Journal of Organometallic Chemistry, 308 (1986) 253–259
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

COPPER(I) AS A PHOSPHINE ABSTRACTOR FROM $(\eta\text{-}C_5H_5)(CO)(PPh_3)FeCOCH_3$

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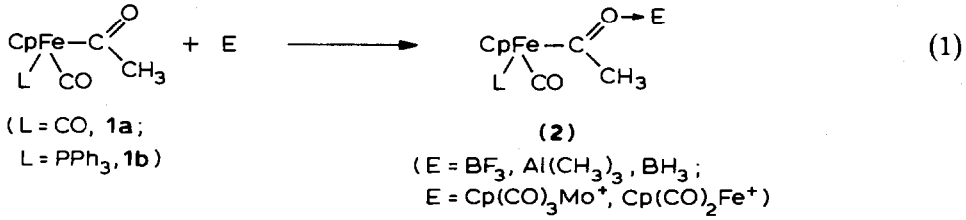
(Received November 4th, 1985)

Summary

The Cu^I complex $Cu(CH_3CN)_4^+ PF_6^-$ chemoselectively abstracts phosphine from $Cp(CO)(PPh_3)FeCOCH_3$ and produces $Cp(CO)_2FeCH_3$ in good yield. No evidence for electrophilic Cu^I coordinating the acetyl ligand on $Cp(CO)(L)FeCOCH_3$ (L = CO, PPh_3), however, was obtained. Reactions of Cu^I and $Cp(CO)(PPh_3)FeCH_3$, with and without the presence of CO, also were examined. With CO, this methyl complex first gives its acetyl derivative $Cp(CO)(PPh_3)FeCOCH_3$ (1 atm CO in CH_2Cl_2 solution, 5 min), and after excess CO is removed (it otherwise blocks further reaction), $Cp(CO)_2FeCH_3$ forms.

Introduction

The coordination of a charged or neutral electrophile to an acyl ligand, forming a Lewis acid-base adduct at the electron-rich acyl oxygen, serves as a general reaction in transition organometallic chemistry [1]. Shriver, in particular, demonstrated that $(\eta^5\text{-}C_5H_5)(CO)_2Fe$ acetyl complexes **1a** reversibly bind Lewis acids such as BF_3 or $Al(CH_3)_3$ (eq. 1) [2]. Presence of an ancillary phosphine ligand on the acetyl



(1)

complex **1b** further enhances both its reactivity and the subsequent thermodynamic stability of the resulting adduct, e.g., $E = H^+$ [3], CH_3^+ [4]. With either **1a** or **1b**, BH_3 (at least 2 eq.) moreover reduces the acetyl ligand by net electrophilic

0022-328X/86/$03.50

activation then hydride transfer by BH_3 [5] (analogous to the reactions of organic ketones and BH_3) [6]. Organometallic Lewis acids, e.g., $Cp(CO)_3Mo^+$ and $Cp(CO)_2Fe^+$, also ligate the acyl ligand; in independent studies, Beck [7] and ourselves [8] have reported several bimetallic μ-(η^1-C,O) acetyl complexes (eq. 1).

The question addressed in this study is if cationic Cu^I complexes, by coordinating **1a** or **b**, will afford analogous bimetallic FeCu μ-acetyl compounds **2**. We accordingly selected the labile Cu^I starting materials [9] $Cu(CH_3CN)_4^+ PF_6^-$ (**3**) [10], its PPh_3 derivatives [11], and $(PPh_3)_3CuFBF_3$ [12] as potential Lewis acids toward **1a,b**. Our ultimate goal is to reduce an acetyl ligand using electrophilic activation (Cu^I) then hydride transfer: chemistry of the postulated bimetallic Cu^I alkoxide could prove relevant to understanding the heterogeneous reduction (by Zn/Cu oxide catalysts plus H_2) [13] of CO to methanol [14]. Of possible relevance to this postulate is Nelson's recent report of using $(Ph_3PCuH)_6$ in generating a formyl complex from $CpRu(CO)_3^+$ [15].

Experimental

All synthetic manipulations were performed under a nitrogen atmosphere using standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air-sensitive organometallics [16]. Solvents for synthetic work and recording of spectral data therefore were deoxygenated by bubbling nitrogen through for ~ 20 min. Camag alumina (neutral, activity 3), was used in column chromatography.

