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Preliminary communication

ACTIVATION OF METAL-ACYL OXYGEN ATOMS BY TRIFLIC ANHYDRIDE: A SIMPLE SYNTHETIC ROUTE TO REACTIVE CATIONIC VINYLIDENE COMPLEXES

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Summary

(η^5-Cyclopentadienyl) (acyl) (carbonyl) (tertiary phosphine)iron complexes react rapidly with trifluoromethanesulfonic acid anhydride to afford cationic vinylidene complexes, via the intermediacy of cationic carbene complexes. Spectroscopic and chemical characterizations of these vinylidene complexes are reported.

There has been a recent upsurge of interest in the synthesis and chemistry of organometallic compounds containing vinylidene ligands. A recent report by Davison indicated that such compounds (I) could be isolated from protonation, or electrophilic alkylation, of the appropriate metal-acetylide precursor [1]. A subsequent report by Bruce described the analogous synthesis of similar vinylidene complexes of ruthenium [2]. Davison had previously demonstrated the intermediacy of highly electrophilic vinylidene ligands in a related system [3]. We now report a facile synthesis of reactive, cationic vinylidene complexes of iron(II) and their spectroscopic characterization.

Reaction of the acyl complex IIa (ν(CO) (CH_2Cl_2) 1918s, 1607m cm^{-1}; ^1H NMR (60 MHz; $CDCl_3$) δ (ppm): 4.40 (5H, d, J(P—H)2)C_5H_5, 2.91 (1H, septuplet, J(H—H)7)CH, 0.99 (3H, d, J(H—H)7)Me, 0.25 (3H, d, J(H—H)7)Me]* with trifluoromethanesulfonic acid anhydride (triflic anhydride, Tf_2O) [5] in CH_2Cl_2 or $CDCl_3$ solution afforded cleanly the dimethylvinylidene complex IIIa [ν(CO) (CH_2Cl_2) 2021s cm^{-1}; ν(C=C) 1621m cm^{-1}; ^1H NMR (60 MHz; $CDCl_3$) δ 5.30 (5H, d, J(P—H)1)C_5H_5, 1.66 (6H, s)Me]. An intermediate cationic

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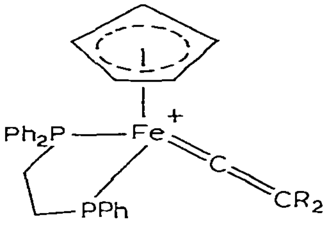
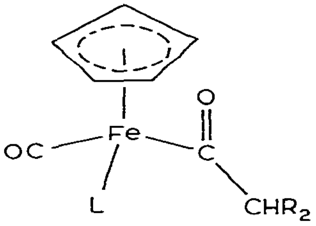
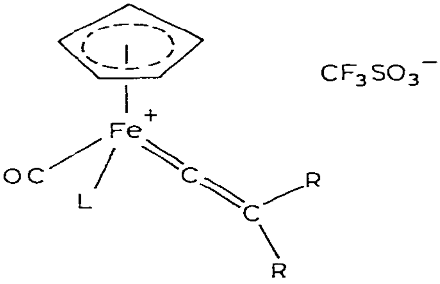
*The ^1H NMR data given in the literature [4] for complex IIa are incorrect. The authors report that the methyl groups of the isopropyl group do not appear to be diastereotopic. Our data shows that they are indeed diastereotopic, that the corresponding methyl groups in IVa are also diastereotopic, but that this nonequivalence is removed on generation of IIIa.



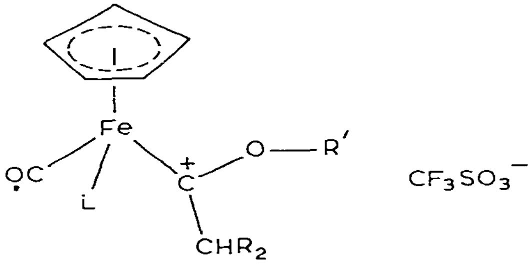
(I) R = H, Me



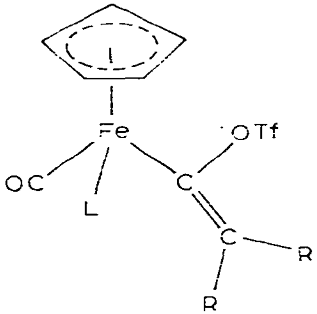
(IIa, R = Me; L = PPh_3)
(IIb, R = H; L = PPh_3)
(IIc, R = H; L = PMe_2Ph)



(IIIa, R = Me; L = PPh_3)
(IIIb, R = H; L = PPh_3)
(IIIc, R = H; L = PMe_2Ph)



(IVa, R = Me; L = PPh_3; R = CF_3SO_2)
(IVb, R = H; L = PPh_3; R′ = CF_3SO_2)
(IVc, R = H; L = PMe_2Ph; R′ = CF_3SO_2)
(IVd, R = H; L = PPh_3; R′ = Me).



