

The effects of counterion and solvent on the reactivity of nickel acylate complexes

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(Received January 24, 1994)

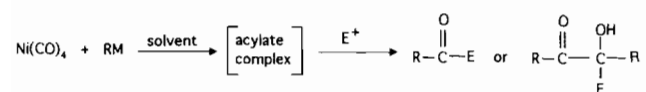
Abstract

Nickel acylate complexes, which can be generated starting with a carbon, nitrogen or oxygen nucleophile, act as acyl anion equivalents and therefore are an excellent method of assembling complex organic molecules from readily available starting materials. In an effort to increase the synthetic utility of these easily formed reagents, a systematic study of the reactivity of the nickel acylate complex generated under a variety of conditions was performed. Those acylate complexes generated with a carbon based nucleophile, such as a butyl or phenyl anion, show a large change in reactivity upon changing, for example, the solvent from THF to Et₂O or the counterion from Li⁺ to MgCl⁺. This reactivity change is due to a large change in the structure of the acylate complex with a different counterion or solvent, as determined by IR and ¹³C NMR spectroscopy and by oxidation potentials. In contrast, when a heteroatom nucleophile is used, such as a dialkyl amide or an alkoxide, the effect of a change in solvent or counterion on the structure, and therefore on the reactivity of the acylate complex, is minimal.

Key words: Nickel complexes; Acylate complexes

Introduction

Nickel acylate complexes are easily generated from the reaction of a carbon, nitrogen or oxygen nucleophile (RM) with Ni(CO)₄. These complexes can be used to generate rather complex organic molecules from readily available starting materials, because upon reaction with an electrophile (E⁺), they act as acyl anion equivalents. Curiously however, sometimes the nickel acylate complex donates one acyl group to the electrophile to generate a simple ketone and sometimes it donates two acyl groups to generate an acyloin derivative [1–5].



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In one particular case in which R=butyl, M=Li, and solvent=THF, we clearly understand the structure of the acylate complex and the conditions under which either of the two different types of products are formed. These results have already been reported [4].

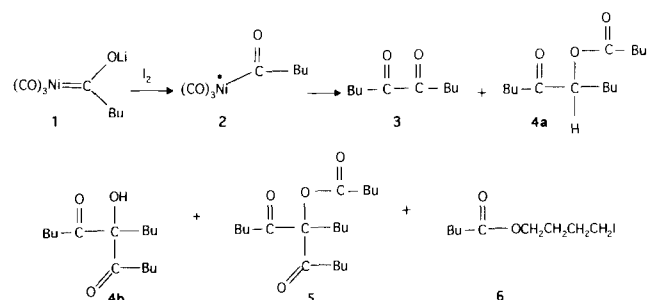
For nickel acylate complexes to become useful reagents for the synthesis of a large variety of organic compounds, this understanding of why sometimes one and sometimes two acyl groups are transferred to the electrophile must be generalized to all cases. In an effort to do so, we have performed a systematic study of the effects of counterion and solvent on the structure, reactivity and types of products that are formed for a large number of different acylate complexes that can be potential synthetic intermediates.

In this manuscript, we report our findings. For each counterion and solvent, first the spectroscopic and electrochemical properties of the acylate complexes generated were determined and then the reactivity of the resulting complex with a variety of electrophiles was studied.

Results and discussion

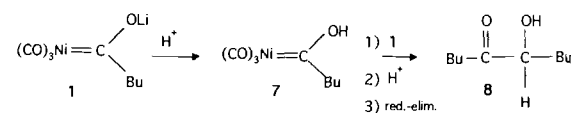
Spectroscopy, electrochemistry and reactivity of the lithium pentanoyl nickel acylate complex in THF

Based on a variety of spectroscopic data [6, 7], the acylate complex **1** is formed by the reaction of BuLi with Ni(CO)₄ in THF. Complex **1** is monomeric and is stable at room temperature for over two days, though we have found it most convenient to prepare a fresh sample of **1** prior to each reaction. This complex is easily oxidized [8] by oxygen, iodine or ferrocenium ion, generating a 17-electron intermediate (**2**) which then decomposes to give organic products **3**, **4a**, **4b** and **5**. When complex **1** is added very slowly to I₂, in addition to these four products, compound **6**, derived from the ring opening of THF, is generated in 25–30% yield.



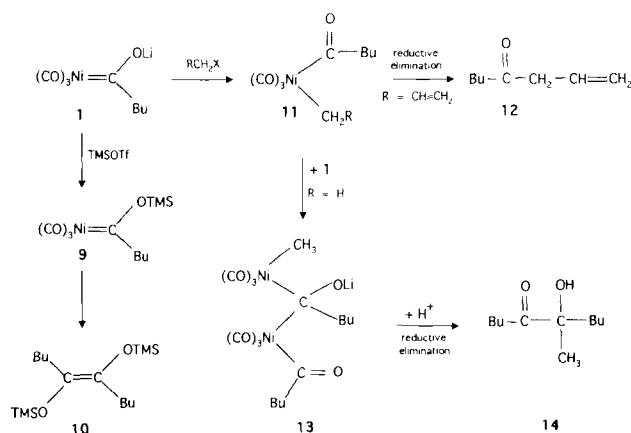
When the acylate complex **1** is treated with a mineral acid or with water, the acyloin derivative **8** is formed in high yield. Acylate complex **1** will not add to the carbonyl of a simple ketone; however, it will deprotonate a ketone which has a p*K*_a of 16 or less. Thus, when 1,3-diphenylacetone (p*K*_a = 16) [9] is added to **1** in THF, followed by an oxidative work-up, the acyloin derivative **8** can be isolated in high yield; but when acetophenone (p*K*_a = 19) is added to **1**, followed by an oxidative work-up, only oxidation products **3**, **4** and **5** are formed.

Kinetics experiments show that **8** is generated from the reaction of acylate complex **1** with a protonated intermediate which is most likely the hydroxy carbene complex **7** [4]. The second proton is added after the coupling of the two nickel complexes. This ease of oxidation and protonation of the acylate complex indicates that **1** is very air sensitive.



When complex **1** is treated with trimethylsilyl triflate, the oxygen is silylated and the resulting Fischer-carbene complex **9** is obtained. Consistent with the protonation experiments, silyl complex **9** only slowly generates 5,6-bis(trimethylsiloxy)-5-decene (**10**), but reacts rapidly

with complex **1**. When complex **1** is treated with allyl bromide, an electrophile with which it reacts quickly (*t*_{1/2} of less than a minute at -78 °C), the nickel is alkylated to give a stable acyl(allyl)nickel complex (**11**), which only after an oxidative work-up generates 1-octen-4-one (**12**). (Both complexes **9** and **11** are stable under an inert atmosphere and have been identified spectroscopically.) When complex **1** is treated with methyl iodide, an electrophile with which it reacts slowly (*t*_{1/2} of hours at room temperature), a second acylate complex attacks the initially formed acyl(alkyl) complex to generate, after oxidation and protonation, the acyloin derivative 5-hydroxy-5-methyl-6-decanone (**14**). No 2-hexanone was ever detected. Therefore, whether ketone **12** or acyloin derivative **14** is generated, in this case, depends upon the rate of the reaction of the monomeric acylate complex **1** with the electrophile [4].



