# Preparation and Reactions of Triphenylphosphine and Triphenyl Phosphite Complexes of (Benzylideneacetone)dicarbonyliron(0) †

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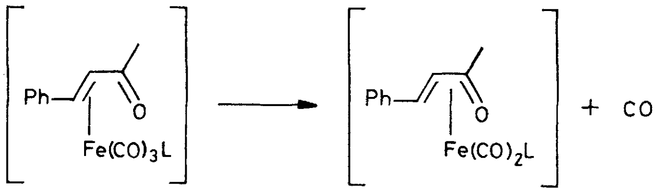
(Benzylideneacetone)dicarbonyl(triphenylphosphine)iron(0), [Fe(bda)$(CO)_2(PPh_3)$], has been prepared by irradiating [Fe$(CO)_4(PPh_3)$], in benzene, in the presence of benzylideneacetone (bda). The related triphenyl phosphite complex has been prepared thermally. These complexes are found to be useful precursors for the preparation of complexes of the type [Fe(diene)$(CO)_2$L] (L = a phosphine or phosphite ligand), offering a significant advance over the previously reported routes.

SEVERAL years ago we reported the synthesis of the complex (benzylideneacetone)tricarbonyliron(0) and commented on its usefulness as a precursor to many previously inaccessible [Fe(diene)$(CO)_3$] derivatives.[1] Since that time the complex has been applied by other workers in related syntheses.[2] The usefulness of this reagent led us to consider the preparation of its close relatives [Fe(bda)$(CO)_2$L] (bda = benzylideneacetone, L = tertiary phosphine or phosphite) since existing routes to the complexes [Fe(diene)$(CO)_2$L], which are of some importance, are not particularly good. The preparation of complexes of the type (1) and their conversion to (2) is dependent on the basicity of the Group 5 ligand L employed.[3] While (1; L = CO) is unstable with respect to conversion into (2; L = CO), (1; L = $PMe_2Ph$) is stable in refluxing benzene and [1; L = $P(OMe)_3$] is converted only slowly into (2) in competition with thermal decomposition.[4] This conversion is satisfactorily achieved when L = triphenyl phosphite.[5]



(1) (2)

## RESULTS AND DISCUSSION

In this work we have shown that, whereas reaction of [Fe(bda)$(CO)_3$] with tertiary phosphines leads to the complexes [Fe$(CO)_3(PR_3)_2$] on heating, irradiation of [Fe$(CO)_4(PPh_3)$] in the presence of bda leads to CO elimination and the formation of the very useful derivative [Fe(bda)$(CO)_2(PPh_3)$] (2). Although this work concentrates on L = $PPh_3$, other phosphine complexes may be accessible by this route. Irradiation of a mixture of [Fe$(CO)_3(PPh_3)_2$] and bda in benzene leads to the formation of the same product. In contrast, the corresponding triphenyl phosphite complex could not be produced photolytically. This complex, [2; L = $P(OPh)_3$], may be prepared in one step by treatment of [Fe(bda)$(CO)_3$] with $P(OPh)_3$ in refluxing benzene. We found that, like [Fe(bda)$(CO)_3$], the substituted complexes readily undergo bda displacement and, in the presence of cyclic dienes, *e.g.* cyclohexa-1,3-diene and cyclohepta-1,3-diene, give high yields of the appropriate [Fe(diene)$(CO)_2$L] derivative.

The complex [Fe(bda)$(CO)_2(PPh_3)$] was readily characterised on the basis of its analytical and spectroscopic properties. The $^1$H n.m.r. in $CDCl_3$ exhibited five resonances: a triplet at $\tau$ 8.10(relative intensity 1), a singlet at 7.63(3), a doublet at 4.32(1), a multiplet at 2.90(5), and a multiplet at 2.66(15). These were readily assigned to protons $H^1$ and $H^2$, the methyl group, the phenyl group (bda), and the triphenylphosphine ligand, respectively (see Table). On electron bombardment at 8 eV,† peaks at *m/e* 374 [Fe$(CO)_2(PPh_3)^+$], 346 [Fe(CO)-$(PPh_3)^+$], 318 [Fe$(PPh_3)^+$], and 262 [$PPh_3^+$] were observed. No molecular peak was observed. The i.r. spectrum exhibited two carbonyl-stretching frequencies at 1 999 and 1 939 cm$^{-1}$. On the basis of these data the structure shown in the Scheme was derived. This has been confirmed by full *X*-ray analysis.[6]

