiron tricarbonyl which has been prepared by this method. King has obtained such a complex in 5% yield from 1,3,3-trimethylcyclopropene and nonacarbonyldiiron [3]. However the available data were not sufficient to distinguish between the two possible structures IIb and IIc. We were able to decide by comparing the $^1H$ NMR spectra of IIa and IIb/IIc (see below).



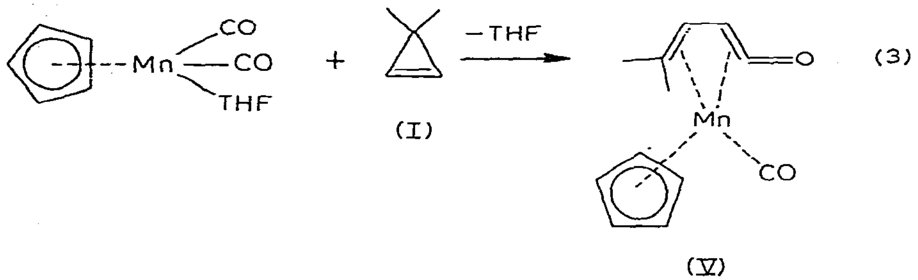
(IIb)



(IIc)

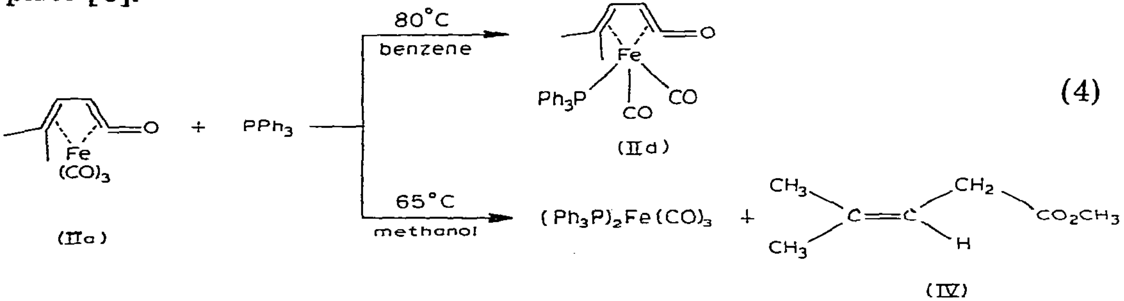
Recently (3-methoxy-1,3-butadienone)iron tricarbonyl (IIe) has been synthesised from 2-methoxyallyl chloride and nonacarbonyldiiron [4].

Besides nonacarbonyldiiron ($\eta^5$-cyclopentadienyl)(tetrahydrofuran)manganese dicarbonyl reacts with I under mild conditions. In tetrahydrofuran, the THF is displaced and at 0°C the red, crystalline(4,4-dimethylbuta-1,3-dienone)($\eta^5$-cyclopentadienyl)manganese carbonyl (V) is obtained in 57% yield.



Decacarbonyldimanganese and other carbonylmetals, such as $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$ or $Cp_2Co(CO)_2$ behave in the same way as $Fe(CO)_5$. At room temperature no reaction occurs with I, whereas at higher temperatures (>60°C) the cyclodimer III is formed catalytically without evolution of CO. At the end of the reaction the carbonylmetals can be recovered unchanged. Previously only tetracarbonylnickel [2] and octacarbonyldicobalt [5] have been shown to react with I catalytically with displacement of CO; e.g. octacarbonyldicobalt catalyses the reaction of I, carbon monoxide and methanol to give 3-methyl-2-butenemethylcarboxylate (IV) [5].

The reaction of IIa and triphenylphosphine is also solvent dependent. In boiling benzene one carbon monoxide ligand is liberated, and the new (4,4-dimethylbuta-1,3-dienone)iron complex IId is formed in 85% yield (eq. 4). In boiling methanol, however, triphenylphosphine displaces the dimethylvinylketene from IIa to give *trans*-$(Ph_3P)_2Fe(CO)_3$ in over 80% yield. The dimethylvinylketene is found as 3-methyl-2-butene-methylcarboxylate (IV) in 29% yield. The remainder apparently polymerises before the reaction with methanol takes place [6].



