

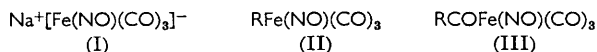
Hydrocarbon–Metal Nitrosyls. Part II.† Acyl Derivatives of Tricarbonylnitrosyliron, and their Reactions with Dienes

By F. M. Chaudhari, G. R. Knox, and P. L. Pauson, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow

Sodium tricarbonylnitrosylferrate reacts with alkyl halides to give tricarbonylnitrosylacylirons. These react with dienes to yield allyl complexes substituted by acyl groups on the terminal carbon atom of the diene used. Reaction with triphenylphosphine led to displacement of one molecule of carbon monoxide from these products: with the allyl complexes there was also some replacement of nitric oxide and hydrogen with formation of acyldienedicyliron(triphenylphosphine)irons.

ACYL derivatives of tetracarbonylcobalt are recognised as important intermediates in hydroformylation and related carbonylation reactions. Their formation and reactions have been studied extensively and have shed much light on the mechanisms of such cobalt carbonyl catalysed processes. It appeared worthwhile to study other analogous systems in this connection and the ready availability¹ of sodium tricarbonylnitrosylferrate, iso-electronic with sodium tetracarbonylcobaltate, provided an ideal opportunity to do so.

The present studies were therefore closely modelled on those of Heck and Breslow²⁻⁸ and others⁹⁻¹¹ in the cobalt series. As in the previous studies, we find that reaction of the sodium salt (I) with alkyl halides normally leads to the acyl complexes (III) without



isolation of the expected intermediate alkyls (II). Thus, methyl iodide, ethyl iodide, benzyl chloride, chloromethyl methyl ether, and ethyl chloroacetate reacted to give the corresponding acyls (III; R = Me, Et, PhCH₂, MeO·CH₂ and EtO·CO·CH₂, respectively). Due to their low stability these were only identified spectroscopically and by further conversion to the triphenylphosphine substituted products (IV). Most conveniently the latter were isolated by adding the phosphine to the initial reaction mixture. However, by isolation, in selected



cases, of the crude tricarbonyl (III) it was possible to demonstrate that the reaction with phosphine involves displacement of carbon monoxide from a preformed

acyl derivative [reaction (1)]. Alkyl migration during phosphine addition to an alkyl complex [reaction (2)], may be an additional pathway. Reaction of the sodium salt (I) with acyl halides proceeds much less smoothly and gives the acyl complexes (IV) only in low yield. Whereas the acetyl compound (IV; R = Me) was obtained in moderate amount by this route, the unstable aromatic derivative (IV; R = Ph), accessible only through the acid chloride, was obtained only in trace quantities. By contrast, the acyl halide approach was found to be preferable to the alkyl halide method in the cobalt series.³ While the present work was in progress, Hieber, Klingshirn and Beck¹² reported the perfluoroacyl derivatives (IV; R = CF₃ or C₂F₅). A more complex acyl derivative has been prepared¹³ from triphenylcyclopropenyl bromide.

The reaction of the salt (I) with bromoacetonitrile was unique, in that the alkyl derivative (II) was apparently produced and isolated as the phosphine substituted complex (V). Although its formulation is not proved rigorously by the available evidence, both the analytical and infrared data suggest structure NC·CH₂·Fe(NO)(CO)₂(PPh₃) (V). Although most of the acyl complexes [(III) and (IV)] are characterised by their acyl–CO stretching frequencies near 1670 cm.⁻¹ this peak may be obscured by overlap with the NO stretching frequency as appears to happen in the phenacyl complex (IV; R = PhCH₂). The other halides which react without carbonyl insertion are the allylic halides, e.g., allyl or but-2-enyl bromide. These give the π-allylic complexes (VI; R = H or CH₃). The cyclopentenyl and cyclohexenyl complexes (VII; n = 2 or 3) were prepared similarly. σ-Allyl complexes have been shown to be intermediate in the corresponding reactions of the pentacarbonylmanganese¹¹ series, but no attempts were made to isolate such intermediates [e.g., (II);

† Part I, Mushtaq Ahmad and G. R. Knox, *J. Organometallic Chem.*, 1967, in press.

¹ U.S.P. 2,865,707/1958 (*Chem. Abs.*, 1959, **53**, 9592); W. Hieber and H. Beutner, *Z. Naturforsch.*, 1960, **15b**, 323; *Z. anorg. Chem.*, 1963, **319**, 285; 1963, **320**, 101.

² R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1962, **84**, 2499.

³ R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 4023.

⁴ R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 651.

⁵ R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 750.

⁶ R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 1097.

⁷ R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 655.

⁸ R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 3381, 3383.

⁹ W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, 1958, **13b**, 192.

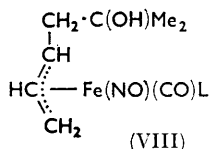
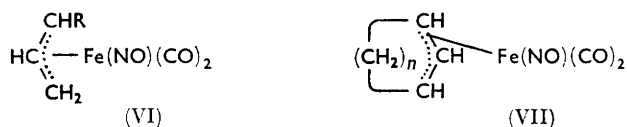
¹⁰ U.S.P. 2,600,571/1952; H. B. Jonassen, R. I. Stearn, J. Kentamaa, D. W. Moore, and A. G. Whittaker, *J. Amer. Chem. Soc.*, 1958, **80**, 2586; C. L. Aldridge, H. B. Jonassen, and E. Pulkkinen, *Chem. and Ind.*, 1960, 374; D. W. Moore, H. B. Jonassen, T. B. Joyner, and A. J. Bertrand, *ibid.*, p. 1304; A. J. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, 1963, **2**, 601.

