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REACTION OF YLIDES WITH CATIONIC TRANSITION METAL OLEFIN AND TETRAHYDROFURAN COMPLEXES

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Summary

The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)(THF)]^+$ (L = CO, PPh_3) with CH_2PPh_3 yields $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)CH_2PPh_3]^+$ complexes. This ylide reacts with $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}C_2H_4)]^+$ to yield $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}(CH_2CH_2CH_2PPh_3)]^+$ and $[PO(OMe)_2]^-$ reacts with this cationic olefin complex to yield $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)[CH_2CH_2PO(OMe)_2]$.

Introduction

Ylides, which have been used extensively for the synthesis of carbon—carbon bonds [1], have not been applied often in the preparation of new carbon—transition metal σ bonds. Recently, a number of reactions of ylides with transition metal complexes has been reported [2]. The most extensively used ylide has been $(CH_3)_3PCH_2$ [2a] which has been shown to bond to transition metals in a number of different ways. This work demonstrated that transition metal ylide complexes are quite stable. As part of our general interest in the synthesis of metal—carbon σ bonds [3] it was decided to treat ylides with $[(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}(L)(THF)]^+$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)(\eta^2\text{-}C_2H_4)]^+$ (L = CO, PPh_3) to form new transition metal ylide, phosphonium and phosphonate complexes.

Experimental

All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen. Melting points and decomposition points were determined in sealed and evacuated capillaries and are uncorrected. The ^{13}C spectra were run in CH_2Cl_2 and chemical shifts are reported versus TMS using $\delta_C(CH_2Cl_2)$ 54.0 ppm and are proton decoupled.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2PPh_3)]BF_4$ (III)

A THF (125 ml) solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (I) [4] (2.0 g, 5.95 mmol) was treated with CH_2PPh_3 (prepared from 2.40 g, 6.7 mmol of $[CH_3PPh_3]Br$ and 4.09 ml of 1.6 *M* n-butyllithium in 25 ml of benzene) which was added by syringe. The resulting mixture was stirred for 15 h. The reaction mixture was filtered, reduced to half of the original volume, and 100 ml of ether was added. The yellow powder which precipitated was collected, washed with pentane (4 × 25 ml) and dried in vacuo (2.15 g, 56%), decomp. pt. 181—182.5°C. (Anal: Found: C, 49.38; H, 3.41. $C_{26}H_{22}BF_4FeO_2P \cdot LiBr$ calcd.: C, 49.44; H, 3.49%). ^1H NMR spectrum (δ(ppm) in $CDCl_3$): PPh_3, 7.80 and 7.55 (15, multiplets); η^5-C_5H_5, 5.12 (5, singlet); CH_2, 2.17 (2, doublet, *J* 12.6 Hz). IR spectrum (cm^{-1}): ν(CO) 2040vs, 2008vs (mull); 2020vs, 1965vs (CH_2Cl_2). ^{13}C NMR spectrum: CO, 216.37 (doublet, *J* 1.3 Hz); *para*-phenyl carbons, 133.92 (doublet, *J* 2.6 Hz); *ortho*-phenyl carbons, 133.34 (doublet, *J* 9.0 Hz); *meta*-phenyl carbons, 129.89 (doublet, *J* 11.8 Hz); P-bound phenyl carbons, 123.88 (doublet, *J* 83.9 Hz); η^5-C_5H_5, 86.86 (singlet); CH_2, —23.33 (doublet, *J* 36.5 Hz).

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2PPh_3)]BF_4$ *(IV)*

A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ (1.89 g, 3.5 mmol) and $AgBF_4$ (0.75 g, 3.85 mmol) was stirred in THF (125 ml) for 15 min. To this solution, CH_2PPh_3 (prepared from $[CH_2PPh_3]I$ (1.74 g, 4.3 mmol) and 2.6 ml of 1.6 *M* n-butyllithium in benzene (25 ml)) was added by syringe. This solution was stirred for 15 h. The reaction mixture was filtered, reduced to half of the original volume, and 100 ml of ether was added. The yellow powder that formed immediately was collected, washed with pentane (4 × 25 ml), and dried in vacuo (1.31 g, 41%) decomp. pt. 68—70°C. (Anal: Found: C, 56.92; H, 4.12. $C_{43}H_{37}BF_4FeOP_2 \cdot LiI$ calcd.: C, 56.83; H, 4.07%. ^1H NMR spectrum (δ(ppm) in $CDCl_3$): PPh_3's, 7.85 and 7.65 (30, multiplets); η^5-C_5H_5, 5.65 (5, doublet, *J* 1.5 Hz); CH_2, 3.18 (2, doublet, *J* 14.4 Hz). IR spectrum (cm^{-1}): ν(CO) 1951vs (mull), 1948 (CH_2Cl_2). ^{13}C NMR spectrum: CO, 208.99 (doublet, *J* 24.1 Hz); carbons of PPh_3 and triphenylphosphonium, 134.93—129.08 (multiplet); P-bound phenyl carbons of triphenylphosphonium, 118.48 (doublet, *J* 88.4 Hz); η^5-C_5H_5, 89.35 (singlet); CH_2, 9.6 (double doublet, *J*(CP) 43.0 Hz, *J*(CP^+) 102.0 Hz).