The addition of $P(OPh)_3$ in benzene to a refluxing benzene solution of [Fe(bda)$(CO)_3$] gives [Fe(bda)-$(CO)_2\{P(OPh)_3\}$] as a deep red gum. The reaction is rapid and can conveniently be followed by i.r. spectroscopy, the addition of phosphite solution being continued until the bands due to the starting material had disappeared.

The complex [Fe(bda)$(CO)_2$L] readily underwent reaction with cyclohexa-1,3-diene or cyclohepta-1,3-diene. These reactions are shown in the Scheme. In a typical experiment [Fe(bda)$(CO)_2(PPh_3)$] and the diene were heated together in benzene under nitrogen for *ca.* 12 h. After removal of the solvent and chromatography on silica, the required product [Fe(diene)$(CO)_2(PPh_3)$] was obtained in yields of *ca.* 90%. The products of these reactions, [Fe(diene)$(CO)_2$L] [L = $PPh_3$ or $P(OPh)_3$], were readily characterised on the basis of their spectroscopic data (Table) and their chemical reactivity

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† Throughout this paper: 1 eV ≈ $1.60 \times 10^{-19}$ J.

[1] J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organometallic Chem.*, 1972, **39**, 329.

[2] (*a*) D. H. R. Barton, A. A. L. Gunatilaka, T. Nakanishi, H. Patin, W. A. Widowson, and B. R. Worth, *J.C.S. Perkin I*, 1976, 821; (*b*) G. Scholes, C. R. Graham, and M. Brookhart, *J. Amer. Chem. Soc.*, 1974, **96**, 5665; (*c*) L. A. Paquette, J. M. Photis, and G. D. Ewing, *ibid.*, 1975, **97**, 3358; (*d*) M. Brookhart, G. O. Nelson, G. Scholes, and R. A. Watson, *J.C.S. Chem. Comm.*, 1976, 195.

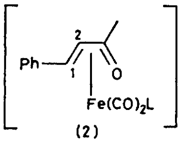
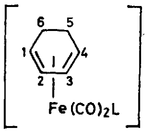
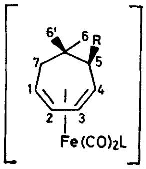
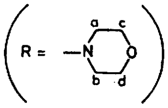
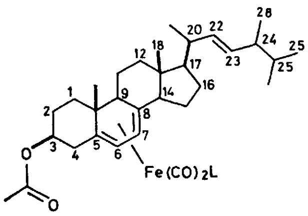
[3] G. Cardacci and G. Concetti, *J. Organometallic Chem.*, 1975, **90**, 49.

[4] A. Vessieres and P. Dixneuf, *Tetrahedron Letters*, 1974, 1499.

[5] A. Vessieres and P. Dixneuf, *J. Organometallic Chem.*, 1976, **108**, C5.

[6] V. Rivera and G. Sheldrick, unpublished work.

