(19) Kato, M.; Jonassen, H. B.; Fanning, J. C. *Chem. Rev.* **1964**, *64*, 99.
(20) Kishita, M.; Muto, Y.; Kubo, M. *Aust. J. Chem.* **1957**, *10*, 386.
(21) Lundquist, R. T.; Cais, M. *J. Org. Chem.* **1962**, *27*, 1167.
(22) Cotton, F. A.; Wise, J. J. *Inorg. Chem.* **1967**, *6*, 917.
(23) Barnum, D. W. *J. Inorg. Nucl. Chem.* **1961**, *21*, 221.
(24) Aaasa, R.; Vanngard, T. *Ark. Kemi* **1965**, *24*, 331.
(25) McGarvey, B. R. *J. Chem. Phys.* **1964**, *40*, 809.
(26) Gersmann, H. R.; Swalen, J. D. *J. Chem. Phys.* **1962**, *36*, 3221.
(27) Belford, R. L.; Duan, D. C. *J. Magn. Reson.* **1978**, *29*, 293.
(28) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135.
(29) Cotton, F. A.; Harris, C. B.; Wise, J. J. *Inorg. Chem.* **1967**, *6*, 909.
(30) Graddon, D. P. *Coord. Chem. Rev.* **1969**, *4*, 1.
(31) Wayland, B. B.; Kapur, U. K. *Inorg. Chem.* **1974**, *13*, 2517.
(32) Wisniewski, M. D.; Wayland, B. B. *J. Chem. Soc. A* **1971**, 2727.
(33) Wayland, B. B.; Wisniewski, M. D. *Chem. Commun.* **1971**, 1025.

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Preparation of Cationic η^2-Alkene and η^2-Alkyne Complexes of the $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]$ System and Reduction of These Complexes to σ-Alkyl and Vinyl Derivatives

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New π-alkene and π-alkyne complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3](\eta^2\text{-un})]BF_4$ (un = unsaturated hydrocarbon) have been prepared in high yield from the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ and $AgBF_4$ in CH_2Cl_2, followed by addition of 3 equiv of the alkene or alkyne. These complexes are much more stable in solution that the triphenylphosphine analogues reported previously. These new complexes can be reduced by hydride reagents to the corresponding alkyl and vinyl derivatives. The alkyl complexes in this system are very stable and do not thermally decompose by a β-elimination pathway. The *sec*-butyl complex formed from the hydride reduction of the *cis*-2-butene complex also shows no tendency to undergo alkyl isomerization on the metal to yield the *n*-butyl derivative. Thermal decomposition studies of the *sec*-butyl complex indicate that the diastereomer which forms preferentially is actually the less stable isomer.

Introduction

The synthesis and reaction of complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-olefin})]BF_4$ have recently become well developed. Rosenblum has shown that these complexes may be useful intermediates in organic synthesis.[1] We have recently reported a convenient synthesis of η^2-olefin and η^2-alkyne complexes in this system by the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $AgBF_4$ in methylene chloride solution, generating the highly reactive intermediate $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$, which is then treated with 2 or 3 equiv of the olefin or alkyne to produce the complexes in ca. 70% yield.[2] This procedure may also be used in an analogous manner with $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ to synthesize compounds of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-olefin})]BF_4$.[2] In contrast to the dicarbonyl system, almost no η^2-olefin complexes had been reported in the phosphine system. These complexes were of particular interest to us because of the chirality of the iron atom and the potential for modifying selectivity of nucleophilic additions to the olefin because of the considerable steric and electronic differences between a phosphine and a carbonyl ligand. This potential was diminished, unfortunately, by the relative instability of many of these complexes in solution. The propene and *cis*-2-butene adducts, for example, are thermally unstable and rapidly decompose above −20 °C.

In order to prepare a series of chiral η^2-olefin complexes of greater stability, we chose to use triphenyl phosphite as the phosphorus donor ligand rather than triphenylphosphine. This ligand had been used successfully to prepare the bis(phosphite) complex $[(\eta^5\text{-}C_5H_5)Fe[P(OPh)_3]_2(\eta^2\text{-}C_2H_4)]BF_4$,[3] but no mixed carbonyl–triphenyl phosphite salts had been reported. Also, only a few neutral compounds had been reported. Those of interest here are the methyl, ethyl, and propyl derivatives prepared by Su and Wojcicki[4] and alkyl and silyl derivatives prepared by Stanley and Baird.[5]

In this paper, we report a facile and high-yield preparation of η^2-olefin and η^2-alkyne complexes and the hydride reduction of these complexes to the respective alkyl and vinyl complexes. In addition, we report our observations concerning the thermal stability of the new alkyliron species.

Experimental Section

General Procedure. All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen by using solvents that were purified and degassed before use. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer. Proton NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer and chemical shifts are reported in δ vs. Me_4Si. Carbon-13 NMR spectra were recorded on a Varian CFT-20 spectrometer using CH_2Cl_2, $CHCl_3$, or dichloroethane as the solvent and internal standard. Chemical shifts are reported in δ vs. Me_4Si assigning the CH_2Cl_2 resonance to be at 54.00 ppm, the $CHCl_3$ resonance to be at 77.20 ppm, and the dichloroethane resonance to be at 44.19 ppm. All carbon-13 spectra were run with ^1H decoupling and all resonances may be assumed to be singlets unless multiplicity is specified. The carbonyl resonance was usually not observed because data were collected under conditions (0.5 s acquisition time, 41° flip angle pulse, and no pulse delay) which tended to saturate this carbon atom. The triphenyl phosphite carbon resonances were assigned following Stewart et al.[6] The $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ was prepared and recrystallized by the method of Brown et al.[7] The $AgBF_4$ was purchased from Ozark-Mahoning. The L-Selectride (lithium tri-*sec*-butylborohydride) was purchased from Aldrich as a 1.0 M solution in THF. Product mixtures containing silver salts were filtered through a bed of filter aid to ensure a fast flow rate. This bed was washed with fresh reaction solvent, ca. 15 mL, until the washings were colorless. Melting and decomposition points were determined in sealed evacuated capillaries and are uncorrected.

(Carbonyl)(η^5-cyclopentadienyl)(η^2-ethylene)(triphenyl phosphite)iron(II) Tetrafluoroborate. A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ (1.0 g, 1.7 mmol) and $AgBF_4$ (0.38 g, 1.9 mmol) was stirred in CH_2Cl_2 (30 mL) for 30 min. This mixture was then filtered to yield a dark green filtrate. Ethylene was passed through the filtrate until the color changed to yellow-brown, ca. 4 min. This solution was first concentrated to 25 mL and then diluted with diethyl ether (75 mL). This precipitated yellow, air-stable crystals, which were collected, dried, and recrystallized from CH_2Cl_2–diethyl ether (1:3, v/v, 60 mL) (0.73 g, 75%); mp 135–136 °C. Anal. Calcd for $C_{26}H_{24}BF_4FeO_4P$: C, 54.42; H, 4.18. Found: C, 54.15; H, 4.39. ^1H NMR spectrum (acetone-d_6): 7.44 (15, mult, $P(OPh)_3$), 5.21 (5, d, J = 1.0 Hz, $\eta^5\text{-}C_5H_5$), 3.75, 3.38 (2, 2, mult, CH_2=). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2025. ^{13}C NMR spectrum (CH_2Cl_2): 150.31 (d, J = 10.3 Hz, O-bound phenyl carbons), 130.81 (meta phenyl carbons), 126.92 (para phenyl carbons), 120.90 (d, J = 4.3 Hz, ortho phenyl

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carbons), 86.57 (η^5-C_5H_5), 50.52 (d, J = 3.5 Hz, CH_2=).