Infrared spectra were taken of CH_2Cl_2 solutions (0.10 mmol/1.5 ml) in a NaCl amalgam-spaced (0.10 mm) solution cell and were recorded on a Perkin–Elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200–1500 cm^{-1}) were calibrated against the polystyrene 1601 cm^{-1} absorption. ^1H NMR spectra were taken of concentrated $CDCl_3$ or CD_3NO_2 solutions, after centrifugation of insoluble residues. Varian models T-60 and XL-200 NMR spectrometers supplied the NMR spectra which were reported as δ values in ppm downfield from internal Me_4Si. ^{31}P NMR spectra of CH_2Cl_2 solutions were recorded in ppm relative to external H_3PO_4; the PF_6^- resonance is centered at δ −143.2 (J(P–F) 710 Hz).

Organic reagents were procured commercially and used as received. $Cu(CH_3CN)_4^+ PF_6^-$ [10] and $Cu(PPh_3)_3FBF_3$ [12] were prepared according to literature procedures, as were the organometallic complexes $Cp(CO)(PPh_3)FeCOCH_3$ [17,18], $Cp(CO)(PPh_3)FeCH_3$ [17], $Cp(CO)_2FeCOCH_3$ [19], $Cp(CO)_2FeCH_3$ [16d], $Cp(CO)(PPh_3)FeI$ [17,20], and $Cp(CO)(PPh_3)Fe(CH_3CN)^+ PF_6^-$ [17].

*Reaction between $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**) and $Cu(CH_3CN)_4^+ PF_6^-$*

A CH_2Cl_2 solution (15 ml) containing $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**) (454 mg, 1.00 mmol) and $Cu(CH_3CN)_4^+ PF_6^-$ (**3**) (372 mg, 1.00 mmol) was stirred for 24 h, before evaporating the resulting orange solution to near dryness with a Buchi rotovaporator (25 mm). Ether extracts (5 × 10 ml) of the residue were combined, concentrated to near dryness, and redissolved in a minimum volume of 1/1 CH_2Cl_2/pentane. This solution then was chromatographed on a column containing alumina/pentane (40 g, 1 × 20 cm): $Cp(CO)_2FeCH_3$ was eluted cleanly as a pale yellow band using pentane. This eluate was concentrated on the Buchi, and the remaining solvent was evaporated with a gentle stream of nitrogen. The resulting yellow gum proved to be spectroscopically pure $Cp(CO)_2FeCH_3$ (**4**) (93 mg, 49%

yield). IR (CH_2Cl_2) 2001, 1945 cm^{-1}; NMR ($CDCl_3$) δ 4.68 (s, 5H, Cp), 0.13 (s, 3H, $FeCH_3$). Due to the high volatility of **4**, its solutions cannot be evaporated to dryness on a Buchi rotovaporator (25 mm) without significant product loss. Best results of control experiments, for example, entailed 85% recovery of **4** by first quickly stripping pentane from its cold ($< 10°C$) solution on the Buchi (without using the water bath for the distilling flask), then briefly warming the flask to room temperature with a gentle stream of nitrogen.

Eluting with CH_2Cl_2 next removed a pale orange band, which afforded spectroscopically pure **1b** (223 mg, 49% recovery). It remained as a nonvolatile orange solid after evaporating solvent: IR (CH_2Cl_2) 1916, 1601 cm^{-1}; NMR ($CDCl_3$) δ 7.41 (br s, 15H, PPh_3), 4.43 (d, J 1.5 Hz, 5H, Cp), 2.32 (s, 3H, CH_3).

This reaction was repeated in refluxing 1,2-dichloroethane (15 ml) for 10 min; IR spectral monitoring of the brown solution was consistent with **1b** quantitatively converting to $Cp(CO)_2FeCH_3$ (**4**). The solution was reduced in volume (22°C/10 mmHg), and combined ether extracts were concentrated and chromatographed. The only organometallic detected on the pentane-alumina column (after developing in CH_2Cl_2) was **4**, which was eluted with pentane and collected as a yellow gummy solid (125 mg, 65% yield). Product loss is attributed to the step involving removal of 1,2-dichloroethane.