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2CH_2CH_2PPh_3)]BF_4$ *(VI)*

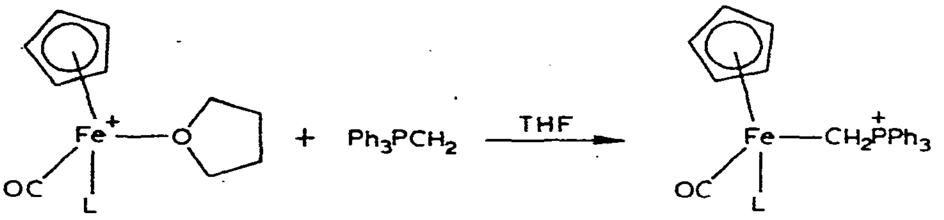
A THF solution (150 ml) of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}C_2H_4)]BF_4 \cdot C_6H_6$ (2.0 g, 3.3 mmol) was treated with CH_2PPh_3 (prepared from $[CH_3PPh_3]Br$ (1.46 g, 4.1 mmol) and 2.5 ml of 1.6 *M* n-butyllithium in benzene (25 ml)). This solution was stirred for 15 h. Hexane (ca. 50 ml) was added to this solution until IR monitoring indicated the complete precipitation of IV which also forms in this reaction to the extent of ca. 35%. This solution was filtered using filter-aid. Addition of more hexane precipitated an orange powder which was collected, washed with pentane (4 × 20 ml) and dried in vacuo (1.19 g, 40%), decomp. pt. 81—83°C. (Anal: Found: C, 60.35; H, 5.18. $C_{45}H_{41}BF_4FeOP_2 \cdot LiBr$ calcd.: C, 60.74; H, 4.61%). ^1H NMR spectrum (δ(ppm) in $CDCl_3$); PPh_3, 7.72 and 7.35 (30, multiplets); η^5-C_5H_5, 4.26 (5, singlet); $CH_2CH_2CH_2$, 3.42 and 1.30 (6, multiplets). IR spectrum (cm^{-1}): ν(CO) 1900vs (mull), 1905vs (CH_2Cl_2). ^{13}C NMR spectrum: CO, 222.33 (doublet, *J* 32.1 Hz); carbons of PPh_3 and triphenylphosphonium, 136.86—127.46 (multiplet); P-bound carbons of triphenylphosphonium, 118.40 (doublet, *J* 85.4 Hz); η^5-C_5H_5, 84.24 (singlet); Fe—$CH_2\underline{C}H_2CH_2$, 30.71 (double doublet, *J*(CP) 3.0 Hz, *J*(CP^+) 3.0 Hz), Fe—$CH_2CH_2\underline{C}H_2$, 26.78 (doublet, *J* 42.6 Hz); Fe—$\underline{C}H_2CH_2CH_2$, 4.17 (double doublet, *J*(CP) 19.1 Hz, *J*(CP^+) 8.2 Hz).

(η^5-C_5H_5)Fe(CO)(PPh_3)($CH_2CH_2P(O)(OCH_3)_2$) (VII)