(Carbonyl)(η^5-cyclopentadienyl)(η^2-propene)(triphenyl phosphite)iron(II) Tetrafluoroborate. This complex was obtained as yellow, air-stable crystals in 78% yield by a procedure analogous to that used for the ethylene complex; dec pt 111–113 °C. Anal. Calcd for $C_{27}H_{26}BF_4FeO_4P$: C, 55.15; H, 4.42. Found: C, 55.42; H, 4.48. ^{1}H NMR spectrum ($CDCl_3$): 7.32 (15, mult, $P(OPh)_3$), 5.25 (1, mult, CH=), 4.87, 4.84 (5, s, η^5-C_5H_5 (both diastereomers)), 4.01 (1, mult, *cis*-CH_2=), 2.94 (1, mult, *trans*-CH_2=), 1.85, 1.66 (3, pair of d, J = 5.2 Hz, J = 6.7 Hz, CH_3 (both diastereomers)). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2021. ^{13}C NMR spectrum (in dichloroethane, both diastereomers are observed, labeled A and B; the ratio A/B is 1.7 to 1): 150.28 (A), 149.99 (B) (pair of d, J = 10.3 and 10.3, O-bond phenyl carbons), 130.58 (meta phenyl carbons), 126.59 (para phenyl carbons), 120.72 (d, J = 4.2 Hz, ortho phenyl carbons), 86.20 (A), 85.90 (B) (η^5-C_5H_5), 82.58 (B), 76.51 (A) (CH=), 51.49 (B), 49.55 (A) (pair of d, J = 4.0 Hz, and J = 7.7 Hz, CH_2=), 21.86 (B), 19.81 (A) (CH_3).

(η^2-1-Butene)(carbonyl)(η^5-cyclopentadienyl)(triphenyl phosphite)iron(II) Tetrafluoroborate. This complex was obtained as yellow, air-stable crystals in 72% yield by a procedure analogous to that used for the ethylene complex; mp 126–128 °C. Anal. Calcd for $C_{28}H_{28}BF_4FeO_4P$: C, 55.88; H, 4.65. Found: C, 55.82; H, 4.88. ^{1}H NMR spectrum ($CDCl_3$): 7.31 (15, mult, $P(OPh)_3$), 5.22 (1, mult, CH=), 4.80, 4.83 (5, s, η^5-C_5H_5 (both diastereomers)), 3.88 (1, mult, *cis*-CH_2=), 3.55 (1, mult, *trans*-CH_2=), 2.87, 2.29 (1, 1, mult, CH_2 (both diastereomers)), 1.18 (3, mult, CH_3). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2017. ^{13}C NMR spectrum (in $CHCl_3$, both diastereomers are observed, labeled A and B; the ratio of A/B is 1.7 to 1): 150.23 (A), 149.96 (B) (pair of d, J = 10.2 Hz and 10.0 Hz, O-bound phenyl carbons), 130.55 (meta phenyl carbons), 126.52 (para phenyl carbons), 120.69 (d, J = 4.1 Hz, ortho phenyl carbons), 86.33 (A), 85.95 (B) (η^5-C_5H_5), 88.27 (B), 82.08 (A) (CH=), 49.74 (B), 48.15 (A) (pair of d, J = 3.9 and J = 5.9 Hz, CH_2=), 30.19 (B), 28.51, (A) (CH_2), 17.37 (A), 17.16 (B) (CH_3).

(Carbonyl)(η^2-*cis*-2-butene)(η^5-cyclopentadienyl)(triphenyl phosphite)iron(II) Tetrafluoroborate. This complex was obtained as yellow, hygroscopic crystals in 68% yield by a procedure analogous to that used for the ethylene complex; dec pt 82 °C. Anal. Calcd for $C_{28}H_{28}BF_4FeO_4P$: C, 55.88; H, 4.65. Found: C, 55.85; H, 4.67. ^{1}H NMR spectrum ($CDCl_3$): 7.27 (15, mult, $P(OPh)_3$), 5.43, 3.90 (1, 1, br mult, CH=), 4.82 (5, s, η^5-C_5H_5), 1.85, 1.67 (3, 3, d, J = 6.7 Hz, J = 6.7 Hz, CH_3). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2009. ^{13}C NMR spectrum (CH_2Cl_2): 150.32 (d, J = 11.8 Hz, O-bound phenyl carbons), 130.71 (meta phenyl carbons), 126.73 (para phenyl carbons), 120.80 (doublet, J = 4.2 Hz, ortho phenyl carbons), 86.37 (η^5-C_5H_5), 77.05, 74.37 (s and d, J = 2.4 Hz, CH=), 16.68, 16.54 (CH_3).

(η^2-Allene)(carbonyl)(η^5-cyclopentadienyl)(triphenyl phosphite)iron(II) Tetrafluoroborate. A mixture of (η^5-C_5H_5)Fe(CO)[$P(OPh)_3$]I (1.0 g, 1.7 mmol) and $AgBF_4$ (0.38 g, 1.9 mmol) was stirred in CH_2Cl_2 (60 mL) for 30 min. This mixture was then filtered and allene was passed through the filtrate for 4 min. The flask was then stoppered and set aside for 1 h. The resulting yellow solution was concentrated to 25 mL and filtered. The filtrate was treated with diethyl ether (30 mL) and this solution cooled at −20 °C overnight. The yellow crystals which formed were collected, washed with diethyl ether (10 mL), and dried in vacuo (0.75 g, 75%); mp 125–127 °C. Anal. Calcd for $C_{27}H_{24}BF_4FeO_4P$: C, 55.35; H, 4.10. Found: C, 55.18; H, 4.21. ^{1}H NMR spectrum ($CDCl_3$): 7.36 (15, mult, $P(OPh)_3$), 6.44, 6.12 (1, 1, mult, free CH_2=), 5.05 (5, d, J = 1.2 Hz, η^5-C_5H_5), 2.84 (2, mult, complexed CH_2=). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2028. ^{13}C NMR spectrum (CH_2Cl_2): 212.26 (d, J = 43.2 Hz, CO), 158.65 (d, J = 4.4 Hz, C=), 150.31 (d, J = 11.5 Hz, O-bound phenyl carbons), 130.68 (meta phenyl carbons), 126.83 (para phenyl carbons), 120.88 (d, J = 4.0 Hz, ortho phenyl carbons), 107.42 (free CH_2=), 88.82 (η^5-C_5H_5), 14.36 (d, J = 6.4 Hz, complexed CH_2=).