Spectroscopy, electrochemistry and reactivity of the lithium pentanoyl nickel acylate complex generated in Et₂O

Turning now to the reaction of BuLi with Ni(CO)₄ in Et₂O, when the reaction solution is maintained at -78 °C at all times, a complex similar to **1** is formed (Table 1). However, unlike complex **1** generated in THF, which is stable both at -78 °C and at room temperature, here as the solution warms to room temperature, complex **1** disappears and new complexes, whose spectroscopic and electrochemical data are reported in Table 2, are generated. The changes in the IR spectrum and in the oxidation potential as the reaction solution is stirred for longer periods of time at room temperature indicate that the complex formed initially at room temperature is only an intermediate in the conversion of **1** to the final organonickel complex. No peaks are observed in the ¹³C NMR spectrum for the acylate complex once the solution warms to room temperature, regardless of whether the actual spectrum is attempted at room temperature or at -80 °C, sug-

TABLE 1. IR CO stretches and ^{13}C NMR CO shifts for the pentanoyl nickel acylate complexes at $-78\text{ }^\circ\text{C}$

Solvent	Counterion	IR CO stretches (cm^{-1})	^{13}C NMR CO shifts (ppm)
THF	Li^+	1980(w)	205.5
		1935(s)	315.6
		1535(w)	
Et_2O	Li^+	2009(w)	205.4
		1943(s)	^a
		1559(w)	
THF	MgCl^+	1978(m)	204.1
		1946(m)	328.6

^aNo peak corresponding to an acyl carbonyl could be observed.

gesting that the new complex is paramagnetic*. Surprisingly, a large, sharp peak due to $\text{Ni}(\text{CO})_4$, which was *not* present before the solution warmed to room temperature, is observed in the ^{13}C NMR spectrum.

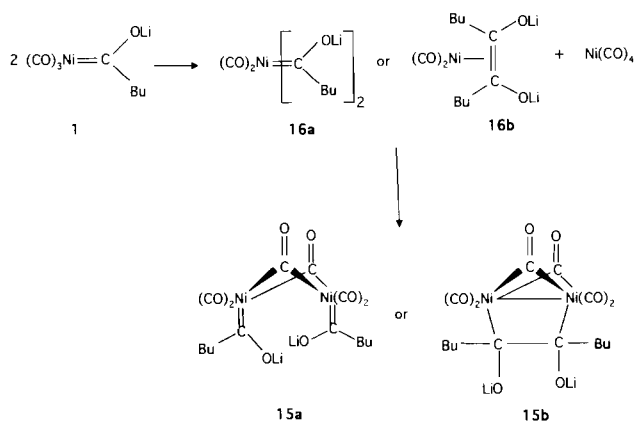
The presence of peaks in the bridging carbonyl region of the IR spectrum is consistent with the final product being a dimeric nickel complex such as the previously suggested [2] structure **15a**. However, if this exact structure is correct, then this type of complex would be rare in that it has bridging carbonyls and no metal-metal bond. A variation of this structure which does have a metal-metal bond and fits all our data is complex **15b**. In either case, a structure with bridging carbonyls may be favored in the less polar Et_2O , as compared with THF, due to the enhanced ability of bridging carbonyls, as compared with terminal carbonyls, to withdraw electron density from the metal [10].

The structure of the intermediate acylate complex is not known at this time. We do know that it is more easily reduced than the final complex, and as we will show, much more basic. Due to these facts and to the reoccurrence of $\text{Ni}(\text{CO})_4$, we are tentatively speculating that the intermediate complex has the bis-acylate structure [11]** shown in **16a** or the nickel coordinated bis-enolate structure shown in **16b**.

* (a) One possible reason for our inability to acquire an NMR spectrum is that the solutions are contaminated by paramagnetic impurities. Though this is a possibility, it seems unlikely due to the variety of preparations and purifications that were performed, due to the broadness of the peaks in the solid state spectrum, and due to the ease of obtaining a well resolved singlet for the ^{13}C NMR spectrum of $\text{Ni}(\text{CO})_4$ in the solution. The more likely alternative is that the dimeric complex generated at room temperature is itself paramagnetic.

(b) Preliminary calculations in our group by Tim Figley using extended Hückel theory indicate that a complex such as **15** is a ground state triplet and not the more common ground state singlet.

**A complex in which four Grignard reagents attack one nickel tetracarbonyl has been previously suggested [11a].



To determine if monomeric complex **1** and dimeric complex **15** are in equilibrium and if the equilibrium constant is just solvent dependent, acylate complex **15** was generated as described above and the Et_2O solvent was removed by a strong stream of argon. The resulting maroon solid has a solid phase (MAS) ^{13}C NMR spectrum which consists of a sharp peak at 14.3 ppm, a broader peak at 23.5 ppm, an even broader peak at 30.0 ppm, and broad peaks at 38.2, 66.0 and 145.3 ppm. These data again are consistent with complex **15** being paramagnetic. When this solid was dissolved in THF, the IR spectrum of the resulting solution is the exact same as that reported in Table 2 for complex **15** in Et_2O . Therefore, once the dimeric complex is generated in Et_2O at room temperature, it will not dissociate to the monomeric complex even if the solvent is changed.

What is needed now is a chemical means (i) to confirm that the acylate complexes formed in Et_2O indeed do contain two acyl groups and (ii) to determine how much $\text{Ni}(\text{CO})_4$ is regenerated when the solution initially warms to room temperature. Because when a room temperature solution of acylate complexes **15** and/or **16** in Et_2O is quenched with water or with aqueous NH_4Cl , compound **8** is formed in high yield, this protonation reaction proved to be an ideal method for making these two determinations.

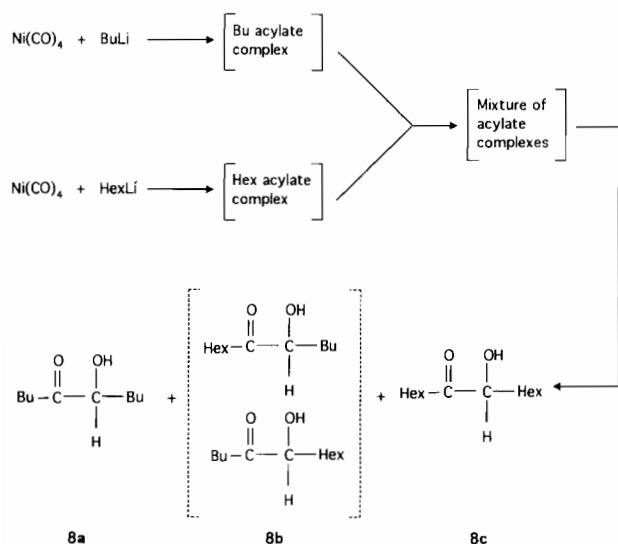
With Et_2O as the solvent, an approximately equal amount of the acylate complex generated from BuLi was mixed with the acylate complex generated from HexLi , and then the mixture was quenched with NH_4Cl . Regardless of whether the acylate complexes were at room temperature for one hour or for one day before being mixed and quenched, only the acyloin derivatives containing two butyl groups (**8a**) or two hexyl groups (**8c**) are formed, i.e. none of the cross products (**8b**) is generated. In contrast, with THF as the solvent, an approximately equal mixture of the butyl and hexyl acylate complexes, after quenching, generates about a 1:2:1 ratio of the acyloin derivatives containing two butyl groups (**8a**), containing one butyl and one hexyl