A mixture of [(η^5-C_5H_5)Fe(CO)(PPh_3)(η^2-C_2H_4)]$BF_4 \cdot C_6H_6$ (0.40 g, 0.66 mmol) and Na[$PO(OCH_3)_2$] (0.11 g, 0.80 mmol) was allowed to react in 20 ml of THF with stirring for 15 h. The solvent was evaporated and the residue extracted with 10 ml of benzene and filtered. The solvent was evaporated to ca. 5 ml and 6 ml of pentane was added. After cooling overnight at −5° C, the resulting red crystals were collected, washed with pentane (2 × 2 ml) and dried in vacuo (0.15 g, 41%), m.p. 150—151.5°C. (Anal: Found: C, 61.44; H, 5.52. $C_{28}H_{30}FeO_4P_2$ calcd.: C, 61.31; H, 5.47%). ^1H NMR spectrum (δ(ppm) in acetone-d_6): PPh_3, 7.45 and 7.05 (15, multiplet); η^5-C_5H_5, 4.10 (5, doublet, *J* 1.2 Hz); CH_3, 3.48 and 3.39 (6, doublets, *J* 10.8 Hz); CH_2CH_2, 2.10 (4, multiplet). IR spectrum (cm^{-1}): ν(CO) 1898vs (mull), 1911 (THF). ^{13}C NMR spectrum: CO, 222.0 (doublet, *J* 48.0 Hz); P-bound phenyl carbons, 135.8 (doublet, *J* 36.0 Hz); *ortho*-phenyl carbons, 133.4 (doublet, *J* 6.0 Hz); *para*-phenyl carbons, 129.3 (singlet); *meta*-phenyl carbons, 128.2 (doublet, *J* 8.0 Hz); η^5-C_5H_5, 85.2 (singlet); CH_3, 51.6 (doublet, *J* 13.0 Hz); Fe—$CH_2\underline{C}H_2$, 33.0 (doublet, *J* 120.0 Hz); Fe—$\underline{C}H_2CH_2$, −7.8 (multiplet).

Results and discussion

The new transition metal ylide complexes III and IV * have been prepared as shown in eqn. 1. These complexes crystallize with an equivalent of lithium halide salt generated when the ylide is prepared. The tetrahydrofuran (THF) adducts I and II used in this preparation are critical to the success of these reactions because this ylide will not react directly with the appropriate (η^5-C_5H_5)Fe(CO)(L)I complex. The THF adducts are prepared by the reaction of the metal iodide and $AgBF_4$ in THF and can be brought into reaction in situ or can first be isolated as crystalline solids [4] and then brought into reaction.



(1)

(I) L = CO
(II) L = PPh_3

(III) L = CO
(IV) L = PPh_3

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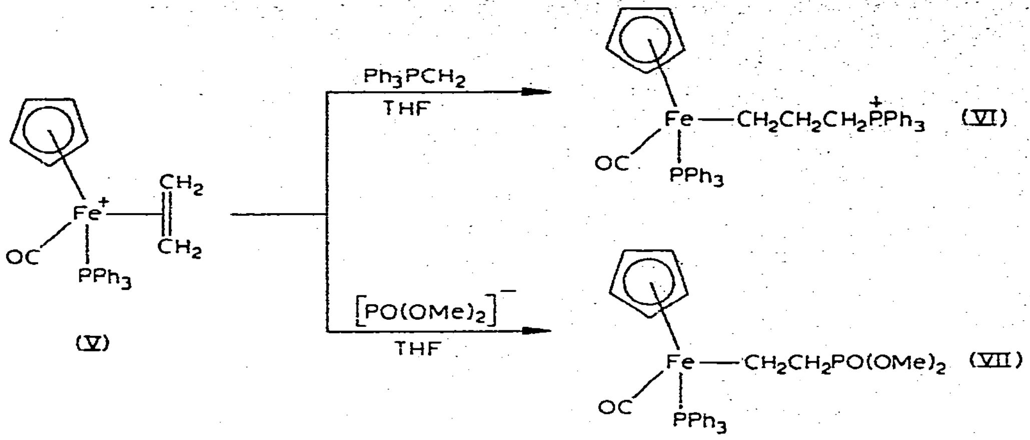
* These are possibly best referred to as phosphonium complexes in order to distinguish them from transition metal ylide complexes such as Ta(η^5-C_5H_5)$_2$(CH_3)(CH_2) [5].

The phosphonium complex VI and the phosphonate complex VII are prepared as shown in eqn. 2. The complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2[CH_2CH_2PO(OEt)_2]$ which is



(2)

analogous to VII, has been prepared by the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-}C_2H_4)]^+$ (VIII) with $P(OEt)_3$ followed by treatment with LiCl [7]. Compound VIII also reacts with PPh_3 to yield $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2CH_2\overset{+}{P}Ph_3)$ [7].

Some displacement of the olefin was observed in the reaction of V with CH_2PPh_3, but the complex IV thus produced is easily separated from VI. No displacement of the olefin was observed in the reaction of V with $Na[PO(OMe)_2]$. This displacement reaction is a potential restriction in the synthesis of complexes such as VI and VII. The reaction of VIII with Ph_3PCH_2 is dominated by displacement of ethylene to yield III. In a somewhat different system, the sulphonium ylide CH_2SMe_2 displaces olefin in neutral palladium olefin complexes [6].

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