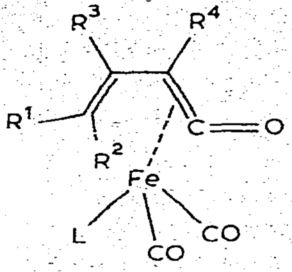
Other reactions of interest for the characterisation of IIa either did not take place or gave no definite products. Treatment of IIa with an ethereal solution of hydrochloric acid or with aqueous $H_2SO_4$ led to recovery of the starting material. This observation is interesting in view of the fact that other (1,3-diene)-iron tricarbonyls react with hydrochlorid acid to give allyliron complexes [7]. Oxidation occurred with $Ce(NH_4)_2(NO_3)_6$ at room temperature in acetone or methanol, and tars were obtained from which no definite compound could be isolated.

### Identification of the new complexes

The new dimethylvinylketenemetal complexes IIa, IId and V were characterised by $^1H$ NMR, IR, and mass spectroscopy. The structure of IIa was proved unequivocally by X-ray structure analysis.

TABLE 1

$^1$H NMR DATA FOR THE VINYLKETENEIRON COMPLEXES [a]



| Compound | L | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|---|
| IIa | CO | $CH_3$ (8.07) | $CH_3$ (8.81) | H (4.33) [b] | H (6.74 [b]) |
| IIc [3] | CO | $CH_3$ (8.10) | $CH_3$ (8.82) | H (4.39) | $CH_3$ (8.20) |
| IId | $PPh_3$ [c] | $CH_3$ (8.13) | $CH_3$ (8.85) | H (4.50) [b] | H (8.13 [d]) |
| IIe [4] | CO | H (7.09) | H (8.53) | $CH_3O$ (6.31) | H (6.48) |

[a] 100 MHz spectra values in $\tau$ (ppm) relative to TMS; measurements in $CS_2$ solutions. [b] Doublet; $J$ 4.5 Hz. [c] H(Phenyl): $\tau$ 2.72 ppm (m). [d] In $C_6D_6$ no overlapping with $R^1$; $\tau$ 8.03 ppm (t = dd; $J$(HH) ~4 Hz; $J$(HP) ~4 Hz).

The molecular weights of IIa, IId and V, as determined by mass spectrometry, were 236 (for $^{56}$Fe), 470 (for $^{56}$Fe) and 244 (for $^{55}$Mn). In the IR spectra of these complexes only the carbonylmetal bands (2050 and 1960 cm$^{-1}$ for IIa; 1985 and 1925 cm$^{-1}$ for IId, 1945 cm$^{-1}$ for V) and the ketone-carbonyl bands (1760 cm$^{-1}$ for IIa; 1690 cm$^{-1}$ for IId; 1755 cm$^{-1}$ for V) could be assigned.

The $^1$H NMR spectra of IIa and IId are shown in Table 1, together with literature data for IIb/IIc [3] and (3-methoxy-1,3-butadienone)iron tricarbonyl (IIe) [4]. The interesting feature is the large difference in the chemical shift of the olefinic protons at the positions $R^3$ (4.33—4.50 ppm) and $R^4$ (6.48—6.74 ppm) in the tricarbonyliron complexes and 8.13 ppm in IId. For IIa the doublet at 4.33 ppm is attributed to the olefinic hydrogen at the $R^3$ position because the signals are fairly broad owing to the coupling with the hydrogens of the methyl group ($R^1$) in the *trans* position. The doublet of the other olefinic