TABLE 2. IR CO stretches, NMR CO shifts, and oxidation potentials for a variety of room temperature nickel acylate complexes^a

Nucleophile	Counterion	Solvent	IR CO stretches (cm ⁻¹)	¹³ C NMR CO shifts (ppm)	E_p^{ox} (V)	
Bu ⁻	Li ⁺	THF	1980(w) 1935(s) 1535(m)	205.3 317.0	-0.62	
		Et ₂ O	1995(m) ^b 1955(w) ^c 1840(w) 1825(w) ^b 1740(w) 1680(w)	no peaks observed for acylate	-0.53 -0.76 ^d -0.49 ^e	
	MgCl ⁺	THF	2005(s) 1996(s) ^c 1948(w) 1822(m) 1799(sh) ^c	no peaks observed for acylate	-0.02 -0.34 ^d -0.01 ^e	
			Et ₂ O	heterogeneous reaction		
		Li ⁺	THF	1955(m) 1941(s) 1523(w)	204.4 311.6	-0.41
			Et ₂ O	2015(m) 1855(w) 1773(w) 1596(w)	no peaks observed for acylate	-0.33
Ph ⁻	Na ⁺	THF	1937(s) 1525(m)	205.4 349.2	-0.41	
		Et ₂ O	heterogeneous reaction			
	MgCl ⁺	THF	2008(s) 1955(m) 1845(sh) 1828(m) 1590(w)	no peaks observed for acylate	-0.02 ^f	
			Et ₂ O	heterogeneous reaction		
		Li ⁺	THF	1942(s) 1928(s) 1901(sh)	204.0 228.9	-0.33
			Et ₂ O	1961(s) 1950(s)	202.2 237.0	-0.21
OCH ₃ ⁻	Li ⁺	THF		no reaction		
		Et ₂ O		no reaction		
	Na ⁺	THF	1996(m) ^b 1979(m) 1804(w) ^b 1615(w)	no peaks observed for acylate	-0.46 (broad) -0.69 ^g	
		Et ₂ O		no reaction		
		CH ₃ OH		no reaction		

^aFor Ni(CO)₄, IR CO stretch = 2040 (THF), 2043 (Et₂O) cm⁻¹; NMR CO shift 193.0 (THF), 193.4 (Et₂O) ppm; E_p^{ox} = +0.8-+0.9 V (broad). In the IR spectra, there is a weak peak at 2025 cm⁻¹ which corresponds to Li⁺ coordinated to Ni(CO)₄ in THF. In all the IR spectra of the phenyl acylate complexes there is a peak at 1817 cm⁻¹ which corresponds to a peak in the spectrum of benzene. ^bPeak strength increases with time. ^cPeak strength decreases with time. ^dFrom a reaction which is 1 to 2 h old. ^eFrom a reaction which is 1 day old. ^fWhen this reaction is allowed to stir for an extended period of time, a small broad peak grows in at -0.20 V. ^gThe reduction potential of CH₃O⁻ is -0.69 V, based on an authentic sample.

group (**8b**), and containing two hexyl groups (**8c**). These results are what would be expected if the acylate complex generated in THF is 'monomeric' and the one generated in Et₂O is 'dimeric'.



To determine how much Ni(CO)₄ is regenerated and to support the idea that due to the formation of complex **16** and to the reappearance of Ni(CO)₄, Ni(CO)₄ must be acting as more than just one carbonyl source [11a], two reactions of BuLi and Ni(CO)₄ were performed in Et₂O as usual. One reaction mixture was allowed to stir at room temperature for 1 h and the other for 23 h. To each, a second equivalent of BuLi was added and the resulting solution was allowed to stir an additional hour. Each of the mixtures then was quenched with NH₄Cl and analyzed by gas chromatography relative to an internal standard. For the 23 h old reaction, which contains mainly dimeric complex **15**, approximately the same amount of acylaldehyde **8** is generated with two equivalents of BuLi as with one; however, for the 1 h old reaction, which contains mainly acylate complex **16** and regenerated Ni(CO)₄, approximately twice the amount of **8** is formed with twice the amount of BuLi. This suggests that about half of the initially added Ni(CO)₄ has been regenerated, consistent with complex **16** being formed in high yield.

As mentioned above, in THF, acylate complex **1** will react with an acid with a pK_a of 16 or less. Thus, **1** will deprotonate water or 1,3-diphenylacetone but not acetophenone. In contrast, a newly warmed Et₂O solution, i.e. one that contains mainly acylate complex **16**, will deprotonate acetophenone. However, an older room temperature solution, i.e. one that contains mainly acylate complex **15**, will not deprotonate acetophenone.

When the acylate complexes generated in Et₂O are oxidized using iodine, organic products, **3**, **4** and **5** are formed, just as in THF; however, here the ratio of

products is highly dependent upon the temperature and the age of the reaction solution. As can be seen in Table 3, as the age of the acylate complex increases, and thus as the amount of **15** which is present increases, the yield of **3** also increases.

When complex **1** in THF reacts with allyl bromide, the acyl(allyl)nickel complex **11** is formed and this complex, after an oxidative work-up, generates **12**. It has been known for some time in the literature [3] that when complex **1** generated in Et₂O reacts with allyl bromide, compound **12** is again the exclusive product. Two important points need to be mentioned at this time: (i) to insure that only complex **1** is present in the Et₂O solution, the reaction temperature must be kept at -78 °C at all times; (ii) in the experiments in the literature, NH₄Cl was added to the reaction mixture before the oxidative work-up; however, the same results were obtained in our laboratories regardless of whether an NH₄Cl/I₂ work-up or just an I₂ work-up was used.

When the Et₂O reaction solution is allowed to warm to room temperature to generate complex **15** before allyl bromide is added, the product is no longer exclusively ketone **12**; acylaldehyde derivative **17** is formed, even when the BuLi to Ni(CO)₄ to allyl bromide ratio is one to one to one (Table 4). (Unfortunately from this reaction, a great deal of complex **15** is recovered in the form of the acylaldehyde derivative **8** or the oxidation products **3**, **4** and **5**, depending on the work-up used.)

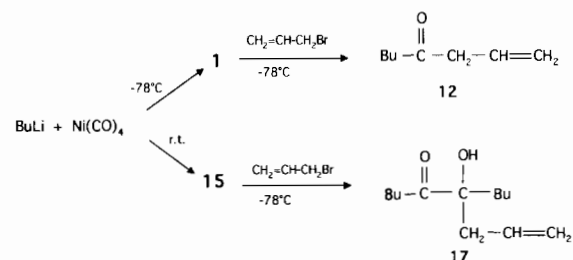


TABLE 3. Products from the I₂ oxidation of the pentanoyl nickel acylate complexes

Counterion	Solvent	Reaction conditions	Yield (%)					
			3	4a	4b	5	6	8
Li ⁺	THF	-78 °C	28	20	10	34	0	0
		r.t., 1 h	22	31	4	32	0	0
		r.t., 1 day	21	29	4	33	0	0
Li ⁺	Et ₂ O	-78 °C	37	57	0	0	0	0
		r.t., 1 h	37	38	15	4	0	0
		r.t., 1 day	75	7	0	8	0	0
MgCl ⁺	THF	-50 °C	3	20	35	12	12	0
		r.t., 1 h	68	5	11	0	0	13
		r.t., 1 day	53	3	6	0	0	34