Reaction between $Cp(CO)(PPh_3)FeCH_3$ (5) and $Cu(CH_3CN)_4^+ PF_6^-$ (3): Presence of CO atmosphere

To a CH_2Cl_2 solution (15 ml) containing $Cp(CO)(PPh_3)FeCH_3$ (**5**) (426 mg, 1.00 mmol) and $Cu(CH_3CN)_4^+ PF_6^-$ (**3**) (372 mg, 1.00 mmol) was passed carbon monoxide for 10 min. An IR spectrum of the resulting orange solution was consistent with quantitative carbonylation of **5** (ν(CO) 1900 cm^{-1}) to $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**) (ν(CO) 1916, 1601 cm^{-1}). This solution was evaporated on a Buchi rotovaporator, and the residue was dissolved in 15 ml of 1,2-dichloroethane and refluxed for 15 min. Solvent was evaporated from the brown solution (room temperature 25 mmHg); the residue was extracted with ether (leaving behind an off-white residue); and the ether was reduced in volume to near dryness. Chromatography of this material using CH_2Cl_2/pentane eluted $Cp(CO)_2FeCH_3$ (**4**) (the only organometallic visible on the column) as a pale yellow band, this affording a 72% yield (139 mg) of the spectroscopically pure **4**.

It is critical to remove the CO completely before the second stage of the above reaction (between **1b** and **3**) will occur. Thus, treating $Cp(CO)(PPh_3)FeCH_3$ (**5**) and $Cu(CH_3CN)_4^+ PF_6^-$ (**3**) with CO (1 atm) in either CH_2Cl_2 or $ClCH_2CH_2Cl$ solution readily afforded solutions containing $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**), which would not react further. Similarly, the room temperature reaction between **1b** and **3** in CH_2Cl_2 solution was inhibited totally in the presence of CO (1 atm).

Reaction between $Cp(CO)(PPh_3)FeCH_3$ (5) and $Cu(CH_3CN)_4^+ PF_6^-$ (3): Absence of CO

A solution of $Cp(CO)(PPh_3)FeCH_3$ (**5**) (427 mg, 1.00 mmol) and $Cu(CH_3CN)_4^+ PF_6^-$ (**3**) (372 mg, 1.00 mmol) in CH_2Cl_2 (15 ml) was stirred at room temperature for 24 h, giving an orange-red cloudy solution and pink precipitate. IR spectral monitoring of this reaction was used to follow **5** converting completely into $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**), $Cp(CO)_2FeCH_3$ (**4**), and the known [17] Cp(CO)-

$(PPh_3)Fe(CH_3CN)^+ PF_6^-$ (**6**) (ν(CO) 1991 cm^{-1}). The resulting suspension was evaporated to near dryness, dissolved in a minimum volume of 1/1 CH_2Cl_2/pentane, and chromatographed on a 40 g alumina-pentane column. Pentane cleanly eluted **4** as a pale yellow band, which afforded 24 mg (13%) of spectroscopically pure product. Methylene chloride removed (**1b**) from the column as a well-defined pale orange band, for a 24% yield (110 mg). Finally, 10% methanol/CH_2Cl_2 eluted a red-brown band (leaving some brown decomposition residues at the top of the column), which gave **6**. This was precipitated, filtered, and vacuum dried as pale orange crystals (189 mg, 32%). NMR ($CDCl_3$) δ 7.4 (br m, 15H, PPh_3), 4.91 (br s, 5H, Cp), 1.99 (s, 3H, CH_3CN).

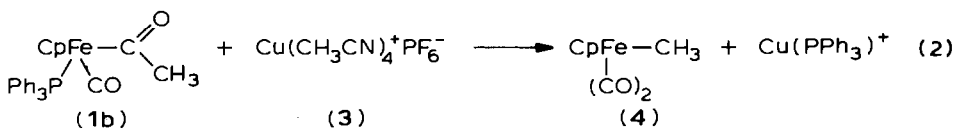
$Cp(CO)(PPh_3)FeI$ (7) and $Cu(CH_3CN)_4^+ PF_6^-$ (3)

$Cp(CO)(PPh_3)FeI$ (**7**) (558 mg, 1.00 mmol) and $Cu(CH_3CN)_4^+ PF_6^-$ (**3**) (372 mg, 1.00 mmol) as a CH_2Cl_2 solution (15 ml) was stirred for 24 h. The resulting olive-green solution, cloudy because of a white precipitate that also was present, was concentrated and transferred to a chromatography column (alumina-CH_2Cl_2). A bright green band was eluted cleanly with CH_2Cl_2; which left starting **7** as olive green crystals (82 mg, 15%) (IR(CH_2Cl_2) 1951 cm^{-1}; NMR ($CDCl_3$) δ 7.42 (br m, 15H, PPh_3), 4.46 (d, J 1.5 Hz, 5H, Cp)), after crystallizing from CH_2Cl_2/ethanol and vacuum drying. A brick-red band then was removed using 10% methanol/CH_2Cl_2, leaving a brown residue on the column. This eluate was treated with pentane in order to precipitate $Cp(CO)(PPh_3)Fe(CH_3CN)^+ PF_6^-$ (**6**) as pale orange crystals, 203 mg (34% yield).