(Carbonyl)(η^5-cyclopentadienyl)(η^2-3-hexyne)(triphenyl phosphite)iron(II) Tetrafluoroborate. A mixture of (η^5-C_5H_5)Fe(CO)[$P(OPh)_3$]I (1.0 g, 1.7 mmol) and $AgBF_4$ (0.38 g, 1.9 mmol) was stirred in CH_2Cl_2 (30 mL) for 30 min. This mixture was filtered and 3-hexyne (0.42 g, 5.1 mmol) was added to the filtrate. After standing for 20 min, this solution was diluted with diethyl ether (85 mL) which precipitated orange crystals. These crystals were collected, dried, and recrystallized from CH_2Cl_2–diethyl ether (1:4, v/v, 75 mL) (0.76 g, 71%); mp 133–134 °C. Anal. Calcd for $C_{30}H_{30}BF_4FeO_4P$: C, 57.39; H, 4.78. Found: C, 57.12; H, 4.78. ^{1}H NMR spectrum ($CDCl_3$): 7.33 (15, mult, $P(OPh)_3$), 4.98 (5, d, J = 1.0 Hz, η^5-C_5H_5), 2.64 (4, br mult, CH_2), 1.43 (6, t, J = 7.2 Hz, CH_3). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2011. ^{13}C NMR spectrum ($CHCl_3$): 149.98 (d, J = 11.3 Hz, O-bound phenyl carbons), 130.24 (meta phenyl carbons), 126.28 (para phenyl carbons), 120.67 (d, J = 4.2 Hz, ortho phenyl carbons), 87.06 (η^5-C_5H_5), 52.44 (d, J = 4.5 Hz, C≡), 20.49 (CH_2), 15.34 (CH_3).

(Carbonyl)(η^5-cyclopentadienyl)(η^2-diphenylacetylene)(triphenyl phosphite)iron(II) Tetrafluoroborate. This complex was obtained as red, air-stable crystals in 78% yield by a procedure analogous to that used for the 3-hexyne complex; mp 129 °C. Anal. Calcd for $C_{38}H_{30}BF_4FeO_4P$: C, 63.01; H, 4.14. Found: C, 62.62; H, 4.54. ^{1}H NMR spectrum (acetone-d_6): 8.02–7.12 (25, mult, C_6H_5C≡ and $P(OPh)_3$), 5.78 (s, η^5-C_5H_5). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2022. ^{13}C NMR spectrum (dichloroethane): 150.24 (d, J = 11.8 Hz, O-bound phenyl carbons), 130.28 (meta phenyl carbons), 126.43 (para phenyl carbons), 120.56 (d, J = 3.9 Hz, ortho phenyl carbons), 132.13, 129.30, 128.39 (phenylacetylene carbons), 87.95 (η^5-C_5H_5), 62.58 (d, J = 5.2 Hz, C≡).

(Carbonyl)(η^2-cycloheptene)(η^5-cyclopentadienyl)(triphenyl phosphite)iron(II) Tetrafluoroborate. This complex was obtained in 73% yield by a procedure analogous to that used for the 3-hexyne complex. This complex is a yellow, crystalline solid which decomposes slowly when exposed to air; dec pt 112 °C. Anal. Calcd for $C_{31}H_{32}BF_4FeO_4P$: C, 58.00; H, 4.98. Found: C, 57.78; H, 5.27. ^{1}H NMR spectrum ($CDCl_3$): 7.35 (15, mult, $P(OPh)_3$), 4.98–4.52 (2, mult, CH=), 4.78 (5, s, η^5-C_5H_5), 2.80–1.35 (10, br mult, CH_2). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2009. ^{13}C NMR spectrum (CH_2Cl_2): 150.36 (d, J = 10.9 Hz, O-bound phenyl carbons), 130.70 (meta phenyl carbons), 126.69 (para phenyl carbons), 120.75 (d, J = 4.0 Hz, ortho phenyl carbons), 86.38 (η^5-C_5H_5), 78.85, 76.43 (CH=), 32.52, 30.97, 27.04, 26.88 (CH_2).

(Carbonyl)(η^2-cyclooctene)(η^5-cyclopentadienyl)(triphenyl phosphite)iron(II) Tetrafluoroborate. This complex was obtained as yellow-orange, air-stable crystals in 76% yield by a procedure analogous to that used for the 3-hexyne complex. These crystals contained 0.5 equiv of CH_2Cl_2 of crystallization; dec pt 85 °C. Anal. Calcd for $C_{32}H_{34}BF_4FeO_4P{\cdot}0.5CH_2Cl_2$: C, 55.88; H, 5.01; Cl, 5.07. Found: C, 55.69; H, 5.21; Cl, 5.25. ^{1}H NMR spectrum ($CDCl_3$): 7.32 (15, mult, $P(OPh)_3$), 5.31 (1, s, CH_2Cl_2), 4.85 (5, s, η^5-C_5H_5), 4.33, 3.51 (1, 1, mult, CH=), 2.62–1.29 (12, br mult, CH_2). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2017. ^{13}C NMR spectrum (CH_2Cl_2): 150.34 (d, J = 10.4 Hz, O-bound phenyl carbons), 130.77 (meta phenyl carbons), 126.81 (para phenyl carbons), 120.82 (d, J = 4.2 Hz, ortho phenyl carbons), 86.33 (η^5-C_5H_5), 81.08, 76.42 (CH=), 32.08, 30.57, 30.05, 25.87 (CH_2).