¹¹ W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.

¹² W. Hieber, W. Klingshirn, and W. Beck, *Chem. Ber.*, 1965, **98**, 307.

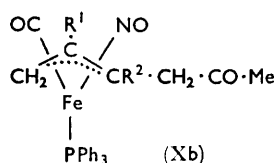
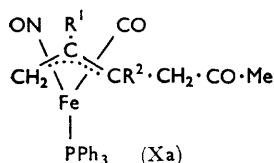
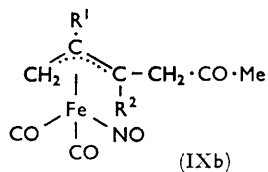
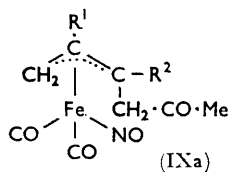
¹³ C. E. Coffey, *J. Amer. Chem. Soc.*, 1962, **84**, 118.

$R = CH_2 \cdot \dot{C}H \cdot CH_2$] in the present work. The but-2-enyl complex (VI; $R = CH_3$) was also prepared by the addition of butadiene to the hydride, $HFe(NO)(CO)_3$ and isoprene reacted similarly. The unstable hydride¹ was prepared by treatment of the sodium salt (I) with



acetic acid at -75° and used without isolation. Due to contamination of the hydride with acetone from the preparation of the salt (I), an interesting by-product was obtained for which we suggest structure (VIII; $L = \text{CO}$) on the basis of spectroscopic data and analysis of this and the derived phosphine complex (VIII; $L = \text{PPh}_3$); similar products were obtained in the isoprene reaction or when diethyl ketone was deliberately added in place of acetone. A somewhat related addition of acetone in nickel carbonyl-allyl chloride reactions has been observed by Cassar and Chiusoli.¹⁴

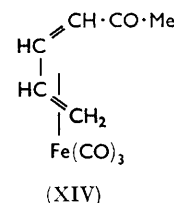
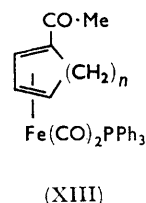
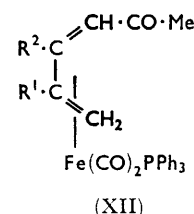
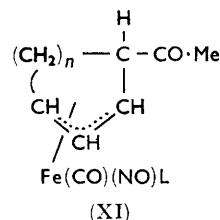
Heck⁸ has shown that acylcobalt tetracarbonyls can also add to conjugated dienes and this behaviour was again paralleled by the compounds (II). Most of these experiments were performed with the acetyl compound (II; $R = \text{Me}$) although preliminary experiments with the propionyl (II; $R = \text{Et}$) and phenylacetyl (II; $R = \text{PhCH}_2$) complexes show clearly that these behave similarly. Unfortunately, none of the initially formed compounds (IX), and only a single example of their triphenylphosphine substitution products (X), could be isolated crystalline and analytically pure. The open chain dicarbonyls (IX) can exist in two isomeric forms (IXa) and (IXb) and *cis-trans* isomerism of a different type arises in the cyclic analogues (XI). Although it



might be expected that one of these isomers should be preferred in these cases, the same cannot be said for the additional diastereoisomerism which arises when any of these compounds (IX) or (XI) is treated with triphenyl

phosphine. This diastereoisomerism is formulated in structures (Xa) and (Xb). In view of the bulky nature of the groups attached to iron in the latter compounds, rotational isomerism may be an additional possibility. We believe that at least in these phosphine-substituted complexes, the presence of more than one isomeric form is a factor preventing crystallisation.

Fortunately the reaction with phosphine did not, in this series, lead exclusively to replacement of carbon monoxide, but always gave, in addition to the products (X) or (XI; $L = \text{PPh}_3$) the corresponding diene complexes (XII) or (XIII) formed by displacement of nitric oxide and hydrogen. These acyl-diene complexes



proved to be readily crystallisable and identifiable. A similar reaction occurs with pyridine, but with abstraction of carbon monoxide from another molecule rather than incorporation of pyridine. In this way the oxohexenyl complex (IX; $R^1 = R^2 = \text{H}$) derived from butadiene gave tricarbonyl-5-oxohexa-1,3-dieneiron (XIV) identical with a sample prepared by acetylation¹⁵ of tricarbonylbutadieneiron.

