



Note

The reactivity of a nucleophilic nickel acylate complex

James R. Hermanson, Timothy M. Figley, Anna L. Seibert, Allan R. Pinhas*

Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, OH 45221-0172, United States

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ABSTRACT

The reactivity of a nucleophilic nickel acylate complex with a tungsten carbene complex, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, PPh_3 , and CO was investigated. With the tungsten carbene complex, a methyl transfer occurred. With the metal carbonyl complexes, the acylate group on the nickel and a carbonyl on the iron or chromium traded places. With the PPh_3 and CO , the acylate anion was replaced by the phosphine or CO ligand.

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Because chromium and iron acylate complexes are important reactants in organometallic chemistry, there have been a large number of studies of these complexes [1]. To further the use of acylate complexes, we have been studying the reactivity of the nickel acylate complex with a variety of electrophiles, including electron-poor double bonds, alkynes, and alkyl halides [2]. In general, when an acylate complex (**1**) reacts with a hard acid/electrophile, such as a trimethyl oxonium or a trimethylsilyl cation, the oxygen is the nucleophilic center to give carbene complex **2**. In contrast, when **1** reacts with a soft acid/electrophile, such as allyl bromide, a double, or a triple bond, the metal is the nucleophilic center to give complex **3**, which when oxidized to force a reductive-elimination reaction, generates ketone **4** [3,4] (see Scheme 1).

As part of our interest in the reactivity of nickel acylate complexes, we wanted to compare their reactivity to that of the chromium and iron complexes. Therefore, we investigated the reaction of nickel complex **1c** ($\text{R} = \text{alkyl}$) with (1) a carbene complex, (2) metal carbonyl complexes, specifically $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$, and (3) triphenyl phosphine and carbon monoxide. In all cases, a ligand exchange reaction occurs. We believe bimetallic complexes are formed as intermediates in some of these exchange reactions.

1. Reaction of **1c** with a tungsten carbene complex

As a test of the nucleophilicity of nickel acylate complex **1c** in comparison to complexes **1a** and **1b**, the reaction of **1c** ($\text{R} = \text{methyl}$ or butyl) with carbene complex **2d** was run. As shown in Scheme 2, nickel carbene complex **2c** and tungsten acylate complex **1d** were

generated. This is the same type of reaction found for a variety of anionic complexes with carbene complex **2d** [5]. Comparing these results to those previously reported indicates that the reactivity of complex **1c** is about the same as $\text{Mn}(\text{CO})_4\text{PPh}_3^-$ and $\text{Co}(\text{CO})_3\text{PPh}_3^-$, and more nucleophilic than **1a** or **1b**.

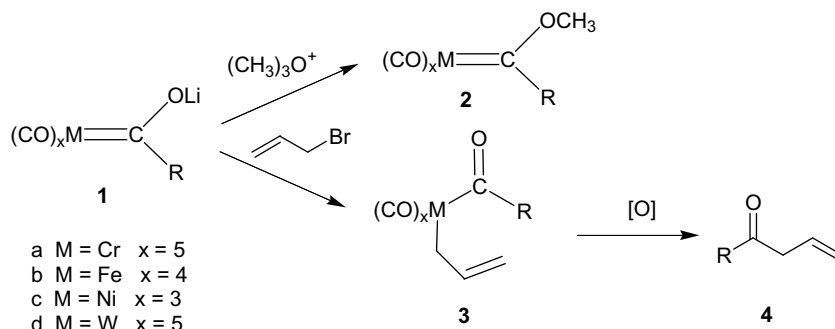
2. Reaction of **1c** with metal carbonyl complexes

As shown in Scheme 3, upon reaction of nickel acylate complex **1c** ($\text{R} = \text{butyl}$) with $\text{Cr}(\text{CO})_6$ or $\text{Fe}(\text{CO})_5$, an acyl or alkyl anion-transfer reaction occurred from the nickel complex to the chromium or iron complex. This reaction is similar to the transmetalation of a Fischer carbene complex [6].