Results

Neither acetyl complex **1a** nor **1b** as CH_2Cl_2 solutions forms an adduct **2** with $Cu(CH_3CN)_4^+ PF_6^-$ (**3**), with **3** plus 1, 2, and 3 eq. of PPh_3 or 1 eq. of $Ph_2PCH_2CH_2PPh_2$, or with preformed $Cu(PPh_3)_3FBF_3$. IR spectra of these solutions, recorded 10 min after mixing, indicated unperturbed terminal carbonyl ν(C≡O) and especially acetyl ν(C=O) (at 1649 and 1600 cm^{-1}, respectively). Dramatic shifts in energy for the latter IR absorptions, in particular, are to be expected for adduct formation [1,2]. No reaction took place (as evidenced by IR spectral monitoring) after prolonged sitting (8 h) of all the above reaction mixtures except one: **1b** and **3**.

Upon sitting at room temperature, a CH_2Cl_2 solution containing $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**) and $Cu(CH_3CN)_4^+ PF_6^-$ (**3**) (1/1) affords the methyl complex $Cp(CO)_2FeCH_3$ (**4**), eq. 2. Although the orange solution remains unchanged in physical appearance, IR spectral monitoring is in accord with **1b**

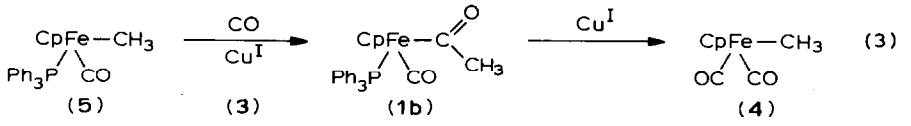


smoothly transforming to **4** (8% conversion, 1 h; 30% conversion, 8 h), with no other metal–carbonyl species detected. ^{31}P NMR spectra of the reaction mixture, likewise, established the presence of only **1b** (δ +76.5) and PPh_3 ligated to Cu^I (δ 6.2).

Neither $Cp(CO)(PPh_3)FeCH_3$ (**5**) (δ 84.6) nor free PPh_3 (δ −6.7) were detected, although the ligated PPh_3 detected undoubtedly is equilibrating between free and ligated (to Cu^I) forms [11].

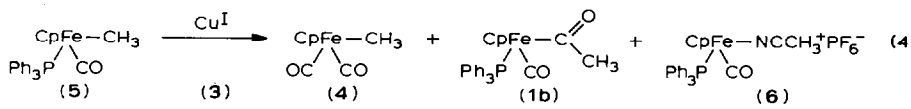
The yield of $Cp(CO)_2FeCH_3$ (**4**) resulting from **1b** and **3** critically depends on the reaction conditions. Thus, the amount of **4** isolated after column chromatography climbed from 49% for the room temperature reaction in CH_2Cl_2 (24 h; 49% recovery of **1b**) to 65% for the reaction in refluxing 1,2-dichloroethane (10 min). IR spectral monitoring of this latter reaction was in accord with **1b** quantitatively converting to **4** – the lower isolated yield of spectroscopically pure product (by NMR) reflected losses due to its volatility. (It is important to note that **1b** is otherwise stable in refluxing dichloroethane (68°C) in the absence of **3**, IR spectra of this solution remaining unchanged after 1 h.) The reaction (eq. 2) also is inhibited completely by the presence of either 1 atm CO * or 1 eq. PPh_3 (24 h, room temperature).

An interesting variant of our procedure for abstracting phosphine from $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**) with Cu^I, is to convert $Cp(CO)(PPh_3)FeCH_3$ (**5**) to $Cp(CO)_2FeCH_3$ (**4**) through the agency of **3** and CO (eq. 3). In the presence of 1 eq.



of **3**, $Cp(CO)(PPh_3)FeCH_3$ (**5**) as a CH_2Cl_2 solution quantitatively carbonylates (1 atm. CO) to **1b** within 5 min; then removing solvent (and excess CO), adding 1,2-dichloroethane, and refluxing for 15 min under nitrogen affords **4** (overall 72% yield) after chromatographic work-up. Since in a previous study we documented that **5** as a CH_2Cl_2 solution only carbonylates in the presence of acid catalysts [22], our present data does not permit us to discern between either Cu^I or traces of protic acid associated with 3 acting as the carbonylation catalyst.