TABLE 4. Product yields for the reactions of the pentanoyl nickel acylate complexes with allyl bromide

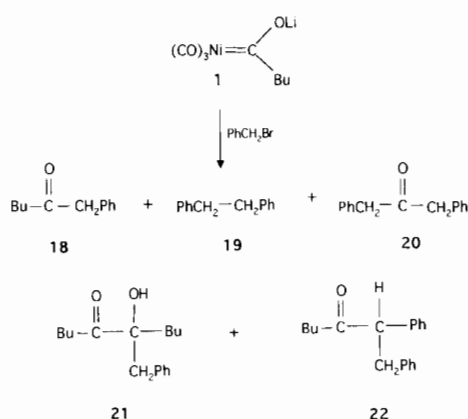
Counterion	Solvent	Reaction temperature	Age of acylate complex (h)	Allyl bromide reaction time (h)	Yield ^a (%)			
					Ox. ^b	12	17	27
Li ⁺	THF	-78 °C or r.t.	1.0	1.0	0	90	0	0
Li ⁺	Et ₂ O	-78 °C	1.0	1.0	11	71	2	0
		r.t.	1.0	1.0	62	5	17	0
		r.t.	23.0	1.0	80	0	14	0
		r.t.	1.0	23.0	47	10	25	0
MgCl ⁺	THF	-50 °C	1.0	1.0	0	92	0	0
		r.t.	1.0	0.5	15	0	25	60
		r.t.	1.0	1.0	15	0	30	47
		r.t.	1.0	24.0	36	0	50	8
		r.t.	24.0	1.0	25	0	17	58
		r.t.	24.0	24.0	42	0	25	33

^aPercentage yields are based on acylate complex. ^bThis represents a mixture of the acylate oxidation products (**3**, **4a**, **4b**, **5**) and the acylate protonation product (**8**).

Nickel acylate complex **1** generated in Et₂O is reported not to react with methyl iodide [3]. Consistent with this observation, when the acylate complex is kept at -78 °C for 1 h, methyl iodide is added, and the resulting solution is maintained at -78 °C for over 6 h, no product which has incorporated a methyl group is formed. However, when the Et₂O solution of complex **1** first is allowed to warm to room temperature to form complex **15** and then is allowed to react with methyl iodide at room temperature overnight, compound **14** is generated.

For acylate complex **1** generated in THF, the rate of the reaction with benzyl bromide, qualitatively, is between that found for the reaction with allyl bromide and that for the reaction with methyl iodide. Consistent with this observation is the formation of both the simple ketone **18** and the acyloin derivative **21**. In addition, three other products (**19**, **20** and **22**) are formed in this reaction. The exact mechanism for formation of these latter products is not known. It is known that they are not generated in a radical reaction, but rather through discrete organometallic complexes [4].

It has been reported that the reaction of the nickel acylate complex generated in Et₂O, when it first is allowed to warm to room temperature before being treated with PhCH₂Br, generates compound **21**, and thus, those authors proposed the dimeric structure **15a** for the acylate complex [2]. In our laboratories, this reaction also gives substantial quantities of **19** and **20**. The yields of these products are the same whether the reaction is oxidized (I₂) directly or first protonated (NH₄Cl) and then oxidized (I₂). In addition, only very small amounts of ketone **18** are formed, and not even a trace of **22** can be detected (Table 5). These results



again are consistent with our spectroscopic determination that the room temperature acylate complex is 'dimeric' (**15**).

To reconfirm the spectroscopic observation that the formation of **15** is irreversible, BuLi and Ni(CO)₄ were mixed together in Et₂O, the solution was allowed to warm to room temperature to generate complex **15**, the solvent was removed, THF was added, and finally benzyl bromide was added. The results for this reaction are virtually the same as for the benzyl bromide reaction performed entirely in Et₂O, and unlike the results when acylate complex **1** is generated in THF.

Thus in summary, solvent, and, as will become apparent in the next section, counterion play important roles in the chemistry of nickel acylate complexes*.

*There are a number of examples in which changing the solvent and/or counterion causes only a modest change in the reactivity of an anionic complex [12]. Changing from THF to Et₂O and from Li⁺ to MgCl⁺ has no effect on the reactivity of the analogous chromium acylate complex [12a].

TABLE 5. Product yields from the reaction of the pentanoyl nickel acylate complexes with benzyl bromide

Counterion	Solvent	Age of acylate complex (h)	Benzyl bromide reaction time (h)	Yield ^a (%)				
				18	19	20	21	22
Li ⁺	THF	1.0	1.0	12	5	0	15	47
		1.0	23.0	12	8	11	12	54
Li ⁺	Et ₂ O	1.0	23.0	3	44	23	18	0
Li ⁺	Et ₂ O/THF ^b	1.0	23.0	0	31	51	19	0
MgCl ⁺	THF	1.0	1.0	0	0	0	2	0
		1.0	24.0	0	17	68	15	0
		24.0	1.0	0	0	0	2	0
		24.0	24.0	0	16	79	5	0

^aPercentage yields are based on benzyl bromide. ^bThe acylate complex was generated in Et₂O and then transferred to THF before the benzyl bromide reaction.

simple ketone products are desired, it is best to use the acylate complex generated in THF because it is monomeric; however, if acyloin type products are desired, it is best to use the acylate complex generated in Et₂O because it is dimeric.

Spectroscopy, electrochemistry and reactivity of the magnesium chloride pentanoyl nickel acylate complex generated in THF

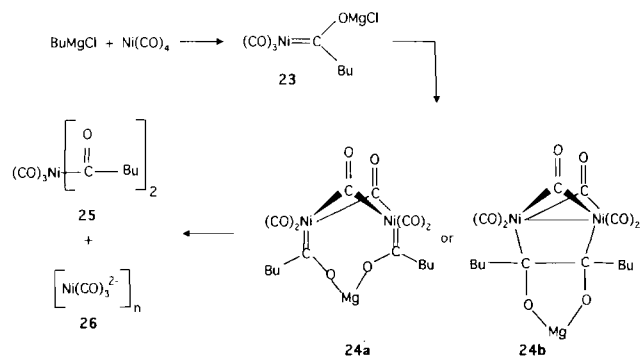
In an effort to extend this study to other carbanions and because a very common alkyl anion source is the Grignard reagent, it was of interest to determine what effect using BuMgCl, as compared with BuLi, would have on the acylate complex. When BuMgCl was added to Ni(CO)₄ at -50 °C and kept at -50 °C in THF (BuMgCl and Ni(CO)₄ do not react at -78 °C), complex **23** was generated within 3 h (Table 1). In THF, acylate complex **23**, in comparison to complex **1**, requires a higher temperature and a longer period of time to form. Two other differences worth noting for complex **23** versus complex **1** in THF are the antisymmetric carbonyl stretch in the IR spectrum is at higher energy (1946 versus 1935 cm⁻¹) and the carbene carbon resonance in the NMR spectrum is at lower field (328.6 versus 317.0 ppm). These two data suggest that the magnesium chloride is more tightly bound to the acylate oxygen than the lithium, and thus, is withdrawing more electron density from the complex [12].

Similar to the reactions of acylate complex **1** in THF, when complex **23** is oxidized with I₂, compounds **3**, **4**, **5** and **6** are generated, and when **23** reacts with NH₄Cl before being oxidized with I₂, mainly the acyloin derivative **8** is formed.