(*n*-Butyl)(carbonyl)(η^5-cyclopentadienyl)(triphenyl phosphite)iron. A slurry of (η^5-C_5H_5)Fe(CO)[$P(OPh)_3$]I in THF (35 mL) was cooled to −78 °C. To this slurry was added *n*-butyllithium (1.1 mL of a 1.6 M solution in hexane). This slurry was warmed to room temperature and stirred for an additional 30 min. The solvent was evaporated from the resulting yellow-green solution to give a light green oil. This oil was extracted with benzene (5 mL) and placed on a chromatography column (alumina, 3 × 20 cm). Elution with a hexane–benzene mixture (3:1, v/v) developed a strong yellow band which eluted well before a weaker green band (not isolated). The yellow band was collected and the solvent evaporated from this solution. The residue was extracted with a warm hexane–CH_2Cl_2 solution (2:1, v/v, 6 mL) and this solution cooled at −20 °C overnight. The yellow crystals which formed were collected, washed with cold pentane (3 mL), and dried in vacuo (0.40 g, 44%); mp 95–96 °C. Anal. Calcd for $C_{28}H_{29}FeO_4P$: C, 65.16; H, 5.62. Found: C, 65.17; H, 5.73. ^{1}H NMR spectrum ($CDCl_3$): 7.25 (15, mult, $P(OPh)_3$), 4.01 (5, d, J = 1.1 Hz, η^5-C_5H_5), 1.42 (6, mult, $FeCH_2CH_2CH_2CH_3$), 0.92 (3, t, J = 5.9 Hz, CH_3). IR spectrum (cm^{-1} in benzene): ν(CO) 1925. ^{13}C NMR spectrum (CH_2Cl_2): 152.06 (d, J = 7.4 Hz, O-bound phenyl carbons), 129.65 (meta phenyl carbons), 124.65 (para phenyl carbons), 121.62 (d, J = 4.5 Hz, ortho phenyl carbons), 83.24 (η^5-C_5H_5), 41.51 ($FeCH_2\mathit{CH_2}CH_2CH_3$), 28.53 ($FeCH_2CH_2\mathit{CH_2}CH_3$), 14.02 ($FeCH_2CH_2CH_2\mathit{CH_3}$), 1.76 (d, J = 28.8 Hz, $Fe\mathit{CH_2}CH_2CH_2CH_3$).

Attempted Thermal Decomposition of (η^5-C_5H_5)Fe(CO)[$P(OPh)_3$](*n*-butyl). A solution of (η^5-C_5H_5)Fe(CO)[$P(OPh)_3$](*n*-butyl) (0.5 g) in a hydrocarbon solvent (bp 126 °C) was refluxed for 24 h. This solution was monitored periodically by IR in an effort to observe a carbonyl band corresponding to (η^5-C_5H_5)Fe(CO)[$P(OPh)_3$]H. At no time was any infrared peak other than that corresponding to the *n*-butyl complex observed. After 24 h the solvent was evaporated to leave a yellow residue. The ^{1}H NMR spectrum confirmed that the residue was exclusively the *n*-butyl compound. The compound remaining in the flask was heated in the melt at 135 °C for 35 min. The ^{1}H NMR spectrum showed the residue to still be the *n*-butyl complex. Heating at higher temperatures, ca. 170 °C, causes the compound to decompose to ferrocene.

(Carbonyl)(η^5-cyclopentadienyl)(ethyl)(triphenyl phosphite)iron. A mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3](\eta^2\text{-C}_2\text{H}_4)]\text{BF}_4$ (1.0 g, 1.7 mmol) and NaBH_3CN (0.16 g, 2.5 mmol) was stirred in THF (20 mL) for 2 h. The solvent was then evaporated, the residue extracted with benzene (40 mL), and this mixture filtered. The filtrate was concentrated to 10 mL and hexane (15 mL) was added. This solution was cooled at −20 °C overnight to yield large yellow crystals which were collected, washed with cold pentane (5 mL), and dried in vacuo (0.51 g, 59%); mp 86–88 °C. Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{FeO}_4\text{P}$: C, 63.98; H, 5.12. Found: C, 64.05; H, 5.27. The ^{1}H NMR spectrum matched that reported by Masters et al.[8] ^{13}C NMR spectrum (CH_2Cl_2): 152.13 (d, J = 7.3 Hz, O-bound phenyl carbons), 129.71 (meta phenyl carbons), 124.70 (para phenyl carbons), 121.65 (d, J = 4.0 Hz, ortho phenyl carbons), 83.34 (η^5-C_5H_5), 22.81 (CH_3), −4.74 (d, J = 29.2 Hz, CH_2).

Reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3](\eta^2\text{-CH}_2{=}\text{CHCH}_2\text{CH}_3)]\text{BF}_4$. To a mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3](\eta^2\text{-CH}_2{=}\text{CHCH}_2\text{CH}_3)]\text{BF}_4$ (1.0 g, 1.7 mmol) and NaBH_3CN (0.16 g, 2.5 mmol) was added THF (20 mL). This mixture was stirred for 2 h and then the solvent was evaporated. The yellow residue was extracted with benzene (25 mL) and this solution filtered. The solvent was then evaporated and the residue extracted with hexane–CH_2Cl_2 (2:1, v/v, 10 mL). The volume of the solution was reduced ca. by half by evaporation until the solution appeared cloudy. Cooling this solution at −20 °C overnight produced yellow crystals which were collected by removing the mother liquor via syringe. The crystals were washed with cold pentane (4 mL) and dried in vacuo (0.55 g, 64%). The spectral properties matched those of an authentic sample of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]$(*n*-butyl) prepared from $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]\text{I}$ and *n*-butyllithium. The reduction of the propene complex was carried out in an analogous fashion.

(*sec*-Butyl)(carbonyl)(η^5-cyclopentadienyl)(triphenyl phosphite)iron. THF (20 mL) which had been cooled to 0 °C was added to a mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3](\eta^2\text{-CH}_3\text{CH}{=}\text{CHCH}_3)]\text{BF}_4$ (1.0 g, 1.7 mmol) and NaBH_3CN (0.16 g, 2.5 mmol). This mixture was stirred at 0 °C for 1 h and the solvent was evaporated. The gummy residue was extracted with benzene (15 mL) and this mixture filtered. The filtrate was concentrated to 3 mL and placed on a short chromatography column (alumina, 3 × 15 cm). Elution with heptane developed a single yellow band. The solvent was evaporated to yield a yellow oil (0.48 g, 56%). Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{FeO}_4\text{P}$: C, 65.15; H, 5.62. Found: C, 65.49; H, 5.29. ^{1}H NMR spectrum (CCl_4): 7.13 (15, mult, P(OPh)_3), 4.13 (5, s, η^5-C_5H_5), multiplet centered at 1.50 (6, $\text{Fe}\mathit{CH}(\mathit{CH}_3)\mathit{CH}_2\text{CH}_3$), 0.98 (3, t, J = 6.2 Hz, $\text{FeCH(CH}_3)\text{CH}_2\mathit{CH}_3$). IR spectrum (cm^{-1} in hexane): ν(CO) 1943. ^{13}C NMR spectrum (in CH_2Cl_2, both diastereomers are observed, labeled A and B; the ratio A/B is 1.5 to 1): 220.74 (B), 220.73 (A) (pair of d, J = 48.1 Hz, J = 48.1 Hz, CO), 152.32 (d, J = 10.2 Hz, O-bound phenyl carbons), 129.81 (meta phenyl carbons), 124.82 (para phenyl carbons), 121.87 (d, J = 4.1 Hz, ortho phenyl carbons), 84.01 (η^5-C_5H_5), 40.28 (A), 39.30 (B) (s, d, J = 2.4 Hz, $\text{FeCH(CH}_3)\mathit{CH}_2\text{CH}_3$), 28.57 (A), 28.42 (B) ($\text{FeCH(}\mathit{CH}_3)\text{CH}_2\text{CH}_3$), 21.35 (A), 21.13 (B) (d, J = 25.6 Hz, J = 26.0 Hz, $\text{Fe}\mathit{CH}\text{(CH}_3)\text{CH}_2\text{CH}_3$), 16.26 (A), 16.15 (B) ($\text{FeCH(CH}_3)\text{CH}_2\mathit{CH}_3$).

