Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221-0172

Reactivity of a Lithium Nickel Acylate Complex in THF

Joan L. Simunic and Allan R. Pinhas*

Received January 3, 1989

The reactivity of the lithium salt of a nickel acylate complex in THF is discussed. Upon reaction with a hard acid, this anionic complex oxygen alkylates, forming a nickel carbene complex. This carbene complex reacts with additional acylate complex to generate an enol ether derivative. When the nickel acylate reacts with a soft acid such as an alkyl halide, the intermediate formed is an acyl(alkyl)nickel complex, which very slowly undergoes a reductive elimination. When the nickel acylate complex is oxidized, products consistent with a radical reaction are observed.

Recently we reported[1] that the pentanoylnickel acylate complex formed from the reaction of nickel tetracarbonyl with butyllithium in tetrahydrofuran (THF), based on infrared and NMR[2] spectral data, is a monomeric complex, $[(CO)_3Ni{=}C(Bu)O^-Li^+]$ (**1**). This thermally stable, air-sensitive complex remains unchanged at room temperature for more than 24 h but readily reacts with both moisture and oxygen.

When the acylate complex is allowed to react with a hard acid such as trimethylsilyl triflate, oxygen silylation occurs forming a nickel carbene complex, $[(CO)_3Ni{=}C(Bu)(OTMS)]$ (**2**), which is stable for a few hours at room temperature. A soft acid such as allyl bromide, on the other hand, metal alkylates the acylate complex, forming a stable acyl(alkyl)nickel complex, $[(CO)_3Ni(COBu)(CH_2CH{=}CH_2)]$ (**3**).

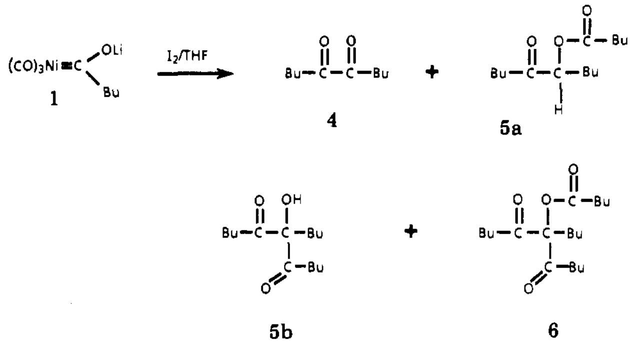
In the present work, we examine the reactivity of the lithium salt of the pentanoylnickel acylate complex in THF with several different electrophiles. In addition, a mechanism is proposed to explain the formation of the products observed.

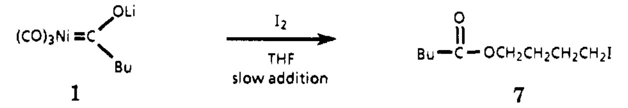
Results

The Nickel Acylate Complex in THF. Before turning to the chemistry of the nickel acylate complex, it is necessary to review its structure. In addition to carbons due to the butyl chain, the ^{13}C NMR spectrum of this complex shows a peak at 205 ppm due to the terminal carbonyls and a peak at 317 ppm due to the acyl carbonyl.[1] The carbonyl stretching region of the infrared spectrum has peaks at 1980 (w), 1935 (s), and 1535 (m) cm^{-1}.[1] The ultraviolet spectrum has two absorptions: 208 nm (ϵ = 20340 L/(mol cm)) and 227 nm (ϵ = 640 L/(mol cm)). These data are consistent with a monomeric acylate complex, **1**, which lacks any nickel–nickel bridging carbonyls.

Since the counterion for the acylate complex is lithium, the possibility of formation of a multinickel complex via lithium–oxygen bridging was considered. When 12-crown-4 was added to the nickel acylate complex **1** in THF, the ^{13}C NMR and infrared spectra are virtually superimposable with those obtained in the absence of the crown ether, thus suggesting that this anionic nickel complex is monomeric as represented by structure **1**; no lithium–oxygen bridging is present.