The unsymmetrical diene, isoprene, undergoes addition of both the hydride $HFe(\text{CO})_3\text{NO}$, and the acyl-complex (III) exclusively at the 1-position, as shown by the properties of the products and the derived diene complex (XII; $R^1 = \text{H}$; $R^2 = \text{Me}$) and in good agreement with studies in the cobalt series.^{8,10}

Nomenclature.—Names based on "allylmetal" have been used to date by all workers in this rapidly expanding field. We believe that this is unsatisfactory for the more complex derivatives (notably the cyclic compounds included in the present and other recent studies). It also contravenes basic rules of established organic nomenclature [and have the Editor's support]. We therefore suggest that the systematic name of the organic ligand should be used and the positions of the enyl system to which the metal is attached should be indicated by a set of three numbers. Thus compound (VIII) ($L = \text{CO}$) is dicarbonylnitrosyl-(5-hydroxy-5-methyl-1,2,3-hexenyl)iron and (XI) ($L = \text{CO}$; $n = 1$)

¹⁴ L. Cassar and G. P. Chiusoli, *Tetrahedron Letters*, 1965, 3295; *Chem. and Ind.*, 1966, 48, 323.

¹⁵ U.S.P. 3,149,135/1964 (*Chem. Abs.*, 1965, 62, 7054).

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is dicarbonylnitrosyl-(4-acetylcyclo-1,2,3-pentenyl)iron. Similar names are employed throughout the following Experimental section.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. Alumina, unless otherwise indicated, refers to Spence's "Grade H," deactivated by exposure to air for 6 hr. "Neutral alumina" refers to the same grade, stored over ethyl acetate (1–2 days), washed with water and methanol, and dried at 160° for 4 hr. Melting points were determined in evacuated capillaries. Infrared spectra, unless otherwise stated, were recorded in KCl discs. N.m.r. spectra were obtained in carbon disulphide solutions on a Perkin-Elmer 40 Mc./sec. instrument with tetramethylsilane as internal standard.

Acyl Complexes.—The following procedure (a) for the acetyl complex is typical of the method used for the subsequent examples of the phosphine-substituted acyls.

Dicarbonylnitrosyl(triphenylphosphine)acetyliron (IV; R = Me). (a) From methyl iodide. To a solution of the salt (I) (2.7 g., 13.5 mmoles) and triphenylphosphine (3.4 g., 13 mmoles) in tetrahydrofuran (50 ml.), methyl iodide (2 ml., 35 mmoles) in tetrahydrofuran (10 ml.) was added, and the mixture stirred for 45 min. After filtration (kieselguhr), the solvent was removed under reduced pressure and the residue chromatographed on alumina. Ligroin removed triphenylphosphine and traces of dicarbonylnitrosyliron. Benzene then eluted the *acetyl complex* (IV; R = Me) (5 g., 80%), which crystallised from ether–n-pentane to give yellow crystals, m. p. 108°; ν_{\max} (in CCl₄) at 2033 and 1969 (–C=O), 1730 (NO) and 1667 cm.⁻¹ (COR). Its n.m.r. spectrum consisted of a complex group of peaks centred at τ 2.6 (aromatic protons) and a singlet at 7.28 (CH₃) of relative intensity 5:1 (Found: C, 59.4; H, 4.0; N, 3.3. C₂₂H₁₈FeNO₄P requires C, 59.1; H, 4.05; N, 3.1%).

(b) From acetyl chloride. To the salt (I) (1.84 g., 9 mmoles) and triphenylphosphine (2.62 g., 10 mmoles) in ether (50 ml.) a solution of acetyl chloride (0.8 g., 10 mmoles) in ether (5 ml.) was added at 0°, and the mixture was stirred at this temperature for 1 hr. Working up as above gave the acetyl complex (IV; R = Me) (0.5 g., 12%) and much dinitrosylbis(triphenylphosphine)iron.

Dicarbonylnitrosyl(triphenylphosphine)propionyliron (IV; R = Et). With ethyl iodide, this was obtained in low yield as an unstable yellow oil; ν_{\max} (in CCl₄) at 2000 and 1942 (–C=O), 1724 (NO) and 1667 cm.⁻¹ (COR).

Dicarbonylnitrosyl(triphenylphosphine)(methoxyacetyl)iron (IV; R = CH₂·OMe). Chloromethyl methyl ether (1.45 g., 18 mmoles) with the salt (I) (3.6 g., 18 mmoles) and triphenylphosphine (4.7 g., 18 mmoles) in ether solution (100 ml.) gave a mixture of Fe(CO)₂(NO)₂, Fe(NO)₂(PPh₃)₂, and the product (IV; R = CH₂·OMe) (0.6 g.) as a yellow oil; ν_{\max} (in CCl₄) at 2020 and 1961 (C=O), 1724 (NO) and 1667 cm.⁻¹ (COR).

Dicarbonylnitrosyl(triphenylphosphine)(phenylacetyl)iron (IV; R = PhCH₂). Benzyl chloride (6 ml., 0.05 mole) in ether (15 ml.) was added to the salt (I) (5 g., 0.025 mole) and triphenylphosphine (6.5 g., 0.025 mole) in ether (100 ml.) and the mixture stirred for 2.5 hr. The *phenylacetyl complex* (IV; R = PhCH₂) (8 g., 59%) was eluted with ligroin and crystallised from dichloromethane–n-pentane; it formed red crystals, m. p. 135°; ν_{\max} (in CCl₄) at 2020

and 1957 (C=O) and 1724 cm.⁻¹ (NO and COR?); τ 2.7 (complex; aromatic protons) and 6.22 (singlet; CH₂) in the intensity ratio 10:1 (Found: C, 64.8; H, 4.5; N, 3.0; P, 6.2. C₂₈H₂₂FeNO₄P requires C, 64.3; H, 4.2; N, 2.7; P, 5.9%).