However, unlike complex **1** in THF, when a solution containing acylate complex **23** in THF warms to room

temperature, peaks due to **23** in both the IR and NMR spectra disappear and the peaks reported in Table 2, appear. As in the Et₂O case, the IR spectrum and electrochemistry change with time suggesting an initially formed room temperature intermediate before the final room temperature complex is generated. By analogy to the chemistry in Et₂O, structure **24** is proposed for the expected dimer. However, complex **24** is formed first and then it disappears and a new complex of unknown structure is generated. In other words, the first type of complex formed at room temperature with magnesium in THF (**24**) is similar to the second type of complex formed with lithium in Et₂O (**15**)*.

The final complex with magnesium is much harder to oxidize and is quite unreactive with electrophiles. Due to these data, we have tentatively assigned the structure of this complex as a neutral bisacyl-mononickel complex (**25**) [11]. The 'missing' electrons most likely have formed an anionic cluster such as **26** and it is this complex which is responsible for the 1822 cm⁻¹ absorbance in the IR spectrum. Consistent with this idea is the observation of a peak at 1819 cm⁻¹ obtained upon partial reduction of Ni(CO)₄ by sodium naphthalide [13].



When a room temperature solution containing complexes **24** and **25** is oxidized with I₂, the major product is diketone **3**. Surprisingly however, the acyloin derivative **8** is also generated from this oxidation reaction (Table 3). Although the ratio of **3** to **4** is about constant, the absolute amount of acyloin **8** produced is a function of the age of the acylate reaction mixture before oxidation. This suggests that one complex generates compounds **3** and **4**, and a second complex generates **8**. More specifically, the older the reaction mixture, the higher the concentration of neutral complex **25** as compared with anionic complex **24**, the higher the yield of compound **8**. In addition, the amount of **8** is dependent upon the length of time for the oxidation and the amount of iodine used for the oxidation (Table 6).

*The IR spectrum of a magnesium acylate complex/lithium chloride mixture has peaks in the carbonyl stretching region at 1993(s), 1946(w), 1820(sh) and 1799(m) cm⁻¹.

TABLE 6. Compound **8** formation from the oxidation of the magnesium pentanoyl nickel acylate complex in THF

Age of acylate complex (h)	Length of time for the oxidation (h)	Amount of I ₂ used (mmol)	Yield of compound 8 (%)
0.17	0.25	10.0	10
1.0	0.25	10.0	13
2.5	0.25	10.0	15
24.0	0.25	10.0	34
48.0	0.25	10.0	36
72.0	0.25	10.0	36
1.0	1.0	10.0	22
1.0	1.5	10.0	33
1.0	5.0	10.0	44
72.0	1.0	10.0	42
72.0	5.0	10.0	46
72.0	24.0	10.0	46
1.0	1.0	20.0	34

TABLE 7. Ammonium chloride protonation of the room temperature pentanoyl nickel acylate complexes

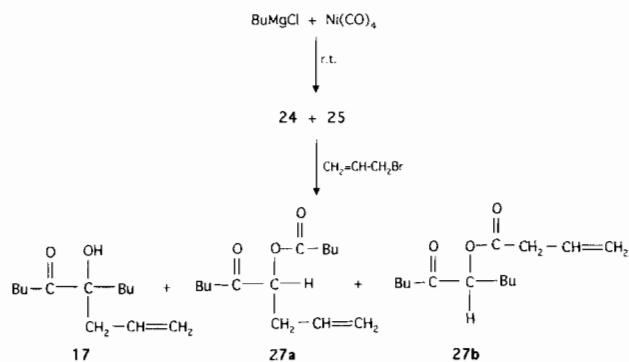
Counterion	Solvent	Age of complex (h)	Yield of 8 (%)
Li ⁺	THF	1.0	77
Li ⁺	Et ₂ O	1.0	82
		23.0	70
MgCl ⁺	THF	0.17	60
		1.0	48
		5.0	45
		24.0	41

Because no proton source is present in these reactions, the most likely source of compound **8** is by a radical reaction involving hydrogen abstraction from THF. However, hydrogen atom sources and a radical trap have little effect on the product composition [14].

As mentioned above, when acylate complex **23** in THF reacts with NH₄Cl before being oxidized with I₂, the acyloin derivative **8** is formed. When a mixture of complexes **24** and **25** reacts with water, NH₄Cl or HI, a mixture of **8** and the oxidation products **3** and **4** is observed. The yield of **8** obtained from these protonation reactions *decreases* as the age of the solution increases, and thus, as the concentration of neutral complex **25** increases (Table 7). The mixture of complexes **24** and **25** will not deprotonate acetophenone, but does deprotonate 1,3-diphenylacetone.

When magnesium acylate complex **23** at -50 °C is treated with allyl bromide, compound **12** is generated in high yield after an oxidative work-up. When the acylate complex first stirs at room temperature to allow for the formation of complexes **24** and **25**, before being treated with allyl bromide, three different allyl sub-

stituted products (**17**, **27a** and **27b**) and a significant amount of diketone **3** are formed; there is no trace of ketone **12** as determined by gas chromatography (Table 4).



Compound **17** is most likely derived from the reaction of allyl bromide with complex **24**, similar to the reaction of allyl bromide with complex **15**. An older reaction solution containing mainly complex **25**, not surprisingly, does not react with allyl bromide under the reaction conditions. Compounds **27a** and **27b** are generated in the oxidative work-up, from complex **25** and any unreacted allyl bromide which is present.

All of the magnesium nickel acylate complexes react with methyl iodide either not at all or only to a very small extent. On the other hand, when the magnesium acylate complex reacts with benzyl bromide, after an oxidative work-up, the products are compounds **19**, **20** and **21**. As with other reactions of this mixture of **24** and **25**, the yield of the product is dependent on the length of time for the reaction with the electrophile and the age of the reaction mixture prior to the addition of the electrophile (Table 5). Monitoring this reaction by IR spectroscopy qualitatively reveals that the reaction of this acylate complex with benzyl bromide is also slower than the reaction with allyl bromide.

By analogy to the reaction of the lithium salt in Et₂O with benzyl bromide and to all the allyl bromide reactions, compound **21** is generated from the reaction of complex **24** with benzyl bromide. The reaction of benzyl bromide with nickel cluster **26** can easily generate compounds **19** and **20**. The analogous reactions of cluster **26** with allyl bromide and methyl iodide would generate hexadiene and ethane, respectively. Though they may be present, both of these compounds would be very difficult for us to detect due to their low concentrations and due to interference from the solvent (THF).

Therefore in summary, Grignard reagents generate acylate complexes which are not synthetically useful. A large variety of metal complexes are present in solution, and this in turn leads to a large number of different organic products being generated.

As an aside, the reaction of BuMgCl with Ni(CO)₄ was also attempted in Et₂O; however, the reaction mixture is heterogeneous at all temperatures, and so no further analysis or reactions were performed.

Phenyl nickel acylate complexes generated in THF and Et₂O

Because of the large effects on the acylate complex due to changing the solvent or counterion, we were curious to determine if these changes were restricted to alkyl acylate complexes or if other carbon based acylate complexes, such as phenyl complexes, would behave similarly. From the reaction of PhLi or PhNa with Ni(CO)₄ in THF, the resulting acylate complex is monomeric, as can be seen from the data in Table 2. Not unexpectedly, the phenyl complexes are more stable, and thus, harder to oxidize by approximately 0.2 V than the butyl complex.