N.m.r. and i.r. data

| Complex | L | Proton | Chemical shift, τ | Intensity | Multiplicity (*J*/Hz) | ν(CO) [a] / cm⁻¹ |
|---|---|---|---|---|---|---|
|  (2) | $PPh_3$ [b] | $H^1$ | 8.10 | 1 | t (9) | |
| | | $H^2$ | 4.32 | 1 | dd (2.5, 9) | |
| | | $CH_3$ | 7.63 | 3 | d (2.5) | 1 999 |
| | | $C_6H_5$<br>$P(C_6H_5)_3$ | 2.90—2.66 | 20 | complex multiplet | 1 939 |
| | $P(OPh)_3$ [b] | $H^1$ | 7.18 | 1 | t (9) | |
| | | $H^2$ | 4.23 | 1 | dd (2.5, 9) | |
| | | $CH_3$ | 7.52 | 3 | d (4.5) | 2 015 |
| | | $C_6H_5$<br>$P(OC_6H_5)_3$ | 2.6—3.0 | 20 | complex multiplet | 1 958 |
|  (3) | $PPh_3$ [c] | $H^2$, $H^3$ | 5.20 | 2 | m | |
| | | $H^1$, $H^4$ | 7.38 | 2 | m | 1 981 |
| | | $H^5$, $H^{5'}$, $H^6$, $H^{6'}$ | 8.35 | 4 | m | 1 927 |
| | | $P(C_6H_5)_3$ | 2.4—2.8 | 15 | m | |
| | $P(OPh)_3$ [c] | $H^2$, $H^3$ | 5.30 | 2 | m | |
| | | $H^1$, $H^4$ | 7.05 | 2 | m | 2 067 |
| | | $H^5$, $H^{5'}$, $H^6$, $H^{6'}$ | 8.4 | 4 | m | 2 021 |
| | | $P(OC_6H_5)_3$ | 2.7—3.1 | 15 | m | |
|  (4) | $PPh_3$ [c] (R = H) | $H^2$, $H^3$ | 5.37 | 2 | m | |
| | | $H^1$, $H^4$ | 7.44 | 2 | m | 1 979 |
| | | $H^5$, $H^{5'}$, $H^7$, $H^{7'}$ | 8.08 | 4 | m | 1 925 |
| | | $H^6$, $H^{6'}$ | 8.76 | 2 | m | |
| | | $P(C_6H_5)_3$ | 2.4—3.1 | 15 | m | |
| (6) | $P(OPh)_3$ [c] (R = H) | $H^2$, $H^3$ | 5.36 | 2 | m | |
| | | $H^1$, $H^4$ | 7.40 | 2 | m | 2 065 |
| | | $H^5$, $H^{5'}$, $H^7$, $H^{7'}$ | 8.22 | 4 | m | 2 019 |
| | | $H^6$, $H^{6'}$ | 8.82 | 2 | m | |
| | | $P(OC_6H_5)_3$ | 2.7—3.1 | 15 | m | |
| (6) | $PPh_3$ [c] (R = OMe) | $H^2$, $H^3$ | 5.32 | 2 | m | |
| | | $H^1$, $H^4$ | 7.38 | 2 | m | 1 978 |
| | | $H^5$ | 6.16 | 1 | m | 1 924 |
| | | $H^6$, $H^{6'}$, $H^7$, $H^{7'}$ | 7.8—8.9 | 4 | m | |
| | | $OCH_3$ | 6.90 | 3 | s | |
| | | $P(C_6H_5)_3$ | 2.5—3.0 | 15 | m | |
| (6) | $P(OPh)_3$ [c] (R = OMe) | $H^2$, $H^3$ | 5.30 | 2 | m | |
| | | $H^1$, $H^4$ | 7.20 | 2 | m | 2 065 |
| | | $H^5$ | 6.48 | 1 | m | 2 018 |
| | | $H^6$, $H^{6'}$, $H^7$, $H^{7'}$ | 8.1—8.5 | 4 | m | |
| | | $OCH_3$ | 6.94 | 3 | s | |
| | | $P(OC_6H_5)_3$ | 2.7—3.1 | 15 | m | |
| (7) | $PPh_3$ [b] | $H^2$, $H^3$ | 5.37 | 2 | m | |
| |  | $H^1$, $H^4$ | 7.42, 7.65 | 1, 1 | m | |
| | | $H^5$ | 6.48 | 1 | m | 1 974 |
| | | $H^{6'}$ | 7.92 | 1 | m | 1 920 |
| | | $H^6$, $H^7$, $H^{7'}$ | 8.5—9.1 | 3 | m | |
| | | $H^a$, $H^{a'}$, $H^b$, $H^{b'}$ | 6.42 | 4 | t | |
| | | $H^c$, $H^{c'}$, $H^d$, $H^{d'}$ | 7.76 | 4 | t | |
| | | $P(C_6H_5)_3$ | 2.5—3.0 | 15 | m | |
|  (8) | $P(OPh)_3$ [b] | $H^6$, $H^7$ | 5.38 | 2 | m | |
| | | $H^3$ | 7.73 | | m | 1 986 |
| | | $H^{22}$, $H^{23}$ | 4.76 | 2 | m | 1 932 |
| | | Acetate | 8.03 | | s | |
| | | $P(OC_6H_5)_3$ | 2.68 | 15 | s | |
| | | Other | 8.47 | | s | 1 730 |
| | | | 8.61 | | m | (acetate) |
| | | | 8.71 | | m | |
| | | | 8.90 | | s | |
| | | | 8.97 | | s | |
| | | | 9.05 | | s | |
| | | | 9.31 | | s | |