Attempted Isomerization of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]$(*sec*-butyl). A solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]$(*sec*-butyl) (0.6 g, 1.2 mmol) in heptane (30 mL) was stirred and heated at 65 °C for 10 h. The solution was filtered to remove decomposition material and the solvent was evaporated from the filtrate to yield a yellow oil. The oil was completely dissolved in CH_2Cl_2 (2 mL) and part of this solution used to obtain a ^{13}C NMR spectrum. This spectrum showed that no $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]$(*n*-butyl) formed under these conditions.

(Carbonyl)(η^5-cyclopentadienyl)(η^1-3,3-hexenyl)(triphenyl phosphite)iron. L-Selectride (3.5 mL of a 1.0 M solution in THF) was added to a −78 °C slurry of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3](\eta^2\text{-3-hexyne})]\text{BF}_4$ (2.0 g, 3.2 mmol) in THF (30 mL). As the orange slurry warmed to room temperature, it slowly became a yellow-orange solution. The solvent was evaporated from this solution, the residue extracted with benzene (5 mL), and this solution placed on a chromatography column (alumina, 5 × 25 cm). Elution with hexane–benzene (2:1, v/v) developed a yellow band which eluted well ahead of a weak orange band (not isolated). The yellow band was collected and the solvent evaporated to yield a yellow oil which was dried in vacuo for 24 h (0.90 g, 52%). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{FeO}_4\text{P}$: C, 66.43; H, 5.76. Found: C, 65.96; H, 5.87. ^{1}H NMR spectrum (CS_2): 7.15 (15, mult, P(OPh)_3), 5.22 (1, t, J = 8.1 Hz, $\text{FeC(CH}_2\text{CH}_3)\mathit{CH}\text{CH}_2\text{CH}_3$), 1.82–0.73 (10, mult, $\text{FeC(}\mathit{CH}_2\mathit{CH}_3)\text{CH}\mathit{CH}_2\mathit{CH}_3$). IR spectrum (cm^{-1} in hexane): ν(CO) 1943. ^{13}C NMR spectrum (CH_2Cl_2): 220.05 (d, J = 49.5 Hz, CO), 152.30 (d, J = 9.0 Hz, O-bound phenyl carbons), 141.39 (d, J = 7.5 Hz, $\text{Fe}\mathit{C}\text{(CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 132.78 (d, J = 6.5 Hz, $\text{FeC(CH}_2\text{CH}_3)\mathit{CH}\text{CH}_2\text{CH}_3$), 129.65 (meta phenyl carbons), 124.71 (para phenyl carbons), 121.90 (d, J = 3.9 Hz, ortho phenyl carbons), 84.07 (η^5-C_5H_5), 45.10 (d, J = 2.8 Hz, $\text{FeC(}\mathit{CH}_2\text{CH}_3)\text{CHCH}_2\text{CH}_3$), 36.30 (d, J = 2.6 Hz, $\text{FeC(CH}_2\text{CH}_3)\text{CH}\mathit{CH}_2\text{CH}_3$), 22.71 ($\text{FeC(CH}_2\mathit{CH}_3)\text{CHCH}_2\text{CH}_3$), 14.44 ($\text{FeC(CH}_2\text{CH}_3)\text{CHCH}_2\mathit{CH}_3$).

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\overline{\text{FeC}_6\text{H}_4\text{OP}}\text{(OPh)}_2\text{(CO)}$. A mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]\text{I}$ (1.0 g, 1.7 mmol) and AgBF_4 (0.38 g, 1.9 mmol) was stirred in CH_2Cl_2 (30 mL) for 30 min. This mixture was filtered and the filtrate was treated with diethylamine (1.0 mL). This solution was stirred for 10 min during which time the color turned brown and a small amount of gray precipitate formed. The solvent was then evaporated, the residue extracted with benzene (4 mL), and this solution placed on a chromatography column (alumina, 3 × 20 cm). Elution with benzene produced a yellow band which separated well from a brown band (not isolated) that remained near the top of the column. The yellow band was collected and the solvent evaporated to yield a yellow residue. The spectral properties of this compound matched those already reported by Stewart et al.[11] for the ortho-metalated complex $(\eta^5\text{-C}_5\text{H}_5)\overline{\text{FeC}_6\text{H}_4\text{OP}}\text{(OPh)}_2\text{(CO)}$ (0.45 g, 57%).

Results

Synthesis and Characterization of New Complexes. A green mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]\text{I}$ and 1 equiv of AgBF_4 first turns brown and then dark green over a 30-min period in CH_2Cl_2. The mixture contains an intermediate which has a carbonyl stretching band at 2005 cm^{-1} and is believed to be the species $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3]]^+$ (**1**). This intermediate is air sensitive and solutions rapidly turn brown if exposed to air. In the absence of air, **1** is fairly stable, showing little decomposition after 2 days at −20 °C. No attempt was made to isolate this intermediate.

Introduction of olefin or alkyne ligands into solutions of **1** leads to the production of new η^2-unsaturated hydrocarbon complexes. The most successful procedure for using **1** synthetically is to first separate **1** from insoluble silver salts by filtration and then to treat the filtrate with 2 or 3 equiv of the ligand. The complexes may then be obtained as yellow or orange crystals in ca. 75% yield by adding diethyl ether and scratching the sides of the container. The complexes obtained from these reactions were usually quite pure and often did not require recrystallization. All of the η^2-unsaturated hydrocarbon complexes reported here are air-stable solids except for the *cis*-2-butene and cycloheptene complexes which are slightly hygroscopic. The complexes are also quite stable in solution under anaerobic conditions although decomposition is extensive if the solutions are exposed to air.

Treatment of a solution of **1** with diethylamine produced a brown solution which did not yield the expected diethylamine adduct. Instead, after this solution was concentrated and chromatographed on alumina, a yellow compound was isolated which was identified by ^{1}H NMR as the known ortho-metalated complex $(\eta^5\text{-C}_5\text{H}_5)\overline{\text{FeC}_6\text{H}_5\text{OP}}\text{(OPh)}_2\text{(CO)}$.[11]

Reactions of New Complexes. The $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(OPh)}_3](\eta^2\text{-olefin})]\text{BF}_4$ complexes are reduced to the corresponding alkyls by NaBH_3CN in THF. These reactions are quite fast and their completion is indicated by the lowering of the carbonyl stretching band from ca. 2015 to ca. 1935 cm^{-1}.