For the analogous reaction of PhLi with Ni(CO)₄ in Et₂O, a dimeric complex similar to **15** is formed. The phenyl analog of complex **15** must be generated more rapidly upon warming to room temperature than the butyl complex because there is no evidence for an intermediate complex such as **16** being formed. No definitive comments can be made about the PhNa reaction in Et₂O, because this reaction mixture is heterogeneous.

In general, the spectroscopy, and therefore the structure, of the complex generated from the reaction of PhMgCl and Ni(CO)₄ in THF is very similar to that obtained from the reaction of BuMgCl. The major difference is that the phenyl complex again rearranges much more rapidly to the final nickel complex than does the butyl complex.

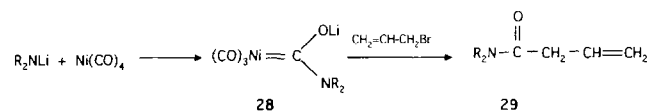
Preliminary results indicate that the reactivity of each phenyl acylate complex is very similar to the reactivity reported for the corresponding butyl acylate complex; thus, phenyl and alkyl acylate complexes behave similarly and generate the same types of solvent and counterion dependent chemistry.

Alkoxy and amido nickel acylate complexes generated in THF and Et₂O

Only for the reaction of LiNEt₂ with Ni(CO)₄ is the resulting (monomeric) nickel complex the same regardless of whether THF or Et₂O is used as the solvent (Table 2). The shift for the acyl carbon in the ¹³C NMR spectrum is upfield in comparison to the shift observed for complex **1**, a result similar to that observed when comparing the spectrum of an organic ketone to the spectrum of an amide. In the IR spectrum, the acyl carbon–oxygen stretch is not observed and most likely is buried under the C–O peak of the solvent. The spectroscopic data and higher oxidation potentials observed here, as compared with the butyl complex,

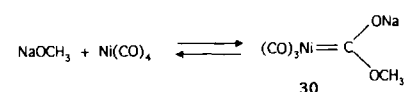
may be indicative of stabilization of the resulting complex by nitrogen–lithium coordination [15]. This intramolecular coordination is probably the reason that of all the complexes studied so far, the amido complex **28** is the only one that does not show either a dramatic change in structure or a dramatic change in reactivity, upon changing the solvent from the more coordinating THF to the less coordinating Et₂O.

For example, the reaction of the amido acylate complex **28** with allyl bromide in either Et₂O or THF generates compound **29**. In addition, the same results are obtained in both solvents for the reactions of amide complex **28** with vinyl halides, aryl halides and acetylenes [2, 3].



Unlike all the reactions reported above, the reaction of NaOCH₃ and Ni(CO)₄ in THF does not go to completion. This most likely is due to the fact that the acylate complex and the alkoxide have approximately the same pK_a values [4, 9]. In Et₂O, no acylate complex is formed, probably due to the lack of solubility of the alkoxide. Although the reagents are soluble in CH₃OH, here also no reaction is observed between NaOCH₃ and Ni(CO)₄ at room temperature as indicated by a lack of change in the spectroscopic data and in the color of the reaction solution.

In spite of our observed lack of formation of the acylate complex at room temperature, numerous reactions have been reported between NaOCH₃, Ni(CO)₄ and an alkyl halide in CH₃OH [2, 3]. However, in all of these reactions, the NaOCH₃, the Ni(CO)₄ and the alkyl halide were mixed together in CH₃OH for an extended period of time, an excess of NaOCH₃ and Ni(CO)₄ was used and many of the reactions were done at elevated temperatures. Taken together, these results are consistent with an equilibrium between the CH₃ONa/Ni(CO)₄ mixture and the methoxy acylate complex **30**, which favors NaOCH₃ and Ni(CO)₄ at room temperature. To confirm this idea, the methoxy acylate complex **30** was generated in THF, the solvent was removed and CH₃OH was added. The peaks in the carbonyl region of the IR spectrum for **30** slowly disappear and only a peak due to Ni(CO)₄ remains. In addition, consistent with the idea of an equilibrium, when the weaker nucleophile LiOCH₃ is mixed with Ni(CO)₄, there is no reaction even when THF is used as the solvent.



The hydroxy analog of the nickel acylate complex could not be generated. No reaction is observed between KOH and Ni(CO)₄ in THF, probably due to the lack of solubility of KOH. Me₄N⁺OH⁻ did react readily with Ni(CO)₄ in THF; however, in all cases the cluster Ni₅(CO)₁₂²⁻ was formed [16]. This same cluster was found even when Ni(CO)₄ was added to a three-fold excess of hydroxide.

In summary, heteroatom acylate complexes are good one acyl group transfer reagents to a large variety of different electrophiles. Although the amido reactions can be done at low temperature, the alkoxy reactions are in many cases restricted to refluxing methanol.

Conclusions

We have reported the IR and NMR spectroscopic data, the oxidation potentials, and the reactivity of alkyl, phenyl, amido and alkoxy nickel acylate complexes in THF and Et₂O with Li⁺, Na⁺ and MgCl⁺ as the counterions. Each nucleophile, regardless of counterion or solvent, initially generates a monomeric nickel acylate complex similar to **1**. However, for many of these complexes, this monomeric structure is not thermodynamically stable, and thus, the complex undergoes further reaction to form other nickel acylate complexes at room temperature. The reactivity of the nickel acylate complexes formed at room temperature with a number of different electrophiles was studied to reveal large variations in the types of organic products which are formed.

Unfortunately, it is hard to generalize, a priori, the exact type of product that will be generated because the product depends on such a large number of variables including the structure of the acylate complex and the rate of the reaction. However, in those cases in which one is fortunate enough to have the desired type of product being formed, nickel acylate complexes are a convenient method of synthesis because fairly complex systems can be generated from readily available starting materials [2–5].

Experimental

General

All reactions were carried out using oven dried glassware that was cooled under an argon atmosphere or in a desiccator. All reactions were conducted under an argon atmosphere. Samples for monitoring by gas chromatography, by NMR or IR spectroscopy, or by cyclic voltammetry were removed via a syringe.

Spectroscopic data for compounds **1**, **3–6**, **8–12**, **14** and **17–22**, have been published previously [4, 6].

Diethyl ether was deaerated with argon for 7–10 min prior to use. Tetrahydrofuran and benzene were freshly distilled from potassium benzophenone ketyl. Water and aqueous NH₄Cl were deaerated with argon immediately prior to use. Tetrabutylammonium perchlorate, employed as the electrolyte for cyclic voltammetry, was dried at 60 °C/0.1 torr for 12 h prior to use.

Nickel tetracarbonyl was transferred from a one pound lecture bottle into a 10 ml sidearm flask, maintaining a strong argon flow, and stored under argon until used. Transfers were made via a syringe and excess Ni(CO)₄ was quenched in an I₂-CCl₄ bath. (**Caution:** Ni(CO)₄ is toxic and flammable when exposed to air. All work with this compound should be conducted in a well-ventilated hood. Maintaining an argon atmosphere during all transfers and using non-flammable solvents in the I₂ bath minimizes the probability of fire.)