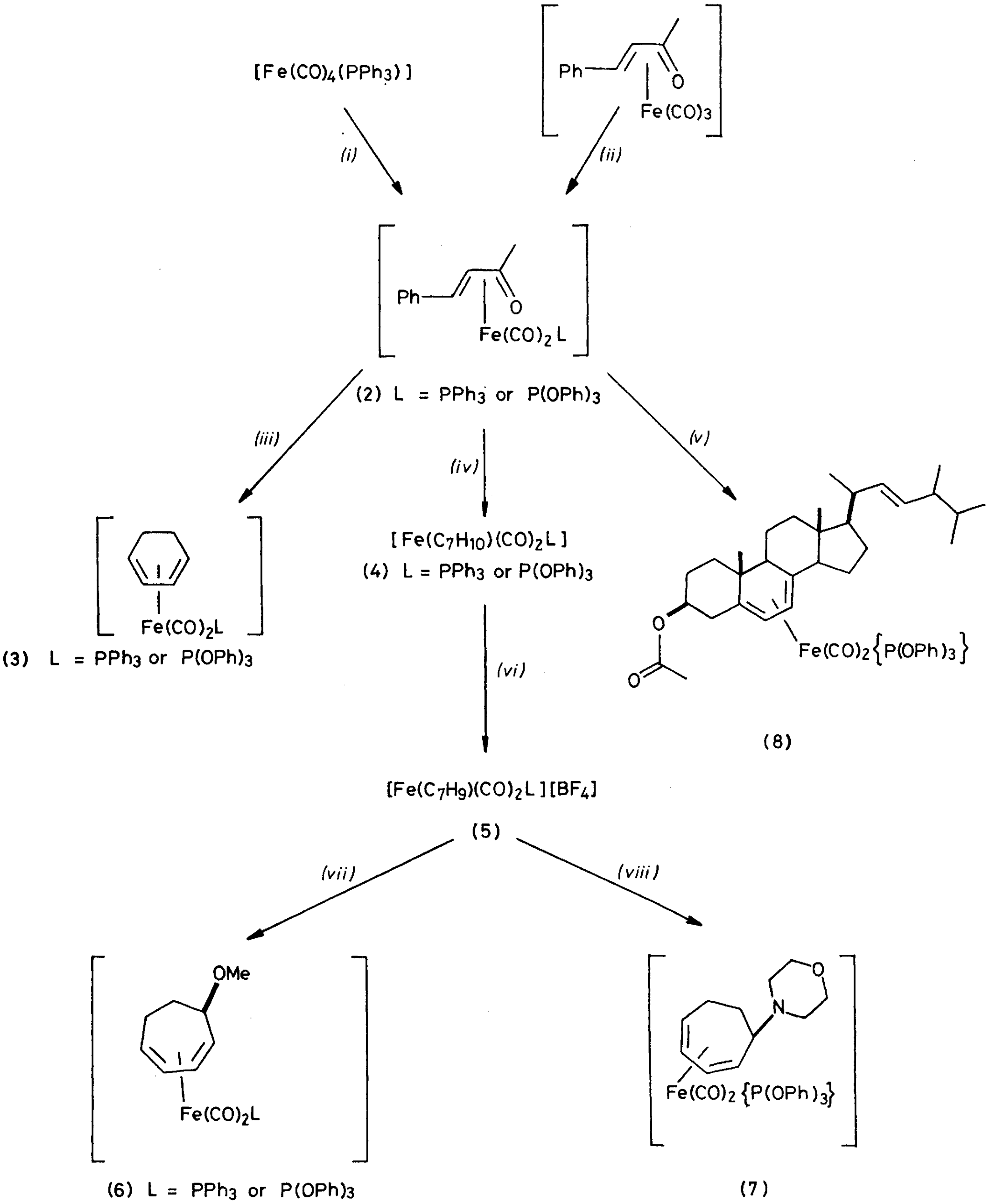
$^{13}C$ N.m.r. data (p.p.m. from $SiMe_4$ [b]): 135.24 ($C^{12}$); 131.95 ($C^{23}$); 129.45, 124.31, 120.93, 120.73 [$P(OPh)_3$]; 80.71 ($C^6$); 78.04 ($C^7$); 73.87 ($C^3$); 57.62; 55.75 ($C^{17}$); 55.33 ($C^{14}$); 42.80 ($C^{24}$); 40.06 ($C^{20}$); 39.60 ($C^{16}$); 37.79 ($C^1$); 37.36; 36.96; 36.82; 36.70; 36.62; 33.09 ($C^{25}$); 27.42; 27.17; 25.50; 23.25; 21.17; 19.95 ($C^{26}$); 19.22 ($C^{21}$); 17.58 ($C^{28}$); 11.93; 11.45 ($C^{18}$).