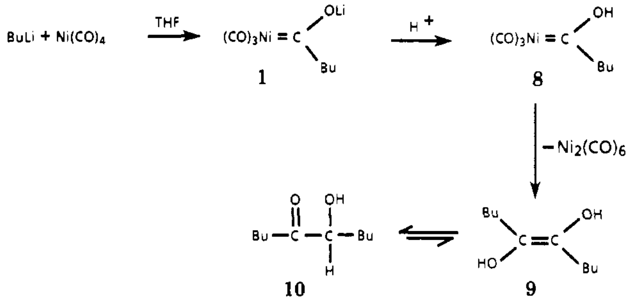
Oxidation of the Nickel Acylate Complex. Oxidation of acylate complex **1** by rapid addition of the acylate complex to iodine produces six products: the butylacyl dimer 5,6-decanedione (**4**); the trimers 5-pentanoate-6-decanone (**5a**) and 6-butyl-6-hydroxy-5,7-undecadione (**5b**); the tetramer 6-butyl-6-pentanoate-5,7-undecadione (**6**); and very small amounts of two additional unidentified tetramers (1% yield). By their nature, it is most likely that these products are formed in a radical reaction; however, at this time it is unknown if the radical is metal-centered or is a free acyl radical.[3]





If the acylate complex is slowly added to iodine, in addition to the aforementioned compounds, compound **7** is formed in 25%–30% yield. To determine if the source for the alcohol of this ester is the ring opening of the solvent THF, the butyllithium/nickel tetracarbonyl reaction was repeated in THF-d_8, and then, this solution of the acylate complex was slowly added to iodine. The alcohol part of ester **7** was deuterated.

Protonation of the Nickel Acylate Complex with Excess Acid. The reactivity of the acylate complex **1** was studied with four different proton sources, and in each case, the only product is the acyloin **10**: NH_4Cl (77% yield); HBF_4 (68% yield); HI (91% yield); H_2O (81% yield). No aldehyde, the expected product from nickel protonation, was ever observed.[4,5] A possible mechanism for this reaction is



Because water proves to be so reactive with the nickel acylate complex, the significantly higher yields of **10** obtained in the reactions with aqueous NH_4Cl and aqueous HI as compared with HBF_4 are probably due to the large amounts of water present in these acids. Consistent with this idea, when water is added to the HBF_4 reaction, the yield of acyloin (80%) is not significantly different from that for the other aqueous acidic solutions. Second, the significant reactivity of water with the nickel acylate leads

---

[1] Simunic, J. L.; Pinhas, A. R. *Organometallics* **1987**, *6*, 1358.

[2] Porschke, K. R.; Wilke, G. *Chem. Ber.* **1984**, *117*, 56.

[3] Goldberg, K. I.; Bergman, R. G. *Organometallics* **1987**, *6*, 430; *J. Am. Chem. Soc.* **1989**, *111*, 1285.

[4] (a) For a previous suggestion of dimerization after nickel protonation see: Ryang, M.; Kwang-Myeong, S.; Sawa, Y.; Tsutsumi, S. *J. Organomet. Chem.* **1966**, *5*, 305. (b) Also see: Sawa, Y.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 4183.

[5] Previous studies[6] have shown that aldehydes do not react with the acylate complex; if valeraldehyde was formed in the reaction, it would have been detectable by gas chromatography.

Table I. Determination of pK_a of the Nickel Acylate Complex at Various Reaction Times

	1.0 equiv of **11**		2.86 equiv of **11**	
time, h	amt of unreacted **1**, mmol	pK_a of **8**	amt of unreacted **1**, mmol	pK_a of **8**
0	10.0		10.0	
1	9.66	13.09	9.54	12.90
6	8.43	14.54	7.95	14.30
23	5.76	15.74	4.26	15.53
50	4.40	16.21	2.45	16.05

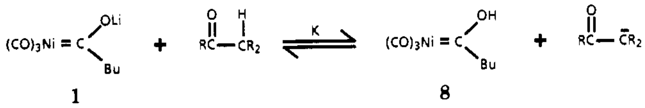
Table II. 5-Hydroxy-6-decanone (**10**) Formation (mmol) vs Time as a Function of Added Acid[a]

	formation of **10**		
time, h	0.25 equiv of water	1.0 equiv of water	1.0 equiv of **11**
23	0.75	2.96	2.12
50	0.78	3.21	2.80

[a] Based upon a 10 mmol reaction; thus, 5 mmoles of acyloin **10** is the theoretical yield.

to the conclusion that the nickel acylate complex **1** must be a strong base whose conjugate acid, **8**, has a pK_a of approximately 16.