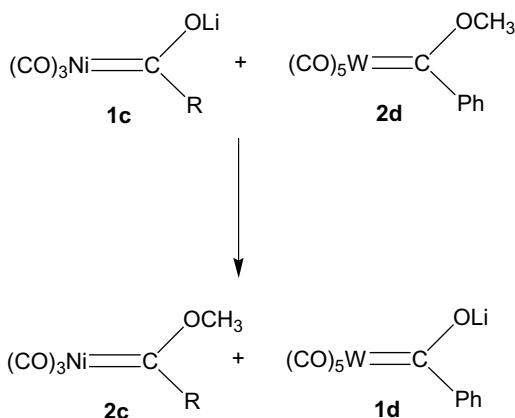
It was found that these reactions are irreversible. The reaction of either chromium acylate complex **1a** or iron acylate complex **1b** with nickel carbonyl generates none of nickel acylate complex **1c**. In addition, chromium acylate complex **1a** does not react with iron carbonyl and iron acylate complex **1b** does not react with chromium carbonyl.

For many compounds, the $\text{p}K_a$ directly correlates with the nucleophilicity of that compound's conjugate base. Although the $\text{p}K_a$ values of the conjugate acids of the three acylate complexes are not known, nickel complex **1c** must be a stronger base than complexes **1a** and **1b** based on the observation that **1c** is protonated by water and **1a** and **1b** are stable in aqueous solution [4,7]. The basicities and the reactions shown in Scheme 3 indicate that **1c** is a stronger nucleophile than **1a** or **1b**. This result is again consistent with reactivity of complex **1c** being about the same as $\text{Mn}(\text{CO})_4\text{PPh}_3^-$ and $\text{Co}(\text{CO})_3\text{PPh}_3^-$, which are stronger nucleophiles than compounds **1a** and **1b** [5].

* Corresponding author. Tel.: +1 513 556 9255; fax: +1 513 556 9239.
 E-mail address: allan.pinhas@uc.edu (A.R. Pinhas).



Scheme 1.



Scheme 2.

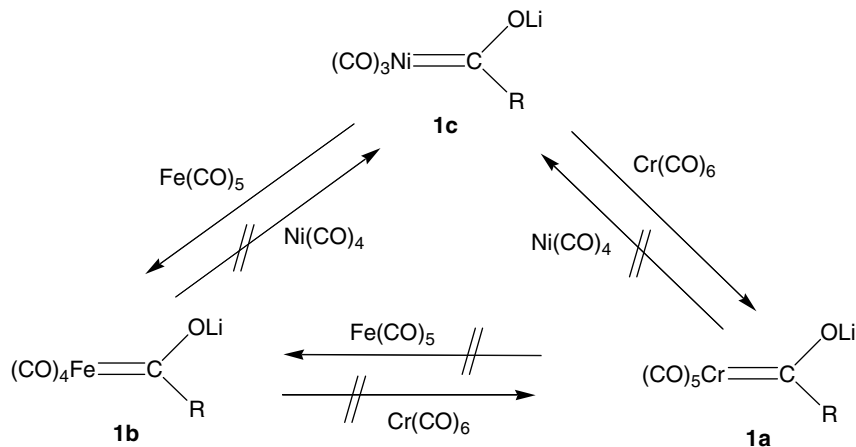
In an effort to determine if this reaction goes by an acyl transfer, as has been reported previously for the reaction of an iron anion with a neutral manganese acyl complex [8], or an alkyl transfer, as has been reported for an iridium complex [9], the reaction of nickel acylate complex **1c** with $\text{Fe}(\text{CO})_5$ was run in the presence of cyclohexanone. It is known that nickel complex **1c** does not react with a simple ketone; however, an alkyllithium readily reacts with a ketone [2,3]. Thus, if RLi were regenerated, it would react with the cyclohexanone and a cyclohexanol derivative would be generated. In contrast, if RLi were not generated, the cyclohexanone would remain unreacted. The latter result was observed,

and thus, we believe that an acyl transfer occurs (Scheme 4). A mechanism similar to this one has been proposed for an allenylidene transfer reaction [10]. Note in Scheme 4, in contrast to Scheme 2, it is the nickel that is the nucleophilic center.