These hydride reductions are clean and remarkably free of side reactions. In particular, in no case was any of the known hydrido complex,[8] $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]H$, observed in these reactions. The known ethyl[4b] and the new butyl complexes were isolated in ca. 60% yield without need of column chromatography. The butyl complex produced from the 1-butene adduct consisted solely of the *n*-butyl derivative. This complex is also produced from the direct reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ and *n*-butyllithium. The reduction of the propene complex yielded both *n*-propyl and the isopropyl isomers in a ratio of 4 to 1. The amount of the isopropyl product increased when $NaBH_4$ was used as the reducing agent and was the predominant isomer when L-Selectride, $LiB[CH(CH_3)_3]_3H$, was used. Reduction of the *cis*-2-butene complex yielded the new *sec*-butyl complex in reasonably good yield. Both of the possible diastereomers of this complex were obtained from this reaction in a ratio of ca. 1.5 to 1. This compound was quite soluble even in cold hydrocarbon solution and could not be induced to crystallize. It was obtained as a pure yellow oil after chromatography on a short alumina column. In general, the branched-chain alkyls are more soluble in hydrocarbon solution and, accordingly, are more difficult to crystallize than the straight-chain alkyls.

The alkyliron complexes in this system are very stable to thermal decomposition. The *n*-butyl derivative did not undergo extensive decomposition when heated in boiling hydrocarbon solution at 126 °C for 24 h. This compound also remained essentially intact after being heated in the melt at 135 °C for 30 min. The complex finally decomposed at ca. 170 °C to yield a dark oil from which crystals of ferrocene sublimed. Also, the *sec*-butyl complex did not isomerize to the *n*-butyl derivative when heated in hydrocarbon solution at 65 °C for 10 h. This experiment did indicate that one of the two diastereomers of this compound is significantly less stable to thermal decomposition than the other. Integration of the ^{13}C NMR spectra of a sample of this compound taken before and after heating for 10 h revealed that the diastereomer which had predominated in the hydride reduction was in lower relative concentration after heating.

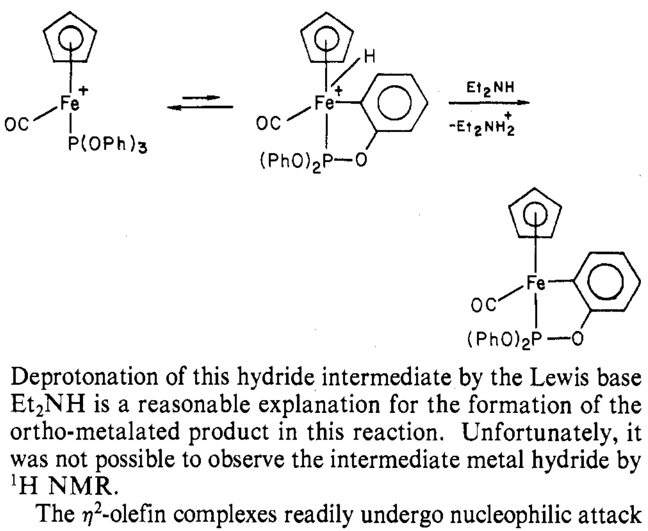
The alkyne complex $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3](\eta^2\text{-}3\text{-hexyne})]BF_4$ is smoothly reduced to the σ-vinyl complex by L-Selectride in THF at −78 °C. This complex was obtained as a yellow oil which is thermally stable and only slowly decomposes in air. This complex was fully characterized and its spectral properties are consistent with σ-vinyl complexes previously reported in the dicarbonyl[12] and triphenylphosphine systems.[2] The reduction of this acetylene complex was not successful when $NaBH_3CN$ was used as the reducing reagent.

Discussion

Our previously reported[2] route to $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)(\eta^2\text{-un})]BF_4$ (L = CO, PPh_3; un = unsaturated hydrocarbon) complexes from the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(L)I$ and $AgBF_4$ in CH_2Cl_2 followed by addition of the ligand proved very successful for the preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3](\eta^2\text{-un})]BF_4$ complexes. The potential synthesis of η^2-unsaturated hydrocarbon complexes is much greater than in the triphenylphosphine system and comparable to the extensively explored dicarbonyl system. The only ligand that failed in this new system that works quite well in the dicarbonyl system is cyclopentene. The stability of these new complexes is very similar to the dicarbonyl analogues with respect to air oxidation and to displacement of the unsaturated ligand by donor solvents such as acetone. In contrast, the triphenylphosphine complexes are much less stable. For example, in the former two systems, the propene complex is quite robust whereas in the latter it can only be observed in solution at low temperature. These trends had been anticipated because, like a carbonyl group, the triphenyl phosphite ligand is smaller and a stronger π-accepting[13] ligand than triphenylphosphine. In terms of size the triphenyl phosphite cone angle[14] is similar to that of trimethylphosphine, a ligand much smaller than triphenylphosphine.

An alternate, but very similar, route to these complexes is to prepare the appropriate $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)(THF)]BF_4$ (THF = tetrahydrofuran) complex as a solid and make the η^2-unsaturated hydrocarbon complexes by a simple exchange reaction in CH_2Cl_2.[15] This route is not very successful in the triphenyl phosphite system because the exchange reaction is slow and only low yields of the desired products could be obtained.

Although the intermediate $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]]^+$ is presumed to be formed in the halide abstraction reaction in CH_2Cl_2,[9] the reaction of this intermediate with Et_2NH to yield the known ortho-metalated species $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_5OP}(OPh)_2(CO)$ indicates that this 16-electron intermediate may be in equilibrium with the 18-electron ortho-metalated hydride species.



Deprotonation of this hydride intermediate by the Lewis base Et_2NH is a reasonable explanation for the formation of the ortho-metalated product in this reaction. Unfortunately, it was not possible to observe the intermediate metal hydride by ^1H NMR.

The η^2-olefin complexes readily undergo nucleophilic attack to yield the corresponding alkyls when treated with a slight excess of $NaBH_3CH$ in THF. The yields for these reactions are good and are not diminished by formation of either the hydride complex $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]H$ or a dimeric product analogous to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. The metal hydride and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ are often byproducts of reductions in the triphenylphosphine and dicarbonyl systems, respectively. These reductions are, therefore, an effective route to simple alkyls and more convenient than the published method[4] of ligand exchange with the appropriate $(\eta^5\text{-}C_5H_5)Fe(CO)_2(alkyl)$ complex since these complexes themselves are at times fairly difficult to prepare. For straight-chain alkyls, the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ and alkyllithium reagents is the most direct route to these complexes. An aspect of these reductions of particular interest was whether the presence of the triphenyl phosphite group would have any influence on the direction of the hydride attack. In the dicarbonyl system, the propene complex was reduced by $NaBH_4$ to yield both the isopropyl and *n*-propyl derivatives in a 3 to 1 ratio[16] and by $NaBH_3CN$ to yield the isopropyl derivative exclusively.[17] The triphenyl phosphite analogue yielded the *n*-propyl over the isopropyl in a ratio of 2 to 1 when $NaBH_4$ was used and in a ratio of 4 to 1 when $NaBH_3CN$ was the reducing agent. This tendency to form the straight-chain isomer was even more pronounced in the case of the 1-butene complex as $NaBH_3CN$ reduced this complex to yield the *n*-butyl complex exclusively. Apparently some selectivity can be achieved in isomer formation by proper choice of hydride reagent as the propene complex yielded the isopropyl derivative almost exclusively when reduced by the bulky hydride reagent L-Selectride. The

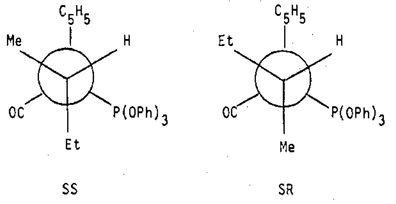


Figure 1.

reductions also proceed smoothly with the *cis*-2-butene and 3-hexyne complexes yielding the *sec*-butyl and σ-vinyl complexes, respectively.