Heating this compound (3.2 g., 6 mmoles) in tetrahydrofuran (100 ml.) under reflux with sodium methoxide (0.33 g., 6 mmoles) in methanol (10 ml.) for 3 hr., gave, after removal of solvent and chromatography, methyl phenylacetate (0.56 g., 62%) characterised by conversion into *N*-benzylphenylacetamide, m. p. 120°.

Reduction of the complex (IV; R = PhCH₂) (2.1 g.) by stirring with lithium aluminium hydride (1 g.) in ether (150 ml.) yielded phenylethanol (0.3 g.), identified by comparison of its i.r. spectrum with that of an authentic sample.

Dicarbonylnitrosyl(triphenylphosphine)(ethoxymalonyl)iron (IV; R = EtO·CO·CH₂). Ethyl chloroacetate (5 ml., 45 mmoles) in tetrahydrofuran (10 ml.) was added to the salt (I) (3.4 g., 17 mmoles) and triphenylphosphine (4.5 g., 17 mmoles) in tetrahydrofuran (50 ml.) at 0° and the mixture was stirred for 2 hr. Following bands containing Fe(CO)₂(NO)₂ and PPh₃, and then Fe(NO)₂(PPh₃)₂, eluted from the chromatogram with ligroin and benzene–ligroin (1:1), respectively, benzene–ether (1:1) eluted the *ethoxymalonyl complex* (IV; R = EtO·CO·CH₂) (4 g., 45%), m. p. 108° (decomp.); (from ether–n-pentane); ν_{\max} (in CCl₄) at 2033, 1965 (–C=O), 1754 (NO and ester CO), and 1689 cm.⁻¹ (COR); there were n.m.r. peaks at τ 2.6 (complex; aromatic protons), 6.05 (quadruplet; CO₂·CH₂·CH₃), 7.4 (singlet; CH₂·CO₂Et) and 8.88 (triplet; CO₂·CH₂·CH₃) of relative intensity 15:2:2:3 (Found: C, 57.5; H, 4.5; N, 2.8. C₂₅H₂₆FeNO₆P requires C, 57.8; H, 4.3; N, 2.7%).

Dicarbonylnitrosyl(triphenylphosphine)(cyanomethyl)iron (V). Chloroacetonitrile (3 g., 40 mmoles) in ether (5 ml.) was added to the salt (I) (3.4 g., 17 mmoles) and triphenylphosphine (4.5 g., 17 mmoles) in ether (100 ml.) at 0°; the mixture was stirred at this temperature for 4 hr. and then left overnight. After removal of the solvent under reduced pressure the residue was chromatographed on alumina. Ligroin–benzene (1:1) eluted dinitrosylbis(triphenylphosphine)iron, and ether–benzene (1:1) then eluted the *cyanomethyl complex* (V) (4 g.; 50%) which crystallised from dichloromethane–n-pentane to give red crystals, m. p. 130–140° (decomp.); ν_{\max} (in CCl₄) at 2222 (CN), 2020 and 1976 (CO), and 1751 cm.⁻¹ (NO); there were n.m.r. peaks at τ 2.5 (complex; aromatic H) and 7.7 (singlet CH₂) of relative intensity 15:2 (Found: C, 58.9; H, 4.1; N, 6.4. C₂₂H₁₇FeN₂O₃P requires C, 59.5; H, 3.9; N, 6.3%).

Dicarbonylnitrosyl(triphenylphosphine)benzoyliron (IV; R = Ph). Benzoyl chloride (3 g., 21 mmoles) in ether (10 ml.) was added to the salt (I) (3.4 g., 17 mmoles) and triphenylphosphine (4.5 g., 17 mmoles) in ether (100 ml.) at 0°, and the mixture was stirred for 1 hr. Filtration (kieselguhr) and evaporation was followed by chromatography on silica gel. Ligroin–benzene (4:1) eluted Fe(CO)₂(NO)₂, PPh₃, and Fe(NO)₂(PPh₃)₂, and benzene–ether (1:1) then eluted the *benzoyl compound* (IV; R = Ph). Only a very small amount was isolated and this could not be further purified due to its instability; it had ν_{\max} (in CCl₄) at 2000 and 1942 (CO), 1724 (NO), and 1653 cm.⁻¹ (COR).

Dicarbonylnitrosyl- π -allyliron (VI; R = H).—Allyl bromide (4.2 g., 35 mmoles) in ether (10 ml.) was added to the

salt (I) (6.7 g., 34 mmoles) in ether (150 ml.) and the mixture stirred for 2 hr. at 25°, then filtered (kieselguhr) and the filtrate evaporated at 0° under reduced pressure. The residue was chromatographed on alumina. Elution with pentane and distillation at 20°/20 mm. gave the complex (VI; R = H) (4.5 g.; 71%) as a red oil, whose i.r. spectrum was identical with that of an authentic specimen.

When this compound (2.1 g., 11.4 mmoles) and triphenylphosphine (3 g., 12 mmoles) were heated under reflux in tetrahydrofuran (60 ml.) for 6 hr. and the resultant product, after evaporation, was chromatographed on alumina, benzene-ligroin (1:4) eluted carbonylnitrosyl(triphenylphosphine)- π -allyliron (2.6 g., 55%). This formed shiny red crystals, m. p. 174°, from ether-pentane and was identified by mixed m. p. and i.r. comparison with an authentic sample.