CH₃OLi, CH₃ONa, BuLi, BuMgCl, PhLi, PhMgCl, PhBr, Et₂NH and Na dispersion were purchased from Aldrich. Some of the BuLi and the hexyllithium (HexLi) were a generous donation from FMC Corporation. Et₂NNa [17], PhNa [17], and Et₂NLi [18] were synthesized according to the literature methods.

Instrumentation

All GC analyses were made using a Varian model 3300 gas chromatograph with a flash vaporization injector: 225 °C; a flame ionization detector: 325 °C; and a 12' × 1/8" 5% SP-2100 on a 100/200 Supelcoport column. Temperature programming was used: initial temperature of 50 °C for 2 min; increased by 10 °C per min to 250 °C; increased by 20 °C per min to 300 °C; and held at 300 °C for 6.5 min. Gas sample analysis for the presence of carbon monoxide was performed on a 6' × 1/4" 5A molecular sieves column.

Separations were made using a Kratos high pressure liquid chromatograph with a Kratos Spectroflow 783 detector, two Spectroflow 400 pumps, a Spectroflow 591 static mixer/injector, a 250 × 7.0 mm reverse phase C₁₈ column, gradient programming, and a 1 ml/min flow rate. The solvents were deaerated HPLC grade CH₃CN and H₂O filtered with the Nanopure II system.

All IR spectra were recorded on a Perkin-Elmer model 599 IR spectrophotometer or a 1600 series FTIR with KBr cells and a scan range of 4000 to 500 or 2500 to 1000 cm⁻¹.

All NMR spectra were recorded on a Nicolet NT-300 or a Bruker 250 MHz spectrometer. All chemical shifts are referenced to tetramethylsilane at 0.00 ppm.

All GC/mass spectra were recorded on a Hewlett-Packard model 5995 spectrometer using a 0.25 mm × 15 m fused silica capillary SPB-1 column and temperature programming. The exact mass spectra were recorded on a Kratos model mass spectrometer.

Cyclic voltammetry

Cyclic voltammetry was performed with a BAS-100 electrochemical analyzer employing a Pt disc working electrode, and, in the same compartment, a Pt wire counter electrode. The solvent was THF with 0.2 M tetrabutylammonium perchlorate. The reference electrode (saturated NaCl SCE) was immersed in a reservoir of solvent and electrolyte which was isolated from the working compartment by a cracked glass junction designed to minimize solution transfer. The cell was oven dried and cooled under a stream of argon prior to each use. An argon atmosphere was maintained over the working solution at all times.

Cyclic voltammograms were obtained at low substrate concentrations, typically 5×10^{-4} M, to minimize IR drop error inherent in a low-conductivity non-aqueous medium. Low substrate concentrations were required to minimize fouling of the working electrode. At higher concentrations, passivation of the electrode occurred after, and even during, a single scan. Once passivated, a working electrode could only be restored by polishing with alumina.

The acylate complexes exhibited well-defined irreversible oxidation processes at the potentials given in Table 2. These results are for a scan rate of 100 mV/s; however, the peak potentials are nearly constant at scan rates ranging from 50 to 200 mV/s. The methoxy complex is an exception to this in that the peak is broad and scan rate dependent. The values of the peak potentials were ascertained by their positions relative to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ redox couple, which was taken as having $E^\circ = +0.31$ V [19]. A typical protocol involves addition of Cp_2Fe to the anolyte, after the measurement of the acylate complex was complete, in order to scale the voltage axis with a scan of the reference complex. This protocol guarded against errors arising from variations in the response of the reference electrode, which was rendered somewhat unreliable by variable junction potentials.

Determination of the number of electrons (n) involved in the anodic processes was not attempted. In principle, the peak currents, i_p , may be used for the determination of n , but i_p is dependent upon the substrate concentrations. Owing to the extreme sensitivity of these nickel complexes to air and moisture, the sub-millimolar concentrations of nickel complexes are only approximately known.

General procedure for nickel acylate complex synthesis

The syntheses of the acylate complexes from $\text{Ni}(\text{CO})_4$ and BuLi, BuMgCl, PhLi, PhMgCl, PhNa, Et_2NLi , Et_2NNa or Me_4NOH in THF or Et_2O all were performed in a similar manner. The general procedure involves the slow addition (typically about 15 min) of a solution of the nucleophile (10 mmol) to a -78 °C solution of

$\text{Ni}(\text{CO})_4$ (1.2 ml, 10 mmol) in 30 ml of Et_2O or THF. This was followed by an additional 15 min at -78 °C, and then by 1 h at ambient temperature, except as noted. For the reactions of CH_3OLi and CH_3ONa , the solid alkoxide was added all at once to a cold solution of $\text{Ni}(\text{CO})_4$. In the reactions with the alkyllithium reagents, the solution changed color while still cold; however, in the reactions of the Grignard reagents, the solution changed color only after removal of the cold bath or when the reaction is performed at -50 °C.

For those reactions of the acylate complex with an electrophile, the electrophile was then added dropwise at -78 °C. The cold bath was removed after 15 min and the reaction was allowed to warm slowly. After the appropriate time, usually 1 or 23 h, excess $\text{Ni}(\text{CO})_4$ was quenched by quickly pouring the reaction mixture into a flask containing slightly more than 2.5 g (10 mmol) solid I_2 and stirring for 15 min. The mixture was washed with aqueous sodium bisulfite until the water layer was colorless. The combined aqueous layers then were washed with approximately 50 ml of Et_2O . The organic layers were combined and dried with potassium carbonate.

The lithium acylate complex **1** in Et_2O was prepared as above except the reaction mixture was maintained at -78 °C at all times prior to the oxidative work-up. The magnesium acylate complex **23** in THF was prepared as above except the reaction mixture was maintained at -50 °C or below at all times prior to the oxidative work-up.

Electrophiles

H_2O , 1.0 ml (55.5 mmol); NH_4Cl , 7.0 ml saturated aqueous solution; HI, 1.5 ml 47% aqueous solution; 1,4-cyclohexadiene, 0.94 ml (10 mmol); tri-*n*-butyltin hydride, 2.7 ml (10 mmol); 1,1-diphenylethylene, 1.8 ml (10 mmol); acetophenone, 2.4 ml (20.6 mmol), 1,3-diphenylacetone, 6.0 ml (28.6 mmol); allyl bromide, 0.9 ml (10 mmol); methyl iodide, 0.6 ml (10 mmol); benzyl bromide, 1.2 ml (10 mmol).

Spectroscopic data for the acylate complexes

Most of the spectroscopic data may be found in Table 1 or Table 2. A room temperature UV spectrum of the lithium pentanoyl complex in Et_2O was obtained: 204 nm ($\epsilon = 20\,450$ l mol $^{-1}$ cm $^{-1}$), 238 (shoulder, 5400), 345 (590).

The magnetic moment of a 1 h old, room temperature, lithium acylate complex in Et_2O was found using the Evans method [20]. Freshly prepared solid lithium pentanoyl acylate complex (**23** mg) was dissolved in 1 ml of solvent. This gives a 14 Hz solvent shift at $T = 295$ K, corresponding to a magnetic moment of 0.80 BM. A similar experiment on a 23 h old acylate complex (19 mg) gives a shift of 8 Hz ($T = 293$ K), corresponding

to a magnetic moment of 0.88 BM. Similar experiments were performed on the magnesium pentanoyl acylate complex in THF: a 95.8 mg sample of a 0.5 h old, room temperature complex in 1 ml of solvent gives a 12 Hz shift ($T=293$ K) which decreases to 5.1 Hz ($T=294$ K) for a sample that is 19.5 h old.