TABLE 2

CRYSTALLOGRAPHIC DATA OF COMPLEX IIa

Formula $C_9H_8FeO_4$, mol. weight 236.00.
Cell data: $a$ 9.977(5), $b$ 8.995(4), $c$ 11.579(4) Å, $\beta$ 103.36(4)°, $V$ 1011.0 Å$^3$, $Z = 4$, $d_c$ 1.550 g cm$^{-3}$.
Space group *Cc*.
Nonius CAD-4-Diffractometer, equipped with graphite monochromator, $\lambda$(Mo-$K_{\bar{\alpha}}$) 0.71069 Å. Data collected: 1039 reflections $hkl$, $\bar{h}kl$, of which 143 were considered unobserved ($I/\sigma I$) $\leq$ 2.0). Final $R$-value 0.033 ($R_w$ = 0.037) including hydrogen atoms. Anomalous dispersion of Fe was taken into account; parameters as given refer to the correct enantiomer as tested by a Hamilton significance test [a].

[a] For details of data collection and computational procedures see ref. 14. A list of structure factor may be obtained on request from the authors (C.K.).

TABLE 3

FINAL ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS (×$10^4$)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Fe | −5000(1) | −3508(1) | −2500(1) |
| O(1) | −5570(7) | −6325(6) | −3767(6) |
| O(2) | −3398(6) | −4999(7) | −334(5) |
| O(3) | −7710(6) | −3049(6) | −2006(7) |
| O(4) | −5974(5) | −2501(6) | −5013(4) |
| C(1) | −5291(7) | −5252(7) | −3267(6) |
| C(2) | −4012(7) | −4396(7) | −1146(5) |
| C(3) | −6643(6) | −3269(6) | −2190(7) |
| C(4) | −5255(6) | −2599(6) | −4044(5) |
| C(5) | −3828(6) | −2319(6) | −3491(5) |
| C(6) | −3575(5) | −1771(5) | −2323(5) |
| C(7) | −4645(5) | −1171(6) | −1848(5) |
| C(8) | −4364(9) | −909(9) | −541(6) |
| C(9) | −5700(7) | −92(7) | −2531(7) |
| H(5) | −2928(79) | −2702(88) | −3636(64) |
| H(6) | −2645(59) | −2006(58) | −1790(47) |
| H(8A) | −3579(72) | −1496(68) | −29(55) |
| H(8B) | −5299(74) | −1063(74) | −354(56) |
| H(8C) | −4038(87) | 104(99) | −289(72) |
| H(9A) | −5866(53) | −131(62) | −3350(53) |
| H(9B) | −6737(99) | −287(99) | −2480(77) |
| H(9C) | −5297(78) | 1108(82) | −2208(66) |

TABLE 4

THERMAL PARAMETERS (×$10^4$)

| Atom | $U_{1,1}$ | $U_{2,2}$ | $U_{3,3}$ | $U_{1,2}$ | $U_{1,3}$ | $U_{2,3}$ |
|---|---|---|---|---|---|---|
| Fe | 42 | 35 | 46 | −4 | 13 | 3 |
| O(1) | 113 | 57 | 115 | −27 | 46 | −28 |
| O(2) | 98 | 84 | 71 | 6 | 14 | 35 |
| O(3) | 58 | 85 | 173 | −10 | 55 | −11 |
| O(4) | 75 | 82 | 51 | −12 | −12 | 7 |
| C(1) | 64 | 44 | 76 | −10 | 27 | −3 |
| C(2) | 65 | 44 | 56 | −5 | 21 | 8 |
| C(3) | 49 | 49 | 81 | −6 | 14 | 2 |
| C(4) | 49 | 49 | 41 | −6 | 3 | −0 |
| C(5) | 40 | 45 | 50 | −6 | 11 | 7 |
| C(6) | 34 | 41 | 43 | −8 | 2 | 4 |
| C(7) | 43 | 35 | 46 | −3 | 7 | 3 |
| C(8) | 80 | 60 | 51 | 3 | 18 | −11 |
| C(9) | 55 | 46 | 69 | 10 | 15 | 10 |
| H(5) | 64 | | | | | |
| H(6) | 31 | | | | | |
| H(8A) | 42 | | | | | |
| H(8B) | 54 | | | | | |
| H(8C) | 95 | | | | | |
| H(9A) | 35 | | | | | |
| H(9B) | 113 | | | | | |
| H(9C) | 70 | | | | | |

