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Preliminary communication

ACETYLATION OF DICARBONYL(η^4-CYCLOHEXADIENE)TRIPHENYLPHOSPHINEIRON

ARTHUR J. BIRCH*, WARWICK D. RAVERTY,
Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600 (Australia)
SHIH-YING HSU and ANTHONY J. PEARSON*
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106 (U.S.A.)

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Summary

Friedel—Crafts acetylation of dicarbonyl(η^4-cyclohexadiene)triphenylphosphineiron is accomplished in 96% yield under mild conditions to give dicarbonyl(η^4-5-*endo*-acetylcyclohexa-1,3-diene)triphenylphosphineiron. The structure of the product was established by direct comparison with the epimeric complex dicarbonyl(η^4-5-*exo*-acetylcyclohexa-1,3-diene)triphenylphosphineiron produced by reaction of methyl magnesium iodide with dicarbonyl(η^4-5-*exo*-cyanocyclohexa-1,3-diene)triphenylphosphineiron.

Despite the intrinsic simplicity of the reaction, Friedel—Crafts acetylation of tricarbonylcyclohexadieneiron 1 has been the subject of conflicting reports in the public literature. One group has reported [1] that the reaction proceeds *endo* to the metal to give the product 2, whilst another [2,3] has cited evidence in favor of formation of the product 3 of M-*exo* acylation. As it turns out, the reaction described is of little synthetic value, since the yields of product are usually low (20—30%), the major side reaction being hydride transfer from 1 to the acylium cation to give the dienyl salt 4 (after anion exchange) [2]. Provided the stereochemistry of product is conclusively established, and that conditions are found which give high yields, reaction of dieneiron complexes with electrophiles might provide synthetic methodology complementary to the known reactions of dienyliron complexes with nucleophiles [4]. Therefore, we have addressed ourselves to the two problems of yield and stereochemistry of acetylation.

*Address correspondence to this author at Case Western Reserve University.

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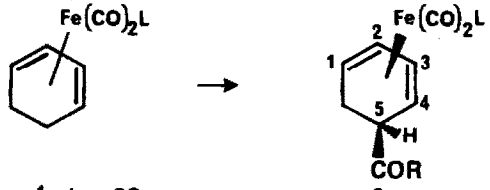


1 L = CO

5 L = PPh_3

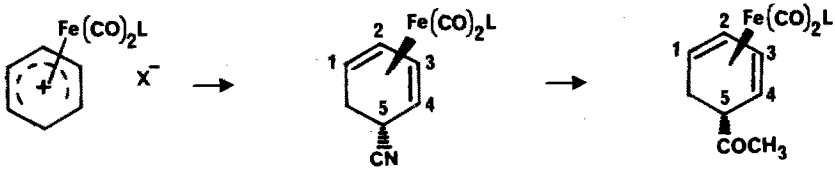
2 L = CO

9a L = PPh_3, R = $COCH_3$

9b L = PPh_3, R = COPh

9c L = PPh_3, R = CH_2OMe

Since the low reactivity of 1 towards electrophiles appeared to us to be due to a lack of electron density on the metal—diene system, we decided to alter the ligand environment of the metal. Treatment of 1 with triphenylphosphine under thermal conditions (cyclohexanol, reflux, 15 h) gave the known complex 5 as a pale yellow crystalline solid, m.p. 120—121°C, in 71% yield [5]. Hydride abstraction from 5 ($Ph_3C^+PF_6^-$, 20°C 1 h) gave the ether insoluble salt 6 in 99% yield [6], and reaction of this with cyanide (1.5 equiv. NaCN, wet THF, 20°C, 30 min) gave the crystalline nitrile 7, m.p. 163—164°C, in quantitative yield [6]. The stereochemistry of this compound may be assigned on the basis of the known reactivity of a wide range of similar dienyliron complexes toward nucleophiles [4], and also by analogy with the reaction of complex 4 with cyanide, the stereochemical course of which has been established by X-ray crystallography [3]. Reaction of the nitrile 7 with methylmagnesium iodide (15 equiv. Et_2O/THF, 1/1, 20°C, 1.5 h), followed by preparative TLC, proceeded without event to give the acetyl derivative 8 in 60% yield as an oil which could not be crystallized [6], the stereochemistry of which is defined by the structure of 7, thereby providing an appropriate reference compound.