In the absence of carbon monoxide, **5** reacts with **3** to give **4** in only 13% yield (eq. 4). Other products of this obviously complicated process are **1b** (24% yield) and the known [17] acetonitrile solvate $Cp(CO)(PPh_3)Fe(CH_3CN)^+ PF_6^-$ (32%). This solvate also results as the major product of **3** apparently abstracting iodide **



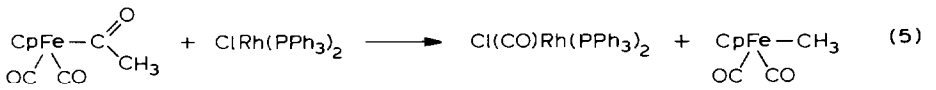
from $Cp(CO)(PPh_3)FeI$ (**7**), with 34% yield of **6** and 15% recovery of **7** after 24 h.

Relevant to this study are results of Wojcicki and Alexander [24] in which

* By IR spectroscopy, however, CO (1 atm) shows no detectable interaction (2300–1600 cm^{-1}) towards **3** in CH_2Cl_2 (with or without PPh_3 – 1–3 eq. – present). The only ν(CO) observed, at 2123 cm^{-1} corresponds to free CO. Other Cu^I-CO complexes, however, are known [21].

** $Ag^+ PF_6^-$ also abstracts iodide from **7** in acetonitrile and gives **6** [23].

$ClRh(PPh_3)_2$, derived in solution from either $ClRh(PPh_3)_3$ or $[ClRh(PPh_3)_2]_2$, readily abstracts CO from **1a** (eq. 5), but is inert towards **1b**. Mechanistic studies of



(5)

this chemistry have implicated as the rate-determining step nucleophilic attack by Rh^I on the terminal CO to be abstracted. In contrast, electrophilic Cu^I in **3** chemoselectively removes phosphine from **1b** and is inert towards **1a**.

The obvious mechanism to consider for Cu^I removing PPh_3 from **1b** entails thermal extrusion of phosphine to give a coordinatively unsaturated acetyl complex $Cp(CO)FeCOCH_3$, which deinserts to $Cp(CO)_2FeCH_3$ [25]. Brunner and Vogt, in fact, established that **1b** equilibrates with **4** plus PPh_3 at elevated temperatures (59°C in C_6D_6), although PPh_3 dissociation evidently does not occur at room temperature [26]. The well-known configurational stability of **1b** – in terms of the chiral Fe center – accordingly derives from the absence of phospine loss * in its solutions kept at room temperature [27]. Nevertheless, Cu^I could drive these equilibria (especially at higher temperatures) by complexing and hence removing the ejected PPh_3 [11], with **3** thus acting as a "phosphine sponge" [28]. We, however, have no explanation for why carbon monoxide inhibits the reaction between **1b** and Cu^I, especially since Cu^I–CO complexes apparently do not form under these conditions.

Cu^{II}, which could be a contaminant of **3**, was ruled out as a participant in this reaction chemistry via the results of the following control experiment. $Cp(CO)(PPh_3)FeCOCH_3$ (**1b**) and one equivalent of $Cu(BF_4)_2$ in 1/1 CH_2Cl_2–CH_3CN (24 h) engenders 80% recovery of **1b** and 20% conversion to $Cp(CO)(PPh_3)Fe(CH_3CN)^+$ BF_4^- (**6**), as ascertained by IR monitoring.

In conclusion, electrophilic Cu^I in $Cu(CH_3CN)_4^+$ PF_6^- (**3**) does not ligate the acetyl group on $Cp(CO)(L)FeCOCH_3$ (**1a,b**). Cu^I (**3**) instead abstracts phosphine from **1b** and gives $Cp(CO)_2FeCH_3$ (**4**), a process synthetically complementing the Rh^I/**1a** chemistry that was elucidated by Wojcicki and Alexander. Apparently Cu^I drives the unfavorable phosphine dissociation equilibrium, **1b** $\rightleftarrows$ **4** + PPh_3, by removing the free PPh_3.

Acknowledgement

Support from the Department of Energy, Office of Basic Energy Sciences is gratefully acknowledged. Initial exploratory studies were carried out by Kevin P. Menard of this laboratory.

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