When the reaction was repeated, but with the addition of triphenylphosphine (12 g., 46 mmoles) to the salt (I) 8.8 g., 44 mmoles) before the addition of allyl bromide (6 g., 50 mmoles), the product was a mixture of the above dicarbonyl (4.8 g.; 58%) and its triphenylphosphine substitution product (3.8 g.; 20%).

Dicarbonylnitrosyl- π -but-2-enyliron (VI; R = Me).—But-2-enyl bromide (2.2 g., 16 mmoles) in ether (5 ml.) was added to the salt (I) (3.2 g., 16 mmoles) in ether (50 ml.). Working up as in the preceding experiment gave the π -but-2-enyl complex (VI; R = Me) (1.6 g.; 49%), b. p. 25°/20 mm., identified by i.r. comparison with an authentic sample and by conversion, by the method described in the preceding experiment, into *carbonylnitrosyl(triphenylphosphine)- π -but-2-enyliron* (46%). The latter formed red crystals, m. p. 119°, from ether-pentane; it had ν_{\max} (in CCl₄) at 1930 (CO) and 1685 cm⁻¹ (NO) (Found: C, 63.7; H, 4.7; N, 3.3. C₂₃H₁₇FeNO₂P requires C, 64.1; H, 5.1; N, 3.3%).

Reaction of Tricarbonylnitrosylhydridoiron with Butadiene.—To butadiene (10 ml.) and the salt (I) (6 g., 30 mmoles) in ether (100 ml.) at -78°, acetic acid (4 ml.) in ether (10 ml.) were added with stirring. After 2 hr. at -78° the mixture was slowly brought to room temperature and then heated under reflux for 0.5 hr. After filtration (kieselguhr) and evaporation under reduced pressure the product was chromatographed on silica gel. Ligroin eluted dicarbonylnitrosyl- π -but-2-enyliron (3 g., 49%) identified by i.r. comparison with the sample from the preceding experiment and by conversion into its triphenylphosphine substitution product. Benzene then eluted *dicarbonylnitrosyl-(5-hydroxy-5-methyl-1,2,3-hexenyl)iron* (VIII; L = CO) (1.5 g.; 19%) which distilled as a thick red oil at 80°/0.005 mm.; ν_{\max} (as liquid film) 3330 (OH), 2041 and 1980 (CO), and 1739 cm⁻¹ (NO); n.m.r. peaks at τ 6.0 (complex), 7.0—8.9 (complex) and 8.69 (singlet; CH₃) of relative intensity 3:4:6 (Found: C, 42.4; H, 5.3; N, 5.7; O, 24.9. C₉H₁₃FeNO₄ requires C, 42.4; H, 5.1; N, 5.5; O, 25.1%).

The latter product was not obtained when the experiment was repeated with a sample of the salt (I) prepared in methanol instead of acetone. When diethyl ketone (5 ml.) was added in a further experiment with this sample of the salt (I), a similar product, presumably *dicarbonylnitrosyl-(5-hydroxy-5-ethyl-1,2,3-heptenyl)iron* (0.3 g.) was obtained as a red oil with ν_{\max} (as liquid film) at 3390 (OH), 2028 and 1965 (CO), and 1730 cm⁻¹ (NO) whose triphenylphosphine substitution product [ν_{\max} at 1927 (CO) and 1681 cm⁻¹ (NO)] was also oily. In both experiments the

yield of π -but-2-enyl complex (VI; R = Me) was unchanged.

Carbonylnitrosyl(triphenylphosphine)-(5-hydroxy-5-methyl-1,2,3-hexenyl)iron (VIII; L = PPh₃).—The dicarbonyl (VIII; L = CO) (1.5 g., 6 mmoles) and triphenylphosphine (1.6 g., 6 mmoles) were heated under reflux in benzene (50 ml.) for 6 hr. The solution was concentrated under reduced pressure and chromatographed on alumina to yield Fe(NO)₂(PPh₃)₂, eluted with ligroin-benzene (1:1) and the *phosphine substituted carbinol* (VIII; L = PPh₃) (1.7 g.; 60%), eluted with benzene-ether (4:1). This formed red crystals, m. p. 130°, from ether and had ν_{\max} at 1915 (CO) and 1685 cm⁻¹ (NO); n.m.r. peaks at τ 2.6 (complex), 6.0—7.0 (complex), 7.0—8.0 (complex), 8.18 (broad singlet; CH₂), and 8.73 (singlet; CH₃) of relative intensity 15:2:3:2:6 (Found: C, 63.7; H, 5.9; N, 3.0; P, 6.3. C₂₆H₂₈FeNO₃P requires C, 63.8; H, 5.8; N, 2.9 and P, 6.3%).

Reaction of Tricarbonylnitrosylhydridoiron with Isoprene.—This was conducted like the above reaction with butadiene and yielded dicarbonylnitrosyl-3-methyl-1,2,3-butenyliron (0.9 g.; 7%) as a red oil identified by i.r. comparison with an authentic sample and by conversion into its triphenylphosphine substitution product. A second red oil was presumed, by analogy with the butadiene experiment, to be *dicarbonylnitrosyl-(5-hydroxy-3,5-dimethyl-1,2,3-hexenyl)iron* (0.5 g.; 3%). This had ν_{\max} (as liquid film) at 3390 (OH), 2008 and 1949 (CO) and 1721 cm⁻¹ (NO). Its oily *triphenylphosphine substitution product* had ν_{\max} (as liquid film) at 1923 (CO) and 1678 cm⁻¹ (NO).