Protonation of the Nickel Acylate Complex by a Ketone. The nickel acylate complex does not add to saturated ketones.[6] However, depending on the pK_a of the α-protons of the ketone, either no reaction or proton transfer is observed. Thus, it was hoped that by using ketones of varying pK_a's and by finding the equilibrium constant K for the proton transfer reaction, one could determine the pK_a of the hydroxy–carbene complex **8**. Therefore, the reaction was run for various times, quenched, and then analyzed.



1 8

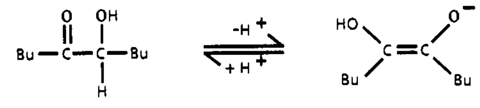
As stated previously, upon rapid addition to iodine, the anionic acylate complex **1** generates the radical-derived products (**4**, two trimers, **5a** and **5b**, and three tetramers, **6**, and the two unidentified products), whereas any of the protonated complex **8** generates the acyloin (**10**). Thus, the acyloin to radical products ratio leads directly to the **8**:**1** ratio.[7]

Ketones whose protons are less acidic than a pK_a of 16, e.g., acetophenone (pK_a = 19), 2-hexanone (pK_a = 21), and 4-heptanone (pK_a = 23),[8] give results after the iodine oxidation that are not significantly different from the results when no ketone is added. On the other hand, 1,3-diphenylacetone (**11**) (pK_a = 16)[8] does react with the nickel acylate complex.

The reaction between the anionic nickel complex and 1,3-diphenylacetone was run at two different concentrations of ketone (1.0 and 2.86 equiv) and for four different times (1, 6, 23, and 50 h) at each concentration. If the pK_a's are calculated, values that change with time are obtained (Table I). Therefore, the equilibrium has never been established; i.e., carbene complex **8** must be generating acyloin product **10** under the reaction conditions and not exclusively in the iodine oxidation reaction.

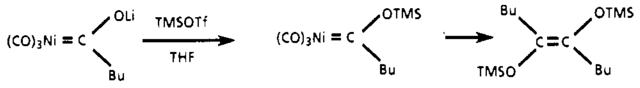
Protonation of the Nickel Acylate Complex by Water. The reaction of the nickel acylate complex **1** with a stoichiometric amount of water also was studied. As judged by the amount of acyloin formed (Table II), water is a slightly better proton source than 1,3-diphenylacetone. In addition, if only 0.25 equiv of water are added, the amount of acyloin formed after the workup is about 25% of that formed with 1 equiv of water.

If the reaction mixture with 1.0 equiv of water is monitored by gas chromatography using an internal standard (4-heptanone), prior to workup the GC trace shows very little acyloin formation (0.44 mmol at 50 h). After workup, the amount of acyloin is the same as in the reactions in which no heptanone was added (3.24 mmol at 50 h). Therefore in solution, the acyloin (**10**) must be as its anion (**12**) rather than as the neutral molecule.



10 12

Silylation of the Nickel Acylate Complex by Trimethylsilyl Triflate. Although the product, **10**, generated by protonation of the nickel acylate complex is consistent with a carbene coupling mechanism,[9] the rapid tautomerization precludes isolation of the kinetic product, **9**. However, the olefin expected from carbene coupling can be isolated by allowing the nickel acylate complex to react with trimethylsilyl triflate. Both cis and trans isomers of olefin **13** are generated.

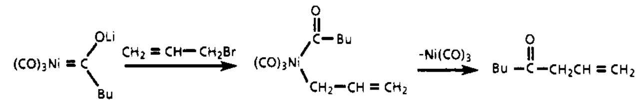


1 2 13

Since the precursor for olefin **13** is believed to be nickel carbene complex **2**, attempts were made to observe complex **2** by ^{13}C NMR spectroscopy. When trimethylsilyl triflate is added to the pentanoylnickel acylate complex, only the acylate and the final organic products are observed, even at −100 °C. However, when the nickel acylate complex is added to a 2-fold excess of trimethylsilyl triflate, the silylated nickel carbene complex **2** is formed. Complex **2** is stable at room temperature for a few hours.