4 L = CO $X^- = AlCl_4^-$

6 L = PPh_3 $X^- = PF_6^-$

7 L = PPh_3

3 L = CO

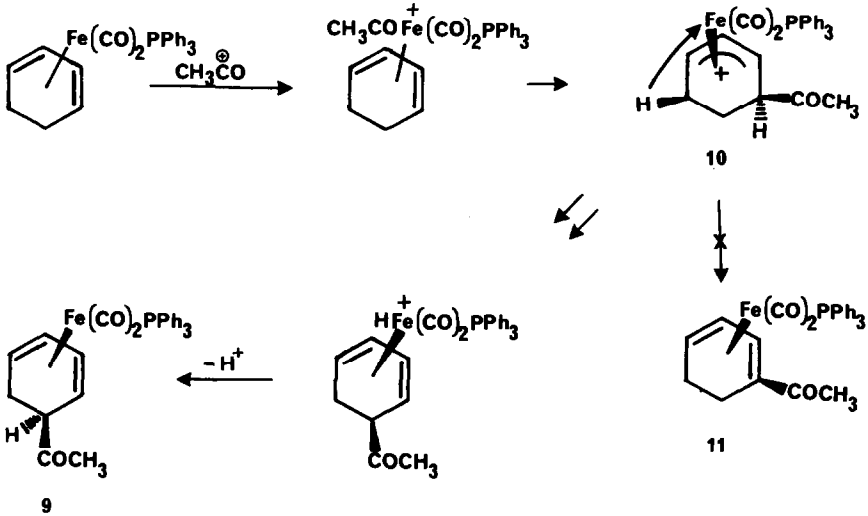
8 L = PPh_3

Acetylation of the diene complex 5 was accomplished under very mild conditions [7], in comparison to the same reaction using 1 [2,3], to give a crystalline acetyl substituted complex, m.p. 128—129°C, in 96% yield. This compound was considerably different in its NMR spectrum [6] to 8, the differences being attributable to the stereochemistry shown by the structure 9a. Thus, the acetyl CH_3 group gives a singlet at higher field for 8 (δ 1.99) than for 9a (δ 2.03), whilst the multiplet due to H(5) occurs at lower field for 8 (δ 2.90) than for 9a (δ 2.30). (The NMR spectrum of a mixture of 8 and 9a also showed two distinct compounds.) These observations are consistent with the known characteristics of cyclohexadiene—$Fe(CO)_3$ complexes, in which groups *endo* to the metal generally give signals at lower field in the ^1H NMR spectrum than do groups *exo* to the

metal [8]. The IR spectra also showed a significant difference in the ketone carbonyl stretching frequency [6].

The ease of reaction of **5** with electrophiles allows us to accomplish benzoylation (PhCOCl, $AlCl_3$, CH_2Cl_2, −78°C) to give **9b** (50% yield, unoptimized) and methoxymethylation (5 equiv. CH_3OCH_2Cl, added to a solution of **5** in CH_2Cl_2 at −78°C; 5 equiv. $AlCl_3$ added in portions; stir 1 h and work up in the usual way) to give **9c** (65% yield, unoptimized). We have assumed that these two reactions take an identical stereochemical course to acetylation.

A plausible mechanism for acetylation of these complexes is shown in the Scheme, in which we have assumed initial attachment of the electrophile to the metal, consistent with the considerably greater reactivity of complex **5** compared to **1**, owing to the poorer π-acceptor capacity of the triphenylphosphine ligand leading to greater electron density at the metal. Whilst we cannot preclude a mechanism involving direct electrophilic attack at carbon [9], it may be noted that protonation is known to occur at the metal, from ^1H NMR studies [12].



The formation of product **9**, as opposed to the alternative compound **11** has two possible explanations. Pauson and coworkers have shown [10] that acetylation of butadieneiron tricarbonyl involves a π-allyl intermediate in which coordinative unsaturation is compensated for by coordination of the acyl oxygen to the metal. In the present case this would probably result in the carbonyl π orbital being orthogonal to a developing carbanion lone pair orbital at the α-position, thereby making the α hydrogen less acidic than the alternative methylene hydrogen [11]. Alternatively, the π-allyl complex **10** is extremely unstable and undergoes very rapid transfer of *endo* proton to the metal, as shown. This is consistent with our inability to isolate η^3-cyclohexenyliron complexes [12] compared with the ease of production of analogous acyclic π-allyliron complexes [13]

It is of course highly improbable that the tricarbonyliron complex **1** shows any mechanistic difference from **5** in its reaction with electrophiles, so we can conclude that acylation of **1** also occurs *endo* to the metal [14]. Further studies into the synthetic utility of the nucleophilic properties of **5** and related complexes are currently being pursued in our laboratory.