[a] In cyclohexane solution. [b] In $CDCl_3$ solution. [c] In $C_6D_6$ solution.

(Scheme). In the $^1H$ n.m.r. spectra, resonances for the olefinic protons of $C^1$ and $C^4$ (outer) are found at higher field for the phosphine complex than for the phosphite, although the signals due to $H^2$ and $H^3$ (inner) occur at similar values for both complexes. This may indicate greater *sp*$^3$ character at $C^1$ and $C^4$ for the phosphine complex. All the olefinic signals are at higher field than those of the tricarbonyliron complex. Interestingly, the aromatic region of all the complexes examined showed two distinct multiplets in the ratio *ca.* 2 : 1 when L = $PPh_3$, while triphenyl phosphite complexes show only one multiplet.

The complexes [Fe(diene)(CO)$_2$L] [4; diene = cyclohepta-1,3-diene, L = PPh$_3$ or P(OPh)$_3$] react with [CPh$_3$][BF$_4$] in CH$_2$Cl$_2$ to produce the cations [Fe(C$_7$H$_9$)(CO)$_2$L]$^+$ (5). Addition of [OMe]$^-$ to these cations yields specifically a 5-*exo*-substituted product [Fe(C$_7$H$_9$OMe)(CO)$_2$L] [6; L = PPh$_3$ or P(OPh)$_3$]. No evidence of the *endo* derivative was found. This is in contrast to our more recent observations of [Fe(C$_6$H$_7$-OMe)(CO)$_3$] for which both *exo* and *endo* isomers have been characterised.[7] Reaction of the cation (5; L = PPh$_3$) with morpholine is similar. In all cases, reaction with a nucleophile leads to the formation of a 1,3-diene derivative rather than the alternative $\sigma,\eta$-allyl complex.

Extension of the synthetic utility of substituted benzylideneacetoneiron(0) complexes with more complicated dienes may, however, be limited by steric effects. Transfer of the tricarbonyliron group from [Fe(bda)(CO)$_3$] has been successfully used to form a



SCHEME (*i*) *hν* and bda, benzene (24 h); (*ii*) P(OPh)$_3$, benzene reflux (15 min); (*iii*) C$_6$H$_8$, benzene reflux (6—12 h); (*iv*) C$_7$H$_{10}$, benzene reflux (6—12 h); (*v*) acetylergosterol, toluene reflux (70 h); (*vi*) [CPh$_3$][BF$_4$], CH$_2$Cl$_2$; (*vii*) Na[OMe], MeOH; (*viii*) morpholine, tetrahydrofuran