Dicarbonylnitrosyl- π -cyclopentenyliron (VII; n = 2).—3-Chlorocyclopentene (5 ml.) in ether (10 ml.) was added to the salt (I) (4 g., 20 mmoles) in ether (100 ml.), and the mixture stirred for 1 hr. at room temperature and then filtered. The filtrate was evaporated under reduced pressure and the residue chromatographed on silica gel. Elution with ligroin gave Fe(CO)₂(NO)₂ first and then the π -cyclopentenyl complex (VII; n = 2) (2.5 g.; 58%), a thick red oil distilling at 60°/0.005 mm. which had ν_{\max} (liquid film) at 2033 and 1980 (CO) and 1742 cm⁻¹ (NO); n.m.r. peaks at τ 4.65 (complex), 5.76 (triplet), and 7.9 (complex) in the ratio 2:1:4 (Found: C, 40.4; H, 3.4; N, 6.6. C₇H₇FeNO₃ requires C, 40.2; H, 3.4; N, 6.7%). This compound and its triphenylphosphine substitution product (below) are the only π -allylic complexes examined by us, where the central hydrogen of the allyl group gives a proton resonance peak at higher field than the protons on the two outer carbons.

This product (1.2 g., 6 mmoles) and triphenylphosphine (1.5 g., 6 mmoles) were heated under reflux in benzene (50 ml.) for 6 hr., to give, after concentration and chromatography, *carbonylnitrosyl(triphenylphosphine)- π -cyclopentenyliron* (1.5 g.; 59%); it formed red crystals, m. p. 125°, from dichloromethane-pentane, had ν_{\max} at 1942 (CO) and 1669 cm⁻¹ (NO); complex n.m.r. peaks at τ 2.5, 5.05, 5.7—7.0, and 8.0 in the ratio 15:2:1:4, but suffered partial decomposition before it could be analysed.

Dicarbonylnitrosyl- π -cyclohexenyliron (VII, n = 3).—The procedure of the preceding experiment was repeated with 3-bromocyclohexene (3.9 g., 24 mmoles) and the salt (I) (4.5 g., 23 mmoles) to give the π -cyclohexenyl complex (VII; n = 3) (2.4 g., 46.2%), a red oil distilling at 60°/0.01 mm.; ν_{\max} (liquid film) at 2020 and 1950 (CO) and 1720 cm⁻¹ (NO); complex n.m.r. peaks at τ 4.85, 7.9, and 9.0 in the ratio 3:4:2 (Found: C, 43.1; H, 4.1; N, 6.3. C₈H₉FeNO₃

Org.

requires C, 43.1; H, 4.1; N, 6.3%). This product (4.35 g., 19 mmoles) and triphenylphosphine (5.24 g., 20 mmoles) yielded *carbonylnitrosyl(triphenylphosphine)- π -cyclohexenyliron* (4.7 g., 66.4%) as red crystals, m. p. 137°, from ether-pentane; ν_{\max} at 1920 (CO) and 1663 cm⁻¹ (NO); complex n.m.r. peaks at τ 2.57, 5.12, 6.35, and 8.45 of relative intensity 15:1:2:6 (Found: C, 65.7; H, 5.0; N, 3.1; P, 6.8. C₂₅H₂₄FeNO₂P requires C, 65.7; H, 5.3; N, 3.1; P, 6.8%).

Formation of Acyl Substituted Complexes (IX)–(XIII).—The following procedures for the reaction of the salt (I) with methyl iodide and butadiene and subsequent reaction of the product with triphenylphosphine are typical and were employed in the subsequent experiments.

Dicarbonylnitrosyl-(5-oxo-1,2,3-hexenyl)iron (IX; R¹ = R² = H). Methyl iodide (10 ml.) in ether (10 ml.) was added to a stirred mixture of the salt (6 g.) and butadiene (10 ml.) in ether (100 ml.). After stirring at room temperature for 1 hr. the mixture was heated under reflux for a few min., then cooled, filtered, and the filtrate evaporated under reduced pressure. Chromatography on silica gel gave first a trace of Fe(CO)₂(NO)₂ eluted with ligroin, and then, on elution with benzene, the *product* (IX; R¹ = R² = H) (5.8 g.; 74%) as an undistillable viscous red oil with ν_{\max} (liquid film) at 2045 and 1980 (–C=O), 1784 (NO), and 1692 cm⁻¹ (COR). When reaction of the salt (I) with methyl iodide was continued at 0° for 1 hr. to complete formation of the acetyl complex (IV; R = Me) before addition of butadiene, the same product was obtained in similar yield.