proton ($R^4$) is found at 6.74 ppm, which is almost the same as in IIe [4]. From these assignments it is evident that Kings vinylketene complex [3] has the structure IIc and not IIb. In the spectrum of IId only the hydrogen in the $R^4$ position couples significantly with the phosphorous, and so we can conclude that the triphenylphosphine group is bonded *trans* to this hydrogen.

In the $^1$H NMR spectrum of the manganese complex V the two olefinic proton are found as doublets at 5.29 and 8.44 ppm, which is in good agreement with the proposed structure (for details see the Experimental).

*X-ray analysis of IIa*

Details of the X-ray analysis are given in Table 2, atomic parameters are listed in Table 3 and Table 4. As Fig. 1 shows, the dimethylvinylketene ligand is complexed to the tricarbonyliron unit as a four-electron ligand. The molecular arrang ment thus bears close similarity to the structure of butadieneiron tricarbonyl, in which the iron atom adopts a square pyramidal configuration [8]. A certain asymmetry is induced into the iron—carbon bonding by the carbonyl function of the ketene group. Whereas the central Fe—C bonds of the planar (±0.07 Å) 1,3-diene unit are as expected, both terminal bonds differ considerably, Fe—C(4) being remarkably short. This shortening stems from the presence of the CO-group at C(4), however, it is not reflected in the C—O bond length which is normal. The linearity of the C=C=O system is distorted on complexation of the C=C part to give an angle of 136.5(6)°. This value may be compared with the distortion angles of complexed allenes, which is found to be in the same order of magnitude (142—152°) [9]. The dihedral angle O(4)C(4)C(5)C(6) is 144.7°. As in butadieneiron tricarbonyl, the Fe—C(3) bond opposite the organic ligand is slightly shorter than the other two Fe—carbonyl bonds. Table 5 lists relevant interatomic distances and angles.

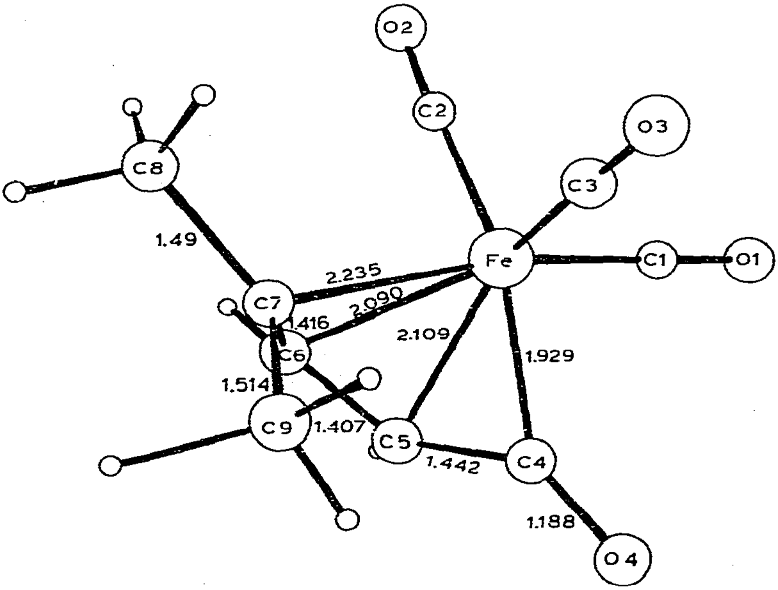


Fig. 1. Structure of (4,4-dimethylbuta-1,3-dienone)iron tricarbonyl (IIa).