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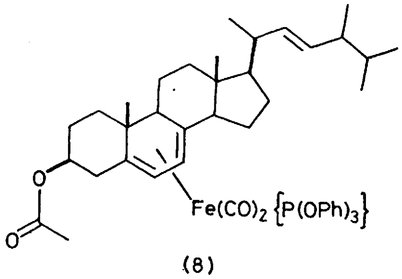
[7] K. E. Hine, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, 1975, 81.

complex at the diene function in the B ring of acetylergosterol.[2a,8,9] In attempts to effect the transfer of [$Fe(CO)_2(PPh_3)$] to the steroid, only [$Fe(CO)_3(PPh_3)_2$] and a trace amount of the tricarbonyliron–steroid complex were detected. The phosphite ligand gives more satisfactory results. Prolonged reflux of the steroid with [2; L = $P(OPh)_3$] led to the production of (8) as the major product detected in the i.r. spectrum of the reaction mixture. Isolation of this pale yellow product is difficult and the overall yield is poor.



(8)

The (acetylergosterol)dicarbonyl(triphenyl phosphite)iron(0) complex (8) is characterised by its spectroscopic properties and by microanalysis. Many resonances are observed in the $^1H$ n.m.r., spectrum: a singlet at τ 2.68 (15), and multiplets at 4.76 (2) and 5.38 (2) corresponding to the triphenyl phosphite ligand, the protons of the free Δ-22,23 olefin, and the inner protons of the complexed diene function, respectively. The many signals occurring at high field include a singlet at τ 8.03 due to the acetate methyl group. Other distinct resonances are found at τ 7.72, 8.47, 8.61, 8.71, 8.90, 8.97, 9.05, and 9.31. The i.r. spectrum exhibits bands at 1 986 and 1 932 cm$^{-1}$ due to the carbonyl ligands, and at 1 730 cm$^{-1}$ due to the acetyl group. The $^{13}C$ n.m.r. spectrum supports the proposed structure, being markedly similar to the spectra of known (acetylergosterol)tricarbonyliron complexes.[9]

These results clearly indicate that, like their parent [$Fe(bda)(CO)_3$], the phosphine and phosphite derivatives [$Fe(bda)(CO)_2L$] are a convenient source of the [$Fe(CO)_2(PPh_3)$] or [$Fe(CO)_2\{P(OPh)_3\}$] units.

## EXPERIMENTAL

Reactions were carried out under a dry dinitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer, $^1H$ n.m.r. spectra on Perkin-Elmer R12B and Varian Associates HA 100 spectrometers, and $^{13}C$ n.m.r. spectra on a Varian Associates XL 100 spectrometer. Elemental analysis was by the microanalytical department of this laboratory.

*Preparations.*— *(Benzylideneacetone)dicarbonyl(triphenylphosphine)iron*(0) (2; L = $PPh_3$). Tetracarbonyl(triphenylphosphine)iron [10] (666 mg, 1.55 mmol) and benzylideneacetone (226 mg, 1.55 mmol) were dissolved in benzene (200 cm$^3$) and the resulting solution was irradiated for 24 h in a quartz annular reactor, using a 125-W medium-pressure mercury lamp. The resulting orange-red solution was chromatographed on $SiO_2$. Elution with benzene gave small amounts of unchanged [$Fe(CO)_4(PPh_3)$] and a second elution with 10% ethyl acetate–benzene gave the product as orange-red crystals [650 mg (80%), m.p. 138—140 °C] after recrystallisation from light petroleum (b.p. 30—40 °C) (Found: C, 69.0; H, 4.90; P, 5.95. Calc. (for $C_{30}H_{25}FeO_3P$: C, 69.2; H, 4.85; P, 5.95%).