(V)

carbene complex IVa [ν(CO) (CH_2Cl_2) 1973s cm^{-1}; ^{1}H NMR (60 MHz; $CDCl_3$) δ 4.85 (5H, d, J(P—H)1) C_5H_5, 3.25 (1H, septuplet, J(H—H)7) CH, 1.11 (3H, d, J(H—H)7)Me, 0.21 (3H, d, J(H—H)7)Me] could be observed by IR or NMR monitoring of the reaction*. We have been unable to obtain the resultant dimethylvinylidene complex in crystalline form; it forms an oily solid on evaporation of its solution. However, its ^{1}H NMR spectrum remains unchanged after 12 h in $CDCl_3$ solution in the absence of nucleophilic species.

The spectroscopic data for IIIa are only consistent with the presence of a dimethylvinylidene ligand. The observation of a singlet peak in the ^{1}H NMR spectrum corresponding to six equivalent methyl hydrogens, with no spin—spin coupling to a methine proton, can only indicate that the dimethylvinylidene ligand is formed, and that the rate of rotation about the iron—carbon bond is fast. This latter observation is consistent with previous reports [1], and with theoretical predictions of very small rotation barrier [7]. In addition the observed high value of ν(CO) (2021 cm^{-1}) for IIIa is consistent with the presence of a potent π-acceptor ligand on the metal [3]; the observation of ν(C=C) at 1621 cm^{-1} is also consistent with previous reports [1,3].

Similarly, treatment of IIb [4] with Tf_2O afforded the unsubstituted vinylidene complex IIIb [ν(CO) (CH_2Cl_2) 2035s cm^{-1}; ν(C=C) (CH_2Cl_2) 1629m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.25 (5H, d, J(P—H)2) C_5H_5, 5.30 (2H, s) CH_2] via the intermediacy of IVb [ν(CO) (CH_2Cl_2) 1973s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.75 (5H, d, J(P—H)2) C_5H_5, 2.38 (3H, s) Me]. Analogous reaction of IIc [4] afforded the unsubstituted vinylidene complex IIIc [ν(CO) (CH_2Cl_2) 2025s cm^{-1}; ν(C=C) (CH_2Cl_2) 1633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.25 (5H, d, J(P—H)2) C_5H_5, 5.41 (2H, s) CH_2, 2.08 (3H, d, J(P—H)11) PMe, 1.98 (3H, d, J(P—H)11) PMe] via the intermediacy of IVc [ν(CO) (CH_2Cl_2) 1968s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.79 (5H, d, J(P—H)2) C_5H_5, 2.73 (3H, s) Me, 1.87 (3H, d, J(P—H)10) PMe, 1.83 (3H, d, J(P—H)10) PMe]**. Compounds IIIb and IIIc are also stable in $CDCl_3$ solution for several hours.

Final structural proof is provided by the rapid reaction of IIIb with methanol to afford the known methyl(methoxy)carbene complex IVd [6]; this reactivity parallels that of the unstable phenylvinylidene ligand system previously reported by Davison [3].

The formation of vinylidene ligands by this route is not surprising. The acyl oxygen in compounds of general structure II is known to be nucleophilic, and can be alkylated with trialkyloxonium cations [6]; similar nucleophilic attack on Tf_2O, analogous to that observed in reactions of enolate anions [8], should readily produce cationic carbene complexes IV. The protons on carbon atoms α to coordinated carbene carbons are known to be both kinetically and thermodynamically acidic [9]. Loss of such a proton from complexes IV would generate the vinyl triflate species V, which contain one of the best known electron releasing substituents [$C_5H_5Fe(CO)PR_3$] and one of the best known leaving groups (OTf^-) [8] bound to the same carbon atom. Generation of vinylidene complexes III by spontaneous dissociation of OTf^- from V seems a

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*Values of ν(CO) and ^{1}H NMR data for complexes IV correspond excellently with those reported for analogous methyl(alkoxy)carbene compounds [6].

**Values of ν(CO) and ν(C=C) for our vinylidene complexes compare very well with those of an unstable phenylvinylidene complex of iron reported by Davison [3].

logical final step; this process would be analogous to the known dissociation of OTf^- in solvolysis reactions of organic vinyl triflates [8].

This method represents an unusually facile activation of a metal-acyl oxygen atom, and a remarkably simple entry into metal-vinylidene chemistry. Studies of the electrophilicity of our cationic vinylidene complexes and the applicability triflate activation to other metal acyls and metal acylates are currently in progress.

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