We have recently shown that (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl) complexes undergo a clean β-elimination reaction to yield (η^5-C_5H_5)Fe(CO)(PPh_3)H and alkene[18]. Also, certain alkyl groups will isomerize on the metal[19] (e.g., the *sec*-butyl compound isomerizes to the *n*-butyl derivative). The first step in each of these processes is the dissociation of the phosphine to yield the 16-electron intermediate (η^5-C_5H_5)Fe(CO)(alkyl). Apparently, the triphenyl phosphite must be considerably less labile than triphenylphosphine because the (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](alkyl) complexes will not undergo a β-elimination reaction nor will the isomerization reaction take place. Heating these complexes to very high temperatures yields only ferrocene. As triphenyl phosphite dissociation would produce the same intermediate as in the triphenylphosphine system, clearly it is the phosphite dissociation that is blocked. Note also in the triphenylphosphine system that the presence of excess triphenylphosphine also blocks the β-elimination reaction by shifting the initial reversible dissociation reaction to the left.[18] Interestingly, these new results substantiate our earlier claims that direct elimination of the olefin without coordination to the metal in the β-elimination process is a high energy process.

The ^{13}C NMR spectrum of (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$]($CH(CH_3)CH_2CH_3$) shows a doubling of all alkyl resonances, indicating that both possible diastereomers for this molecule containing two chiral centers form in the hydride addition reaction. In this mixture, one diastereomer (A) predominates over the other (B) by a ratio of 1.5 to 1. Although favored in this reaction, diastereomer A is less thermally stable than B as shown by the fact that heating the sample at 65 °C for 10 h changes the ratio of A to B to 0.75 to 1. Baird has shown that one diastereomer of (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$]($CHPhSiMe_3$) is considerably less stable than the other, but it was impossible to ascertain the relative amounts of the initial products that formed in the reaction.[5b] He has also shown by using vicinal P–H coupling constant arguments that the more stable isomer is, as expected, the one that places the alkyl substituents in the sterically least hindered position relative to the other ligands on the metal. This makes the *SS–RR* pair lower in energy, one rotamer of which is shown in Figure 1 along with one rotamer of the *SR–RS* pair (note that the *RR–SS* and *RS–SR* enantiomers, respectively, are also present, making each diastereomer an enantiomeric pair). On the assumption that the configuration of the starting material is similar to that shown in Figure 2 which places the *cis*-2-butene group in the least sterically hindered position,[20] the hydride addition must preferentially take place from the carbonyl side of the molecule, thus producing the *SR* isomer as shown in Figure 2. Although the *n*-butyl complex could be readily prepared by the reaction of (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$]I and *n*-butyllithium, unfortunately it was not possible to make the *sec*-butyl complex from *sec*-butyllithium for comparative purposes.

The chemistry of this triphenyl phosphite system offers advantages over both the triphenylphosphine and dicarbonyl derivatives. The main advantage over the triphenylphosphine system is that the η^2-olefin complexes are much more stable. Also, the starting material forms from (η^5-C_5H_5)Fe(CO)$_2$I in 80% yield as compared to about 30% yield in our hands for the triphenylphosphine analogue. The main advantage over the dicarbonyl system is that under reducing conditions one does not have to contend with the formation of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$, a frequently encountered product that lowers yields and makes purification of products more difficult. Also, the alkyls are much more stable in this system than in the dicarbonyl system. A significant advantage of the dicarbonyl system is that [(η^5-C_5H_5)Fe(CO)$_2$]$^-$ can be used as a reagent whereas the analogous anion is unknown in the triphenyl phosphite system.

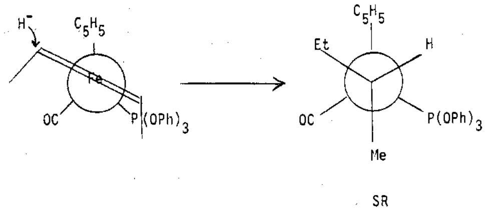


Figure 2.

Note that the NMR spectra reported for the new η^2-ethylene, diphenylacetylene, and 3-hexyne complexes clearly show that these are fluxional molecules at the normal spectrometer temperature in that the nuclei on each side of these symmetrical ligands are reported to be equivalent. In a static structure analogous to that shown in Figure 2 for the *cis*-2-butene complex, each side of these ligands would be nonequivalent. A variable-temperature NMR investigation of these molecules and analogous triphenylphosphine substituted molecules[2] has been carried out and the results are reported separately.[21]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this project.

Registry No. [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-ethylene)]BF_4, 71341-60-1; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-propene)]BF_4 (isomer A), 71359-43-8; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-propene)]BF_4 (isomer B), 71425-14-4; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-1-butene)]BF_4 (isomer A), 71425-16-6; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-1-butene)]BF_4 (isomer B), 71359-45-0; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-*cis*-2-butene)]BF_4, 71359-47-2; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-allene)]BF_4, 71359-49-4; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-3-hexyne)]BF_4, 71341-56-5; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-diphenylacetylene)]BF_4, 71341-58-7; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-cycloheptene)]BF_4, 71359-51-8; [(η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^2-cyclooctene)]BF_4, 71359-53-0; (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](*n*-butyl), 71359-54-1; (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](ethyl), 59140-21-5; (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](*sec*-butyl) (isomer A), 71359-55-2; (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](*sec*-butyl) (isomer B), 71392-86-4; (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$](η^1-3,3-hexenyl), 71359-56-3; (η^5-C_5H_5)$FeC_6H_4OP(OPh)_2$(CO), 56533-24-5; (η^5-C_5H_5)Fe(CO)[P(OPh)$_3$]I, 31988-05-3.