Reaction of the 5-Oxohex-1,2,3-enyl Complex (IX; R¹ = R² = H) with Triphenylphosphine. The preceding product (IX; R¹ = R² = H) (4.9 g., 21 mmoles) and triphenylphosphine (5.5 g., 21 mmoles) were heated under reflux in benzene (100 ml.) for 5 hr., filtered, the filtrate evaporated under reduced pressure, and the residue chromatographed on alumina. Ligroin–benzene (4:1) eluted a mixture of triphenylphosphine and Fe(CO)(NO)₂(PPh₃), ligroin–benzene (7:3) eluted Fe(NO)₂(PPh₃)₂ and ligroin–benzene (1:4) eluted *carbonylnitrosyl(triphenylphosphine)- π -(5-oxo-1,2,3-hexenyl)iron* (X; R¹ = R² = H) (2 g., 20.6%) as a red oil with ν_{\max} (liquid film) at 1925 (CO) and 1690 and 1680 cm⁻¹ (NO and COR). Finally benzene eluted *dicarbonylnitrosyl(triphenylphosphine)- π -(hexa-3,5-dien-2-one)iron* (XII; R¹ = R² = H) (0.06 g., 0.6%) which formed yellow crystals, m. p. 175°, from dichloromethane–n-pentane and had ν_{\max} at 2000 and 1934 (–C=O) and 1658 cm⁻¹ (COR); n.m.r. peaks at τ 2.6 (complex), 4.0–5.0 (complex), 5.0–6.0 (complex), 8.09 (singlet), and 8.5–9.8 (complex) of relative intensity 15:1:1:4:2 (Found: C, 66.6, 64.4, 65.3, 66.3; H, 5.6, 5.3, 4.9, 3.6. C₂₆H₂₃FeO₃P requires C, 66.4; H, 4.9%).

A similar experiment with triphenyl phosphite gave *carbonylnitrosyl(triphenyl phosphite)- π -(5-oxo-1,2,3-hexenyl)iron* (61%) as a red oil with ν_{\max} at 1957 (–C=O) and 1689 cm⁻¹ (NO and COR).

Reaction of the Complex (IX; R¹ = R² = H) with Pyridine.—The complex (IX; R¹ = R² = H) (11.54 g., 46 mmoles) and pyridine (3 ml.) were heated under reflux in benzene (150 ml.) for 24 hr., the mixture filtered, and the residue, from evaporation of the filtrate, chromatographed on alumina. Ligroin first eluted traces of an unidentified yellow oil with ν_{\max} (liquid film) at 2049, 1980, 1709, and 1667 cm⁻¹; ligroin–benzene (4:1) then eluted tricarbonyl- π -(hexa-3,5-dien-2-one)iron (XIV) (0.3 g.) as a yellow oil, i.r.

spectrum identical [ν_{\max} (liquid film) at 2049 and 1980 (–C=O) and 1672 cm⁻¹ (COR)] with an authentic specimen.¹⁵

Dicarbonylnitrosyl- π -(5-oxo-3-methylhex-1,2,3-enyl)iron (IX; R¹ = H; R² = Me).—The salt (I) (4.5 g., 23 mmoles), isoprene (7 ml.) and methyl iodide (7 ml.) yielded this *product* (IX; R¹ = H; R² = Me) as a red oil (4.2 g.; 70%), having ν_{\max} (liquid film) at 2041 and 1976 (–C=O), 1730 (NO), and 1681 cm⁻¹ (COR). This product (4.2 g., 17 mmoles) with triphenylphosphine (4.5 g., 17 mmoles) gave *carbonylnitrosyl(triphenylphosphine)- π -(5-oxo-3-methylhex-1,2,3-enyl)iron* (X; R¹ = H; R² = Me) (1.6 g., 20%) as a red oil, having ν_{\max} (liquid film) at 1923 (–C=O) and 1681 cm⁻¹ (NO and COR), and *dicarbonylnitrosyl(triphenylphosphine)- π -(3-methylhexa-3,5-dien-2-one)iron* (XII; R¹ = H, R² = Me) (0.6 g.; 7.5%) forming yellow crystals, m. p. 117°, from ether-pentane; ν_{\max} (in CCl₄) at 2004 and 1876 (–C=O) and 1667 cm⁻¹ (COR); n.m.r. peaks at τ 2.65 (complex), 4.55 (doublet), 8.02 (doublet), 8.56 (doublet), and 9.1–10.6 (complex) of relative intensity 15:1:3:4:2 (Found: C, 67.0; H, 5.3. C₂₇H₂₅FeO₃P requires C, 66.9; H, 5.2%). Treatment of the dicarbonyl (IX; R¹ = H, R² = Me) (3.8 g., 15 mmoles) with triethyl phosphite (2.5 g., 15 mmoles) gave *carbonylnitrosyl(triethylphosphite)- π -(5-oxo-3-methyl-1,2,3-hexenyl)iron* (2.3 g.; 40%) as a red oil with ν_{\max} (liquid film) at 1908 (–C=O) and 1669 cm⁻¹ (NO and COR).