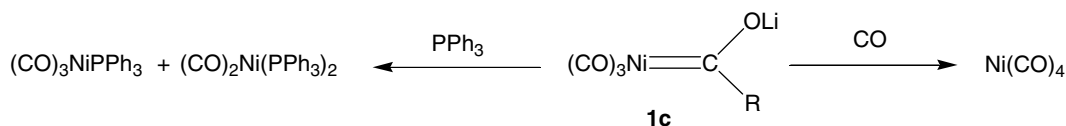
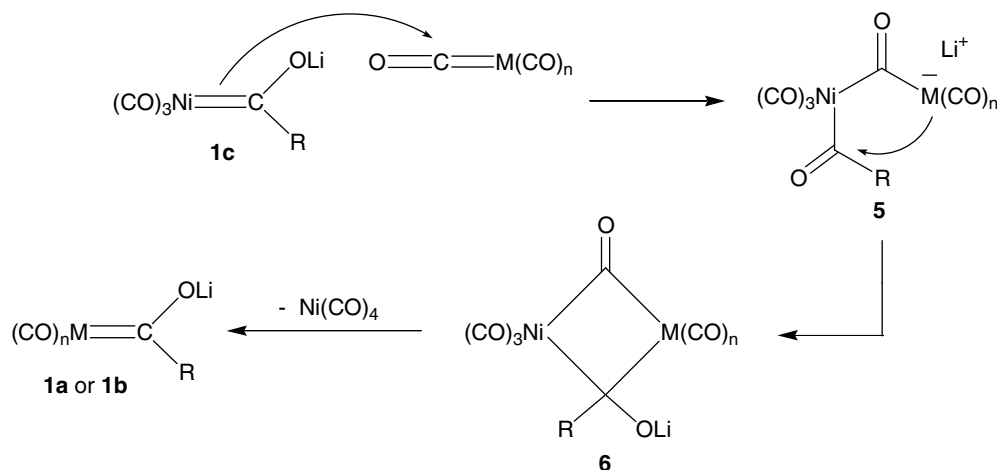
3. Reaction of **1c** with PPh_3 and CO

In the reaction of iron acylate complex **1b** (R = phenyl) with PBu_3 , a ligand substitution of PBu_3 for RCO^- occurs [11]. Unfortunately, the authors do not know what happens to the acyl anion or the phenyl group. Therefore, it was decided to investigate the reaction of complex **1c** (R = methyl or butyl) with PPh_3 . As shown in Scheme 5, the products from this reaction are a mixture of $(\text{CO})_3\text{NiPPh}_3$ and $(\text{CO})_2\text{Ni}(\text{PPh}_3)_2$, with the ratio depending on the amount of triphenyl phosphine used. This reaction is slow, taking about 3 days to go to completion. At the end of 3 days, in the IR spectrum, the peaks for acylate complex **1c** are no longer present; only the peaks for $(\text{CO})_3\text{NiPPh}_3$ and $(\text{CO})_2\text{Ni}(\text{PPh}_3)_2$ are observed. After the 3-day period or even after a shorter time period, when the reaction was quenched with water or CH_3I , no organic compound containing the original methyl or butyl group was detected spectroscopically or chromatographically. In addition, when the reaction was run in the presence of cyclohexanone, no cyclohexanone adduct was observed.

To determine if this type of reaction is unique to a phosphine, acylate complex **1c** (R = methyl or butyl) was synthesized as usual under an Ar atmosphere. When this dark maroon solution was placed under a CO atmosphere and monitored by IR spectroscopy, only the slow formation of $\text{Ni}(\text{CO})_4$ with simultaneous loss of compound **1c** was observed. As above, the reaction took about 3 days



Scheme 3.



for total disappearance of complex **1c**. If at some intermediate time, the solution was again saturated with argon, both the generation of nickel carbonyl and the decomposition of **1c** ceased.