Oxidation by I_2

This was performed as in the general procedure except no additional electrophile was added. Yields may be found in the Tables.

Attempted radical reactions

The magnesium nickel acylate complex in THF was generated as in the general procedure. The reaction mixture was allowed to stir for 24 h with the electrophile and was worked up using 5.0 g of I_2 (20 mmol) for 1 h. Yields (%) with added 1,4-cyclohexadiene: **3**, 33; **4a**, 2; **4b**, 16; **8**, 48. Yields (%) with added 1,1-diphenyl ethylene: **3**, 41; **4a**, 1; **4b**, 33; **8**, 25. Yields (%) with added tri-*n*-butyltin hydride: **3**, 16; **4a**, trace; **4b**, 8; **8**, 2; and 70% of an unidentified compound containing tin. For comparison, % yields from oxidation of an acylate complex after 25 h at room temperature: **3**, 33; **4a**, 3; **4b**, 16; **8**, 42.

Protonation of the lithium pentanoyl nickel acylate complex in ether

These reactions were performed as in the general procedure. Yields for most NH_4Cl reactions may be found in Table 6. One additional yield in H_2O gives 83% of **8**.

20 mmoles BuLi

This was performed as in the general procedure. After 1 or 23 h, the solution was again cooled and an additional 10 mmol of BuLi was added. After 1 h, the solution was quenched with NH_4Cl . After an additional hour, the reactions were worked up. Then 4-heptanone was added as an internal standard. Yields: 10 mmol BuLi generate 4.0 mmol **8** for a 1 h old reaction mixture and 3.4 mmol **8** for a 23 h old reaction mixture; 20 mmol BuLi generate 7.3 mmol **8** for a 1 h old reaction mixture and 4.6 mmol **8** for a 23 h old reaction mixture.

Hexyllithium reactions

A solution of the acylate complex formed from BuLi and a solution of the complex from HexLi were generated as described above. After stirring individually for 1 h or for 23 h at room temperature, the solutions were mixed together and allowed to stir for 1 h. They then were quenched with an aqueous NH_4Cl solution and allowed to stir overnight. The combined solution was worked up in the usual manner and analyzed by

gas chromatography. In Et_2O , only compound **8** and the hexyl analog of **8** are generated; whereas the reactions in THF generate **8**, the hexyl analog of **8**, and the mixed butyl/hexyl analog of **8**, in an approximately 1:2:1 ratio.

Protonation of the magnesium pentanoyl nickel acylate complex in THF

These reactions were performed as in the general procedure. Yields for most NH_4Cl reactions may be found in Table 6. Additional yields: -50 °C reaction mixture, NH_4Cl for 3 h at -50 °C, 71% **8**; 1 h old acylate complex, HI quench for 24 h, 27% **3**, 8% **4a**, 51% **8**, and 14% of a compound tentatively identified by mass spectroscopy as 6-hydroxy-5,7-undecadione. MS (m/e): 200 (1.4%), 158 (7.8%), 116 (11.8%), 85 (100%), 57 (35.4%). H_2O , 1 h old complex quenched with H_2O for 1 h: **3**, 26%; **4a**, 6%; **4b**, 7%; **8**, 59%; quenched for 3 h: **3**, 22%; **4a**, 6%; **4b**, 3%; **8**, 66%; quenched for 5 h: **3**, 26%; **4a**, 6%; **4b**, 3%; **8**, 65%.

Allyl bromide reactions

These reactions were performed as in the general procedure. Most yields may be found in Table 4. Additional yields: -78 °C lithium pentanoyl acylate complex in Et_2O , NH_4Cl/I_2 work-up: 16% oxidation + protonation products (ox.), 62% **12**, 3% **17**; room temperature lithium pentanoyl acylate complex Et_2O , NH_4Cl/I_2 work-up: 31% ox., 32% **12**, 24% **17**.

4-Pentanoate-1-nonene-5-one (**27a**) and 5-(3-butenate)-6-decanone (**27b**): approximately a 7:1 ratio of **27a** to **27b** was obtained. Because it did not prove possible to separate these compounds, the spectral data are reported for the mixture. 1H NMR ($CDCl_3$), δ : 5.80–5.69 (m, 0.7 H), 5.17–5.06 (m, 2.7 H), 3.192 (d, $J=7.4$ Hz, 0.14 H), 2.61–2.34 (m, 4.9 H), 1.70–1.50 (m, 4.9 H), 1.44–1.25 (m, 4.5 H), 0.911 (q, $J=6.9$ Hz, 6.2 H). ^{13}C NMR ($CDCl_3$), δ : 207.123, 173.239, 132.273, 118.606, 94.217, 38.784, 35.023, 33.758, 26.919, 25.103, 22.282, 13.670. IR (neat): 3082(w), 2959(s), 2933(s), 2874(m), 1744(s), 1728(s), 1643(w) cm^{-1} . MS, m/e : 240 (0.14%), 198 (0.7%), 170 (5.3%), 96 (3.7%), 86 (5.2%), 85 (100%), 69 (6.9%), 57 (35.2%), 55 (5.2%), 42 (3.7%), 41 (21.6%); exact mass: 240.1721 (obs.), 240.1725 (calc. for $C_{14}H_{24}O_3$). GC retention time: 15.7 min.

Methyl iodide reaction

These reactions were performed as in the general procedure. Yields and times are given in the text.

Benzyl bromide reaction

These reactions were performed as in the general procedure. Product yields based on benzyl bromide are given in Table 5. Additional yield: 1 h old lithium pentanoyl acylate complex reacting with benzyl bromide

for 23 h, $\text{NH}_4\text{Cl}/\text{I}_2$ work-up, 3% **18**, 43% **19**, 21% **20**, 20% **21**.

As with the reaction of the lithium pentanoyl nickel acylate complex in THF, for the magnesium pentanoyl acylate complex in THF, a mass spectrum of the gas phase above the reaction mixture indicates the presence of 1-butene.

Preparation of the nickel carbonyl anion

This was done by a procedure to generate other metal carbonyl anions. A 0.5 M solution of $\text{NaC}_{10}\text{H}_8$ in THF was added in 1 ml aliquots under argon to a solution of $\text{Ni}(\text{CO})_4$ at $-78\text{ }^\circ\text{C}$ and monitored by IR spectroscopy after each addition.

Acknowledgements

We thank Ms Wilaiporn Chamchaang and Mr James Hermanson for providing some of our preliminary results. We wish to thank the National Science Foundation (Grant No. CHE-8603898 to A.R.P.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (to J.W.H. and to A.R.P.), and the Research Corporation (to J.W.H.) for financial support for this work. We also thank the National Science Foundation for supplemental support to M.J.T. through its REU program, the University Research Council of the University of Cincinnati for a summer fellowship to J.L.S. An Ohio Board of Regents Academic Challenge Award aided in the purchase of the Bruker 250 MHz NMR spectrometer, and Dr Terry Rathman of FMC generously donated the hexyllithium. Finally and most importantly, we thank the large number of chemists with whom we have discussed our results and who have made many valuable suggestions.

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