*(Benzylideneacetone)dicarbonyl(triphenyl phosphite)iron*(0) (2; L = $P(OPh)_3$]. (Benzylideneacetone)tricarbonyliron (292 mg, 1.02 mmol) and triphenyl phosphite (319 mg, 0.71 mmol) were dissolved in benzene (60 cm$^3$) and the solution was heated under reflux for 15 min. More $P(OPh)_3$ was added in benzene solution, in small portions, until all the bands due to the starting material had vanished from the i.r. spectrum of the reaction mixture. The solvent was removed *in vacuo* to leave an orange gum which was recrystallised twice from light petroleum to yield (benzylideneacetone)dicarbonyl(triphenyl phosphite)iron(0) [2; L = $P(OPh)_3$] as orange-red crystals (350 mg, 60%). The product was identified spectroscopically.

*Ligand-substitution Reactions of* [$Fe(bda)(CO)_2L$] [L = $PPh_3$ *or* $P(OPh)_3$].—*(Benzylideneacetone)dicarbonyl(triphenylphosphine)iron*(0) (2; L = $PPh_3$) *with cyclohepta*-1,3-*diene*. Complex (2; L = $PPh_3$) (520 mg, 1 mmol) and cyclohepta-1,3-diene (940 mg, 10 mmol) were heated under reflux in benzene (20 cm$^3$) for 12 h. The reaction mixture was chromatographed on silica. Elution with benzene gave a yellow gum. Recrystallisation from pentane gave dicarbonyl(η-cyclohepta-1,3-diene)(triphenylphosphine)-iron(0) (4; L = $PPh_3$) as yellow crystals (410 mg, 88%) (Found: C, 69.7; H, 5.70; P, 6.45. Calc. for $C_{27}H_{25}FeO_2P$: C, 69.2; H, 5.40; P, 6.60%).

*(Benzylideneacetone)dicarbonyl(triphenyl phosphite)iron*(0) [2; L = $P(OPh)_3$] *with cyclohepta*-1,3-*diene*. Complex [2; L = $P(OPh)_3$] (248 mg, 0.5 mmol) and cyclohepta-1,3-diene (230 mg, 2.5 mmol) were heated under reflux in benzene (10 cm$^3$) for 6 h. The reaction mixture was chromatographed on silica. Elution with benzene gave the dicarbonyl(η-cyclohepta-1,3-diene)(triphenyl phosphite)-iron(0) [4; L = $P(OPh)_3$] as a yellow oil (160 mg, 63%), characterised spectroscopically (see Table).

(2; L = $PPh_3$) *with cyclohexa*-1,3-*diene*. The reaction was carried out as with cyclohepta-1,3-diene. Dicarbonyl-(η-cyclohexa-1,3-diene)(triphenylphosphine)iron(0) (3; L = $PPh_3$) was obtained in 90% yield and identified spectroscopically (see Table).

[2; L = $P(OPh)_3$] *with cyclohexa*-1,3-*diene*. The reaction was carried out as with cyclohepta-1,3-diene. Dicarbonyl-(η-cyclohexa-1,3-diene)(triphenyl phosphite)iron(0) [3; L = $P(OPh)_3$] was obtained in 70% yield and was characterised spectroscopically (see Table).

[2; L = $P(OPh)_3$] *with acetylergosterol*. The complex (480 mg, 0.89 mmol) and acetylergosterol (367 mg, 0.84 mmol) were heated under reflux in toluene (40 cm$^3$) for 70 h. The resulting solution was reduced in volume and filtered, when cool, through a 10-cm column of Mallinckrodt silicic acid (100 mesh). A fast-moving pale yellow band preceded the large yellow band which was collected, eluting with toluene. The solvent was removed *in vacuo* to leave a yellow gum which was extracted overnight with methanol, in which acetylergosterol is insoluble. After filtration, this yellow extract was evaporated to dryness and repeated chromatography on preparative t.l.c. plates ($SiO_2$) eluting with benzene produced a pale yellow gum from which

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[8] G. Evans, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1976, **102**, 507.

[9] G. Evans, Ph.D. Thesis, 1974, University of Cambridge.

[10] A. F. Clifford and A. K. Mukherjee, *Inorg. Synth.*, 1966, **8**, 185.