The ^{13}C NMR spectrum of complex **2** shows a peak at 387 ppm due to the carbene carbon and a peak at 193 ppm due to the terminal carbonyls, in addition to the peaks for the carbons of the butyl chain (38, 35, 24, and 15 ppm) and the silyl methyls (3 ppm). The carbonyl stretching region of the infrared spectrum has a peak at 1990 cm^{-1}, consistent with terminal carbonyls.[10] No peaks due to **13** are observed in the ^{13}C NMR spectrum for a minimum of 2 h after complex **1** is added to trimethylsilyl triflate. Complex **13**, however, does form spontaneously from **2** after several hours at room temperature.

Reactivity of the Nickel Acylate Complex with Allyl Bromide. When the nickel acylate complex **1** is allowed to react with allyl bromide and the reaction mixture is subjected to an oxidative workup, a β,γ-unsaturated ketone, **14**, is generated in over 90% yield in 1 h, either at room temperature or at −78 °C.[11]



1 3 14

If the reaction is monitored by infrared spectroscopy,[12] within 5 min of allyl bromide addition to the pentanoylnickel acylate

---

(6) (a) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233, 4926. (b) Hegedus, L. S. Ph.D. Thesis, Harvard University: Cambridge, MA, 1970.

(7) In determining the **8**:**1** ratio, it must be considered that it takes 2 mol of **1** to form 1 mol of **4**, 3 mol of **1** to generate the trimers (**5a** and **5b**), and 4 mol of **1** to generate the tetramers (**6** and two unidentified compounds). For the pK_a values in Table I, it was assumed that it requires 2 mol of **8** to generate **10**.

(8) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin/Cummings Publishing: Menlo Park, CA, 1972; p 494.

(9) (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122 (see specifically pp 84–86). (b) Casey, C. P. *Transition Metal Organometallics in Organic Synthesis*; Academic Press: Orlando, FL, 1976; Vol. 1. (c) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. (d) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

(10) For the purposes of comparison, the carbene carbon chemical shift in a similar chromium complex is 360 ppm. Kreiter, C. G.; Formacek, V. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 141. The weak, higher energy IR absorption expected for this C_{3v} complex is obscured by the peak for nickel tetracarbonyl.

(11) Care must be taken when this reaction is worked up, as any acid will facilitate the conversion of **14** to its conjugated isomer 2-octen-4-one.

(12) All IR spectra were taken at room temperature.

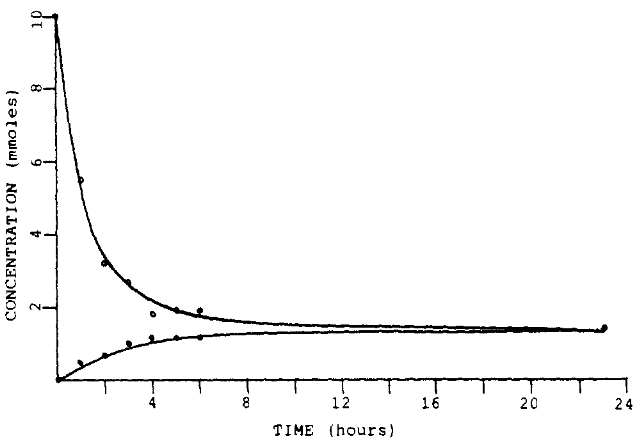
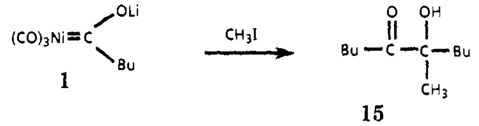


Figure 1. Disappearance of methyl iodide (○) and formation of 5-hydroxy-5-methyl-6-decanone (**15**) (●) in THF vs time, as monitored by gas chromatography.

complex at −78 °C, the carbonyl stretches associated with the acyl carbonyl ligand (1535 cm^{-1}) and with the terminal carbonyl ligands (1980 and 1935 cm^{-1}) of the anionic nickel complex disappear, and carbonyl stretches consistent with an acyl carbonyl ligand (1720 cm^{-1}) and with terminal carbonyl ligands (2040, 1995, and 1960 cm^{-1}) of a neutral nickel complex of C_s symmetry appear. If an IR spectrum is obtained 30 min after addition of the allyl bromide, with the reaction mixture maintained at −78 °C, a shoulder begins to appear at 1710 cm^{-1}, which is probably due to the organic product **14**.