TABLE 5

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

| | | | |
|---|---|---|---|
| Fe—C(1) | 1.794(7) Å | Fe—C(1)—O(1) | 175.1(7)° |
| Fe—C(2) | 1.831(7) Å | Fe—C(2)—O(2) | 177.1(6)° |
| Fe—C(3) | 1.772(7) Å | Fe—C(3)—O(3) | 176.9(6)° |
| Fe—C(4) | 1.929(6) Å | Fe—C(4)—O(4) | 146.0(5)° |
| Fe—C(5) | 2.109(6) Å | Fe—C(7)—C(8) | 118.0(4)° |
| Fe—C(6) | 2.090(5) Å | Fe—C(7)—C(9) | 113.0(4) |
| Fe—C(7) | 2.235(5) Å | C(1)—Fe—C(4) | 86.5(3)° |
| C(1)—O(1) | 1.128(9) Å | C(1)—Fe—C(7) | 170.2(3)° |
| C(2)—O(2) | 1.136(9) Å | C(2)—Fe—C(4) | 155.3(3)° |
| C(3)—O(3) | 1.150(9) Å | C(2)—Fe—C(7) | 96.3(3)° |
| C(4)—O(4) | 1.188(8) Å | C(3)—Fe—C(4) | 101.9(3)° |
| C(4)—C(5) | 1.442(9) Å | C(3)—Fe—C(7) | 84.2(3)° |
| C(5)—C(6) | 1.407(8) Å | O(4)—C(4)—C(5) | 136.5(6)° |
| C(6)—C(7) | 1.416(8) Å | C(4)—C(5)—C(6) | 115.3(5)° |
| C(7)—C(8) | 1.493(10) Å | C(5)—C(6)—C(7) | 121.6(5)° |
| C(7)—C(9) | 1.514(9) Å | C(6)—C(7)—C(8) | 118.2(6)° |
| | | C(6)—C(7)—C(9) | 122.5(6)° |

## Experimental

### *General*

All manipulations were carried out under argon. Solvents were dried in the usual manner and distilled before use. Microanalytical data for C and H were provided by Dornis and Kolbe, 4330 Mülheim a.d. Ruhr, W. Germany, and for Fe and Mn by X-ray fluorescence. Infrared spectra in the range 4000—400 $cm^{-1}$ were recorded on a Perkin—Elmer 521 Grating spectrophotometer. $^1H$ NMR spectra were recorded on a Varian HA-100 spectrometer. Mass spectra were measured on a Varian CH5 spectrometer. GLC determinations were carried out using Varian Aerograph Series 1400 *.

### *Reagents*

Pentacarbonyliron, hexacarbonyl-molybdenum and -tungsten (Merck—Schuchardt) were used without further purification. Published procedures were used to prepare nonacarbonyldiiron [10] ($\eta^5$-cyclopentadienyl)(tetrahydrofuran)-manganese dicarbonyl [11] and 3,3-dimethylcyclopropene (I) [12].

### *Preparation of (4,4-dimethyl-1,3-dienone)iron tricarbonyl (IIa) from $Fe_2(CO)_9$*

I (3.0 ml, 35.3 mmol) was added at 0°C to a suspension of nonacarbonyldiiron (7.28 g, 20.0 mmol) in acetone (50 ml). The mixture was stirred at 30—35°C for 1 h to give a brown solution. The solvent and pentacarbonyliron were removed by distillation in vacuo (25°C/12 Torr). The oily-brown residue was redissolved in acetone (5 ml) and the solution poured onto a kieselgel column. The column was washed with pentane (10 × 10 ml). The combined washings were reduced in volume to ca. 20 ml and cooled at —30°C to give a yellow-orange solid, which

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* NMR, IR and mass spectra were recorded at the Max-Planck-Institut für Kohlenforschung, 4330 Mülheim a.d. Ruhr by Prof. E.G. Hoffmann, Drs. K. Seevogel and D. Henneberg, respectively; the GLC determinations were carried out by Dr. G. Schomburg of this institute.