Dicarbonylnitrosyl- π -(6-oxo-2,3,4-heptenyl)iron.—The salt (I) (4 g., 20 mmoles) and *cis*-penta-1,3-diene (7 ml.) with methyl iodide (7 ml.) gave *dicarbonylnitrosyl- π -(6-oxo-2,3,4-heptenyl)iron* (1.4 g., 27%) as a red oil with ν_{\max} (liquid film) at 2004 and 1946 (–C=O) and 1718 cm⁻¹ (NO and COR). This compound (3 g., 12 mmoles) and triphenylphosphine (3.2 g., 12 mmoles) gave *carbonylnitrosyl(triphenylphosphine)- π -(6-oxo-2,3,4-heptenyl)iron* as a red oil which decomposed on elution from an alumina column and *dicarbonylnitrosyl(triphenylphosphine)- π -(hepta-3,5-dien-2-one)iron* (0.5 g., 9%). The latter formed yellow crystals, m. p. 138°, from dichloromethane–pentane, had ν_{\max} at 2000, 1934, and 1886 (–C=O), and 1655 cm⁻¹ (COR); n.m.r. peaks at τ 2.55 (complex), 4.4–5.4 (complex), 8.69 (singlet), 8.98 (doublet), and 9.7–10.1 (complex) of relative intensity 15:2:3:3:2 (Found: C, 67.1; H, 5.55. C₂₇H₂₅FeO₃P requires C, 67.0; H, 5.3%).

Dicarbonylnitrosyl- π -(5-oxo-2,3-dimethyl-1,2,3-hexenyl)iron (IX; R¹ = R² = Me).—The salt (I) (4.5 g., 23 mmoles), 2,3-dimethylbutadiene (5 ml.), and methyl iodide (7 ml.) yielded *dicarbonylnitrosyl- π -(5-oxo-2,3-dimethyl-1,2,3-hexenyl)iron* (1.6 g.; 26%) as a red oil with ν_{\max} (liquid film) at 2020 and 1960 (–C=O) and 1720 cm⁻¹ (NO and COR). This product (3 g., 11 mmoles) with triphenylphosphine (3 g., 11 mmoles) gave *carbonylnitrosyl(triphenylphosphine)- π -(5-oxo-2,3-dimethyl-1,2,3-hexenyl)iron* (X; R¹ = R² = Me) (1.2 g.; 21%) which formed red crystals, m. p. 120°, from ether-pentane; ν_{\max} at 1920 and 1910 (–C=O), and 1710, 1688, and 1662 cm⁻¹ (NO and COR); n.m.r. peaks at τ 2.5 (complex), 6.3–6.8 (complex), 7.05 (doublet), 7.84 (singlet), 8.52 (doublet), and 9.17 (singlet) of relative intensity 15:3:1:3:3:3 (Found: C, 64.3; H, 5.7; N, 2.8. C₂₇H₂₈FeNO₃P requires C, 64.7; H, 5.6; N, 2.8%). There was also obtained *dicarbonylnitrosyl(triphenylphosphine)- π -(4,5-dimethylhexa-3,5-dien-2-one)iron* (XII; R¹ = R² = Me) (0.53 g.; 9.5%) which formed yellow crystals, m. p. 161–162°, from ether-pentane; ν_{\max} at 1996 and 1930 cm⁻¹ (–C=O) and 1652 cm⁻¹ (COR); n.m.r. peaks at τ 2.6 (complex), 7.7 (doublet), 8.15 (doublet), 8.62 (singlet), and 10.0—

10·8 (complex) of relative intensity 15 : 3 : 3 : 4 : 2 (Found: C, 67·6; H, 5·75. $C_{28}H_{27}FeO_3P$ requires C, 67·5; H, 5·5%).

Dicarbonylnitrosyl- π -(4-acetyl-1,2,3-cyclopentenyl)iron (XI; L = CO; $n = 1$).—The salt (I) (4 g., 20 mmoles), cyclopentadiene (10 ml.), and methyl iodide (7 ml.) yielded the *acetylcyclopentenyl complex* (XI; L = CO; $n = 1$) (2·3 g., 45%) as a red oil; ν_{max} (liquid film) at 2037 and 1980 ($-C\equiv O$), 1739 (NO), and 1667 cm^{-1} (COR), whose triphenylphosphine substitution product decomposed during attempted chromatography on alumina.

Dicarbonylnitrosyl- π -(4-acetyl-1,2,3-cyclohexenyl)iron (XI; L = CO; $n = 2$).—The salt (I) (4·5 g., 23 mmoles), cyclohexa-1,3-diene (2·5 ml., 25 mmoles), and methyl iodide (7 ml.) yielded the *acetylcyclohexenyl complex* (XI; L = CO; $n = 2$) (2·5 g., 41%) as a red oil; ν_{max} (liq. film) at 2010 and 1950 ($-C\equiv O$), 1710 (NO) and 1650 cm^{-1} (COR). This compound (2·8 g., 11 mmoles) with triphenylphosphine

(2·8 g., 11 mmoles) gave, in addition to the red triphenylphosphine substitution product (XI; L = PPh_3 ; $n = 2$), which decomposed on the alumina column, *dicarbonyl(triphenylphosphine)- π -(1-acetylcyclohexa-1,3-diene)iron* (0·05 g.; 1%), which formed yellow crystals, m. p. 159° (from dichloromethane-pentane); ν_{max} at 1988 and 1934 ($-C\equiv O$) and 1663 cm^{-1} (COR); n.m.r. peaks at τ 2·6 (complex), 4·2 (broad doublet), 5·47 (complex), 7·9 (singlet), and 8·5 (complex) of relative intensity 15 : 1 : 1 : 4 : 4 (Found: C, 67·7; H, 5·2. $C_{28}H_{25}FeO_3P$ requires C, 67·7; H, 5·1%).

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