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6 All new compounds gave satisfactory spectral and analytical data. IR and ^{1}H NMR data are as follows (seelcted compounds):
6. IR (CH_2Cl_2): ν_{max} 2055, 1908, 1605, 850 cm^{-1}; NMR (CD_3CN): δ (ppm) 7.65—7.25 (15H, m, Ph_3P), 6.95 (1H, t, J = 5 Hz, 3-H), 5.13 (2H, dd, J = 5 Hz, 7 Hz, 2-H, 4-H), 3.60 (2H, t, $J_{1,2} = J_{1,6}$ *endo* 7 Hz, 1-H, 5-H), 2.8 (1H, dt, J_{gem} = 14 Hz, $J_{1,6}$ *endo* = $J_{5,6}$ *endo* = 7 Hz), 1.7 (1H, d, br, J_{gem} 14 Hz, *exo*-6-H).
7. IR (CH_2Cl_2): ν_{max} 2218, 1983, 1925, 1605 cm^{-1}; NMR ($CDCl_3$): δ (ppm) 7.5—7.2 (15H, m, Ph_3P), 4.97 (2H, m, 2-H, 3-H), 2.9 (1H, ddd, $J_{4,5} = J_{5,6}$ *exo* = 3.5 Hz, $J_{5,6}$ *endo* = 10 Hz, 5-H), 2.4 (2H, m, 1-H, 4-H), 2.17 (1H, ddd, $J_{5,6}$ *endo* = 10 Hz, $J_{1,6}$ = 4 Hz, J_{gem} = 13 Hz, *endo*-6-H), 1.7 (1H, dd, br, J_{gem} = 13 Hz, *exo*-6-H).
8: IR ($CHCl_3$): ν_{max} 1982, 1920, 1700, 1605 cm^{-1}; NMR ($CDCl_3$): δ (ppm) 7.6—7.2 (15H, m, Ph_3P), 4.92 (2H, m, 2-H, 3-H), 2.90 (1H, m, 5-H), 2.36 (2H, n, 1-H, 4-H), 1.99 (3H, s, $CO \cdot CH_3$), 1.74 (2H, close ABq, 2 X 6-H).
9a. IR ($CHCl_3$): ν_{max} 1985, 1926, 1710, 1605 cm^{-1}; NMR ($CDCl_3$) δ (ppm) 7.7—7.3 (15H, Ph_3P), 4.9 br (2H, m, 2-H, 3-H), 2.6 br (2H, m, 1-H, 4-H), 2.3 (1H, m, *exo*-5-H), 2.03 (3H, s, $CO \cdot CH_3$), 2.0—1.6, br (2H, m, 2 X 5-H).

7 The optimized acetylation procedure is as follows: A solution of the Perrier complex in dichloromethane was prepared by gentle warming of acetyl chloride (1.2 ml) and aluminum chloride (2.94 g) followed by addition of anhydrous dichloromethane (10 ml) to the cooled melt. To a stirred solution of complex 5 (0.50 g, 1.11 mmol) in dry dichloromethane (10 ml) under argon at −78°C was added 1 ml (2 equiv.) of the above Perrier complex solution. Two further portions of the Perrier complex solution (1 ml) were added at half-hourly intervals. After the second addition stirring was continued for 10 min, the reaction mixture was diluted with dry ether at −78°C and was then poured onto ice. The organic layer was washed with water (4 X 15 ml), brine (20 ml), dried ($MgSO_4$) and evaporated. The oily product was crystallized from dichloromethane/pentane to afford the pale yellow crystalline ketone 9 (0.53 g, 96%).

8 See, for example, A.J. Birch and A.J. Pearson, J. Chem. Soc. Perkin Trans., 1 (1978) 638, and ref. cited therein.

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11 We thank a referee for pointing this out.

12 Attempts to protonate 5 to give π-allyl complexes lead only to the formation of diene complexes having proton attached to the metal, evidenced by NMR signal at ca. δ −6.0 (A.J. Pearson, unpublished observations).

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14 We have observed that the *endo*-acetyl complex 2 isomerizes to the *exo* derivative 3 on passage through basic alumina. This might explain the result reported by Johnson et al. (ref. 3) since solutions of these complexes are commonly filtered through basic alumina prior to NMR measurement to remove paramagnetic impurities. We recommend the use of neutral silica gel for this purpose with sensitive complexes.