was isolated by filtration at −30°C. Vacuum sublimation (40°C/0.001 Torr) gave yellow crystalline IIa (3.3 g, 70%), m.p. 58–59°C (Found: C, 46.75; H, 3.46; Fe, 23.34. $C_9H_8FeO_4$ calcd.: C, 45.80; H, 3.42; Fe, 23.66%). IR ($CCl_4$ solution) 2050s, 1960s, 1760s $cm^{-1}$. Mass spectrum (70 eV): *m/e* 236 ($M^+$, rel. int. 2%), 208(18), 180(11), 152(9), 134(9), 124(35), 108(9), 96(10), 82(16), 67(12), 56(27), 28(100). For the $^1H$ NMR spectrum see Table 1.

### *Preparation of IIa from Fe(CO)$_5$*

A mixture of $Fe(CO)_5$ (4.0 ml, 5.83 g, 29.8 mmol) and I (4.8 g, 70.6 mmol) in acetone (100 ml) was irradiated with a medium pressure mercury lamp (Philips HPK 125 W) at room temperature. Gas was evolved for 0.5 h and the mixture slowly darkened. Volatiles were removed under reduced pressure (12 Torr) to give an oily residue, from which IIa (1.2 g, 17%) was sublimed at 40°C/0.001 Torr. Note: no IIa was isolated when this experiment was repeated with pentane as solvent.

### *(4,4-Dimethyl-1,3-dienone)cyclopentadienemanganese carbonyl*

I (20 ml, 23.5 mmol) was added to a solution of $CpMn(CO)_2THF$ (1.5 g, 6 mmol) in THF (90 ml) at 0°C. After stirring for 4 h, volatiles were removed by vacuum distillation (50°C, 0.5 Torr) and the residue was treated with pentane (15 ml). Upon cooling to −30°C a red crystalline solid (0.83 g, 57%) was obtained, which was recrystallised from diethyl ether/pentane (10/15 ml), m.p. 73°C, slow decomposition above 0°C. (Found: C, 59.33; H, 5.16; Mn, 22.13. $C_{12}H_{13}MnO_2$ calcd.: C, 59.03; H, 5.37; Mn, 22.50%). IR ($Et_2O$-solution): $\nu$ 1945s and 1755s $cm^{-1}$. Mass spectrum (70 eV): *m/e* 244 ($M^+$ for $^{55}Mn$). $^1H$ NMR (toluene-$d_1$, 60 MHz): $\tau$ 5.29 (d, $J$ 6.5 Hz, 1H); 6.00 (s, 5H); 8.38 and 8.44 (s + d, 4H), 9.30 ppm (s, 3H).

### *Cyclodimerisation of 3,3-dimethylcyclopropene (I) in the presence of carbonylmetal compounds*

*(a) With pentacarbonyl iron.* A mixture of I (8.0 g, 118 mmol) pentacarbonyliron (10.2 g, 52.1 mmol) and toluene (20 ml) was heated in a steel autoclave at 90–95°C for 3 h. After cooling, the mixture was distilled under vacuum (100°C/0.001 Torr) to give a yellow distillate (32.90 g) and an oily residue (2.40 g). Mass spectrometry showed that the distillate contained only $Fe(CO)_5$, III and toluene.

*(b) With hexacarbonyltungsten.* A solution of hexacarbonyltungsten (0.35 g) and I (8 g) in 10 ml THF were heated at 60°C for 30 h in a 200 ml V2A autoclave. The mixture was distilled under vacuum to give 16.5 g of distillate; b.p. 20–40°C/12 Torr; composition (GLC): 56.1% THF and 42.2% III (6.9 g, 86.5%); 1.7 g oily residue.