(acetylergosterol)dicarbonyl(triphenyl phosphite)iron(0) (8) separated as the last of the toluene was removed on the vacuum line (Found: C, 68.6; H, 7.40. Calc. for $C_{50}H_{61}FeO_7P·MeOH$: C, 68.6; H, 7.35%).

*Proton Abstraction from Complexes* (4).—*Preparation of dicarbonyl*(1—5-η-*cycloheptadienylium*)(*triphenylphosphine*)-*iron*(0) *tetrafluoroborate* (5; L = $PPh_3$). Complex (4; L = $PPh_3$) (300 mg, 0.91 mmol) was dissolved in dry dichloromethane (15 cm$^3$). Trityl tetrafluoroborate (300 mg, 0.91 mmol) was added and the reaction mixture stirred for 20 min at room temperature. The dienylium salt was precipitated by addition of diethyl ether. The product (0.27 g, 76%) was obtained by filtration and washing with diethyl ether and was identified as (5; L = $PPh_3$) by its i.r. spectrum (CO stretching in $CH_2Cl_2$ at 2 045 and 2 004 cm$^{-1}$).

*Preparation of dicarbonyl*(1—5-η-*cycloheptadienylium*)-(*triphenyl phosphite*)*iron*(0) *tetrafluoroborate* [5; L = $P(OPh)_3$]. Complex [4; L = $P(OPh)_3$] (160 mg, 0.31 mmol) was dissolved in dry dichloromethane and treated with trityl tetrafluoroborate (150 mg, 0.45 mmol) as above. Precipitation and washing with diethyl ether produced 0.085 g (46%) of the product as a pale yellow powder (Found: C, 53.0; H, 4.2; P. 5.1. Calc. for $C_{27}H_{24}BF_4FeO_5P$: C, 53.8; H, 4.0; P, 5.1%), CO stretching in $CH_2Cl_2$ at 2 065 and 2 019 cm$^{-1}$.

*Reactivity of Complexes* (5) *towards Nucleophiles*.—(5; L = $PPh_3$) *and methoxide*. The dienylium salt (100 mg, 0.18 mmol) was added to a solution of sodium methoxide (100 mg, 1.8 mmol) in methanol and the reaction mixture was stirred for 30 min at 0 °C. Water was added (30 cm$^3$) and the mixture extracted with diethyl ether (2 × 30 cm$^3$). The extracts were dried over Mg[$SO_4$] and the solvent evaporated without heating. Dicarbonyl(η-5-methoxycyclohepta-1,3-diene)(triphenylphosphine)iron(0) (6; L = $PPh_3$) (80 mg, 89%) was obtained as a yellow powder (Found: C, 67.5; H, 5.80; P, 6.10. Calc. for $C_{28}H_{27}FeO_3P$: C, 67.5; H, 5.75; P, 6.20%), *M* 498 (mass spectrum) (Calc: 498.37).

[5; L = $P(OPh)_3$] *with methoxide*. The reaction was carried out as above. Dicarbonyl(η-5-methoxycyclohepta-1,3-diene)(triphenyl phosphite)iron(0) [6; L = $P(OPh)_3$] was obtained as a yellow oil and identified spectroscopically (see Table).

(5; L = $PPh_3$) *with morpholine*. The dienylium salt (100 mg, 0.18 mmol) was added to a solution of morpholine (150 mg, 0.18 mmol) in tetrahydrofuran (10 cm$^3$). The mixture was stirred at 0 °C for 30 min. Water was added (30 cm$^3$) and the mixture extracted with diethyl ether (2 × 30 cm$^3$). The extracts were dried over Mg[$SO_4$] and the solvent was evaporated without heating, leaving a yellow gum. Recrystallisation from pentane gave dicarbonyl(η-5-morpholinocyclohepta-1,3-diene)(triphenylphosphine)iron as a yellow powder, 100 mg (95%), m.p. 74—77 °C (Found: C, 67.2; H, 6.25; N, 2.45; P, 5.60. Calc. for $C_{31}H_{32}FeNO_3P$: C, 67.3; H, 5.85; N, 2.55; P, 5.60%), *M* 553 (mass spectrum) (Calc: 553.43).

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