Due to our fear that monitoring may be affecting the reaction in some manner, as a control experiment, a solution of complex **1c** was stirred under an argon atmosphere for 3 days and monitored by IR spectroscopy. For this reaction, at no time was any $\text{Ni}(\text{CO})_4$ generated. Therefore, the CO is required for the decomposition of **1** to occur, but as above, the fate of the alkyl group is not known.

4. Conclusion

Thus, nickel acylate complex **1c** is a stronger nucleophile than the analogous chromium (**1a**) or iron (**1b**) complexes, and is approximately in the middle in comparison to other transition metal anionic complexes.

5. Experimental

5.1. General

All reactions were carried out using glassware dried in a 110 °C oven and cooled under an argon atmosphere or in a desiccator. All reactions were run under an argon atmosphere. Tetrahydrofuran was freshly distilled from potassium benzophenone ketyl. Nickel tetracarbonyl was transferred from a one-pound lecture bottle and filtered through celite into a 10 mL sidearm flask, maintaining a strong argon flow, and stored under argon until used. Transfers were made via syringe and excess $\text{Ni}(\text{CO})_4$ was quenched in an iodine/ CHCl_3 bath. ($\text{Ni}(\text{CO})_4$ is toxic and flammable when exposed to air. All work should be conducted in a well-ventilated hood, maintaining an argon atmosphere during all transfers and using non-flammable solvents in the iodine bath to reduce the probability of fire.) Iron pentacarbonyl and chromium hexacarbonyl were used as received.

5.2. Instrumentation

All infrared spectra were recorded on a Perkin–Elmer Model 1600 series FTIR spectrophotometer using KBr cells. All NMR spectra were recorded on a Bruker 250 MHz spectrometer. ^1H and ^{13}C spectra were referenced to tetramethylsilane at 0.00 ppm and ^{31}P spectra were referenced to PPh_3 at -6.0 ppm.

5.3. Syntheses of acylate complexes

These were done in a similar manner to the published procedure. [2] To a 3-neck round-bottom flask, under an inert atmosphere and equipped with a glass stopper, a rubber septum, a stir bar, and a gas inlet adapter, was added approximately 40 mL of degassed THF. The solvent was cooled to -78 °C and 5.0 mmoles of the appropriate metal carbonyl (0.60 mL of nickel tetracarbonyl, 0.66 mL of iron pentacarbonyl, or 1.1 g of chromium hexacarbonyl) were added. To this was added 3.1 mL of 1.6 M butyllithium or 3.6 mL of 1.4 M methyllithium (5.0 mmoles) over a 15 min period. (It has been found that near the end of the addition there is a significant darkening of the color of the reaction mixture. Cleaner reactions result when the addition is stopped at this point.) The reaction was kept at -78 °C for an additional 15 min and then allowed to warm to room temperature for 1 h.

5.4. General procedure

After stirring at room temperature, the metal acylate complex again was cooled to -78 °C. Then, depending on the reaction, 2.2 g (5.0 mmoles) of tungsten carbene complex **2d**, 5.0 mmoles of one of the other metal carbonyl complexes (0.60 mL of nickel tetracarbonyl, 0.66 mL of iron pentacarbonyl, or 1.1 g of chromium hexacarbonyl), 1.0 mL (10.0 mmoles) of cyclohexanone, and/or 1.3–2.6 g (5.0–10.0 mmoles) of PPh_3 were added. In the CO reaction, the solution was saturated with CO and left under a CO

atmosphere. Each reaction was kept at $-78\text{ }^{\circ}\text{C}$ for an additional 15 min and then allowed to warm to room temperature. Each reaction was either monitored by IR spectroscopy, or worked-up in the usual manner (using an I_2 oxidation to destroy the metal complex(es) and then extracting the resulting organic compound(s) into diethyl ether). For those reactions that were worked-up, the resulting products were analyzed by ^1H , ^{13}C , and where appropriate ^{31}P NMR spectroscopy and IR spectroscopy. The spectral data for all compounds have been reported previously [2,5].

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