References and Notes

(1) (a) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974); (b) N. Genco, D. Marten, S. Raghu, and M. Rosenblum, *J. Am. Chem. Soc.*, **98**, 848 (1976).
(2) D. L. Reger, C. J. Coleman, and P. J. McElligott, *J. Organomet. Chem.*, **171**, 73 (1979).
(3) M. C. H. Green and R. N. Whiteley, *J. Chem. Soc. A*, 1943 (1971).
(4) (a) S. R. Su and A. Wojcicki, *J. Organomet. Chem.*, **27**, 231 (1971); (b) *Inorg. Chem.*, **14**, 89 (1975).
(5) (a) K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, **97**, 6598 (1975); (b) *ibid.*, **99**, 1808 (1977).
(6) R. P. Stewart, Jr., L. R. Isbrandt, J. J. Benedict, and J. G. Palmer, *J. Am. Chem. Soc.*, **98**, 3245 (1976).
(7) D. A. Brown, H. J. Lyons, A. R. Manning, and J. M. Rowley, *Inorg. Chim. Acta*, **3**, 346 (1969).
(8) J. A. VanDorn, C. Masters, and H. C. Volger, *J. Organomet. Chem.*, **105**, 245 (1976).
(9) Analogous intermediates have been suggested in closely related systems: [(η^5-C_5H_5)Fe(CO)$_2$]$^+$, ref 10; [(η^5-C_5H_5)Fe{(OPh)$_3$}$_2$]$^+$, ref 3; and [(η^5-C_5H_5)Fe(CO)(PPh_3)]$^+$, ref 2.

(10) (a) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961); (b) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971); (c) P. F. Boyle and K. M. Nicholas, *J. Organomet. Chem.*, **114**, 307 (1976); (d) M. Brookhart and G. O. Nelson, *J. Am. Chem. Soc.*, **99**, 6099 (1977).
(11) R. P. Stewart, Jr., J. J. Benedict, L. Isbrandt, and R. S. Arnpulski, *Inorg. Chem.*, **14**, 2933 (1975).
(12) D. W. Lichtenberg and A. Wojcicki, *J. Organomet. Chem.*, **94**, 311 (1975).
(13) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
(14) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(15) D. L. Reger and C. J. Coleman, *J. Organomet. Chem.*, **131**, 153 (1977).
(16) P. Lennon, M. Madhavarao, A. Rosan, and M. Rosenblum, *J. Organomet. Chem.*, **108**, 93 (1976).
(17) S. M. Florio and K. M. Nicholas, *J. Organomet. Chem.*, **112**, C17 (1976).
(18) D. L. Reger and E. C. Culbertson, *J. Am. Chem. Soc.*, **98**, 2789 (1976).
(19) D. L. Reger and E. C. Culbertson, *Inorg. Chem.*, **16**, 3104 (1977).
(20) (a) J. W. Faller, B. V. Johnson, and C. D. Schaeffer, Jr., *J. Am. Chem. Soc.*, **98**, 1395 (1976); (b) J. W. Faller, private communication.
(21) D. L. Reger and C. J. Coleman, *Inorg. Chem.*, companion paper in Notes section of this issue.

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Fluorinated Alkoxides. 15. Synthesis and Hydrogenation of Iminoalkoxy Complexes of Copper(2+). Influence of Chelate Ring Size on Structure and Magnetic Properties

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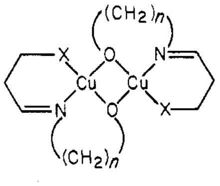
Template condensation of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone, $CH_3COCH_2C(CF_3)_2OH$, with a variety of amino alcohols $NH_2(CH_2)_nOH$ ($n = 2$–6) in the presence of Cu^{2+} leads to stable, neutral, iminoalkoxy complexes with a 1:1 metal/ligand ratio for $n = 2$–4 and a 1:2 metal/ligand ratio for $n = 5$ or 6. These are associated into tetranuclear units for $n = 2$, dinuclear units for $n = 3$ or 4, and mononuclear units for $n = 5$ or 6. Magnetic moments are reduced in the dinuclear but not the tetranuclear complexes; this is ascribed to a lack of planarity around the Cu atoms in the latter. Hydrogenation of the above (aminoalkoxy)copper(II) complexes is achieved with $LiAlH_4$; dinuclear structures, all having reduced magnetic moments, are now found with $n = 2$–4, and mononuclear structures are found with $n = 4$–6. Possible structures consistent with observed magnetic and spectroscopic data are discussed.

Introduction

There is considerable interest in the correlation between magnetic properties and structure in dinuclear[1] copper(II) complexes where spin pairing between copper atoms may occur via bridging oxygen atoms. In particular, studies on complexes of tridentate ligands where each copper atom is included in two chelate rings, as in the general structure **1**, show a critical dependence of the degree of interaction upon the size of the ring containing the bridging oxygen atoms.

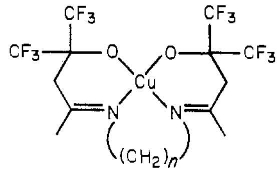


1, X = O or N

Thus, Bertrand and Kelley[2] found that, in the template condensation of acetylacetone with amino alcohols, a planar complex with a substantially reduced magnetic moment was obtained with $n = 3$, whereas the analogous complex with $n = 2$ was nonplanar, was associated into units containing four copper atoms, and was of normal magnetic moment. Curtis and co-workers, in a similar condensation process using acetone, found that the complex with $n = 3$ was planar (with an additional amino alcohol residue incorporated at a fifth, apical, position on copper) and virtually diamagnetic,[3] while the complex with $n = 2$ was nonplanar and paramagnetic.[4] Analogous derivatives incorporating aromatic[5] or pyrrole[6] rings also show very large degrees of coupling between copper atoms when $n = 3$.

From structural studies on numerous examples, it is clear that it is the geometry of the environment around the copper atoms, rather than the electronic properties of the ligands, which determines the degree of coupling, a reduced magnetic moment always being associated with approximate planarity. The geometry may be conveniently expressed either in terms of the departure from planarity toward, in the limit, tetrahedral coordination around copper,[7] or in terms of the Cu–O–Cu bridging angle.[8]

We have recently demonstrated[9,10] that the fluorinated keto alcohol $CH_3COCH_2(CF_3)_2OH$ (hexafluorodiacetone alcohol, HFDA) will readily undergo template condensation with a variety of diamines to give copper(II) complexes of structure **2**.



2, $n = 2$–12

It was reasonable to suppose that the use of amino alcohols in place of diamines in the condensation would result in the formation of dinuclear copper complexes of type **1** in which the value of n could be varied by choice of a suitable amino alcohol. Furthermore, since we have shown that fluorinated imino complexes of copper may readily be hydrogenated to the corresponding amino derivatives,[11] there would be an opportunity to study the effect on the ring geometry and magnetic properties of changing the hybridization at nitrogen from sp^2 to sp^3.

This paper describes the synthesis and properties of iminoalkoxy complexes of copper having $n = 2$–6 and their hydrogenation to the corresponding amino complexes.

Experimental Section

General Methods. Infrared spectra were recorded on a Perkin-Elmer 621 instrument, visible–UV spectra on Cary 14 and 118 spectrometers, and mass spectra on a Varian MAT 311A instrument, and molecular

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