*(c) With hexacarbonyl molybdenum.* A colourless mixture of hexacarbonylmolybdenum (0.2 g), I (6.4 g) and THF (8 ml) was heated in a 100 ml V2A autoclave at 60°C for 16 h. The brown mixture was distilled at 20–40°C/12 Torr to give a colourless liquid (12 g) of the composition (GLC): 6.6% I (0.8 g, 12.4%); 49.9% THF and 41.1% III (4.9 g, 77%); 1.0 g dark brown residue remains

### *Reactions of (4,4-dimethyl-1,3-dienone)iron tricarbonyl (IIa)*

*(a) With triphenylphosphine in benzene.* A solution of IIa (0.38 g, 1.61 mmol)

and triphenylphosphine (1.08 g, 4.12 mmol) in benzene (15 ml) was heated under reflux for 2 h. After cooling to room temperature the volume of the solution was reduced to ca. 5 ml and pentane (15 ml) was added to precipitate yellow crystals. These were filtered off, washed with diethyl ether (15 ml) and dried in vacuum to give IId (0.65 g, 85%), m.p. 120°C decomp. (Found: C, 66.68; H, 4.49; Fe, 11.9. $C_{26}H_{23}FeO_3P$ calcd.: C, 66.40; H, 4.93; Fe, 11.87%). IR ($CCl_4$ solution): 1985s, 1925s, 1690s $cm^{-1}$. Mass spectrum (70 eV): *m/e* 470 ($M^+$, rel. int. 1%), 442(2), 414(3), 386(20), 318(60), 262(100), 240(12), 183(77), 108(39), 28(70). $^1H$ NMR see Table 1.

*(b) With triphenylphosphine in methanol.* A solution of IIa (0.49 g, 2.08 mmol) and triphenylphosphine (1.32 g, 5.04 mmol) in methanol (20 ml) was heated under reflux for 16 h. A yellow solution was formed from which a yellow precipitate separated after 1/4 h. After cooling to room temperature, the volatile material (17.0 g) was collected at —196°C by distillation under vacuum ($10^{-2}$ Torr, oil-bath temperature 40°C) and analysed by GLC: 99.73% methanol, 0.22% IV (37 mg, 29% yield; retention time identical with an authentic sample [5]).

The residue was redissolved in hot benzene (10 ml). Upon cooling, yellow crystalline *trans*-$Fe(CO)_3(PPh_3)_2$ separated. This was filtered off, washed with pentane (15 ml) and dried in vacuum (0.5 g, 39%). (Found: C, 71.50; H, 4.50. $C_{39}H_{30}FeO_3P_2$ calcd.: C, 70.58; H, 4.52%.) IR ($CS_2$ solution): $\nu$ 1882 $cm^{-1}$ (lit. [13] for *trans*-$Fe(CO)_3(PPh_3)_2$ 1887 $cm^{-1}$).

From the combined filtrates a yellow crystalline solid [0.39 g; mixture of 65% IIa and 35% $Fe(CO)_3(PPh)_2$ (estimated from its $^1H$ NMR spectrum)] was obtained by cooling to —20°C. Note: In the absence of $PPh_3$ IIa reacts with methanol to yield mainly a non-distillable tar. Only traces of IV are present in the distillate.

*(c) Attempted reaction of IIa with HCl.* A standard (0.35 *M*) solution of HCl (3 ml, ca. 1 mmol) was added to a solution of IIa (0.18 g, 0.76 mmol) in diethyl ether (7 ml). The solution was stirred at 25°C for 4 h, then the volatile components were removed. The residue was dissolved in pentane (5 ml) and the starting material (0.17 g) was recovered by filtration at —30°C.

*(d) Attempted reaction of IIa with $H_2SO_4$.* A mixture of IIa (1.60 g, 6.78 mmol), $Et_2O$ (10 ml) and $H_2SO_4$ (10 *M*; 25 ml, 0.25 mmol) was stirred at 25°C for 40 h. The organic layer was separated and dried over $MgSO_4$. After filtration volatiles were evaporated off and the residue was dissolved in pentane (20 ml). After cooling (—30°C), 1.50 g of starting material was recovered by filtration and drying.

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