Although spontaneous reductive elimination has been observed in other nickel(II) complexes,[13] the amount of product formed from **3** by reductive elimination before oxidation by iodine *is small*, based on the fact that even after 90 min at room temperature, only trace amounts of **14** are observed. By ^{13}C NMR spectroscopy, as expected, only a small amount of 1-octen-4-one (**14**) is evident, consistent with the nickel complex being paramagnetic.

Alkylation of the Nickel Acylate Complex by Methyl Iodide. On the basis of the allyl bromide results, it was expected that methyl iodide would also nickel alkylate the acylate complex. The anticipated product after reductive elimination of the alkyl and acyl ligands from the acyl(alkyl)nickel(II) complex is 2-hexanone. In fact, 2-hexanone is only a minor product of the reaction; the major product is the acyloin derivative 5-hydroxy-5-methyl-6-decanone (**15**).[14]



The reaction of the pentanoylnickel acylate complex with methyl iodide is significantly slower than the reaction of the nickel acylate complex with allyl bromide. Whereas the later reaction has a half-life of minutes at −78 °C, the former has a half-life of 1.5 h at room temperature, as determined by product formation and methyl iodide disappearance (Figure 1).

Similar rate data are obtained by monitoring the loss of the nickel acylate complex. Changes in the chemical shift of the ^{7}Li NMR spectrum indicate that the lithium salt of the anionic nickel complex is being replaced by lithium iodide (Figure 2).

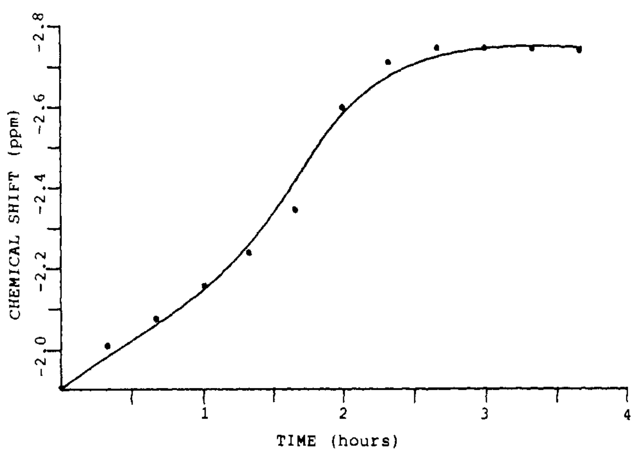


Figure 2. Change in the ^{7}Li NMR chemical shift for the reaction of the nickel acylate complex **1** with methyl iodide. The chemical shift of an external butyllithium standard was arbitrarily taken as zero ppm.

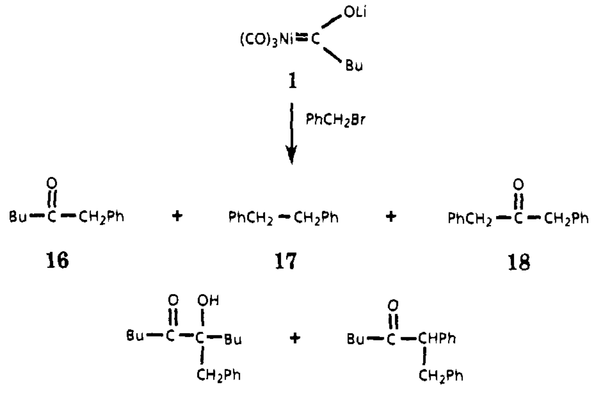
Table III. Product Formation vs Time for the Reaction of **1** with Benzyl Bromide

	% product formation					
time, h	16	17	18	19	20	$PhCH_2X$
1[a]	14	30	2	15	34	2
1[b]	12	5	0	15	47	20
23[a]	13	8	12	9	54	1
23[b]	12	8	11	12	54	1

[a] Percent yields are based on benzyl bromide and are obtained from monitoring the reaction by GC *before* workup. [b] Percent yields are based on benzyl bromide and are obtained *after* an oxidative workup.

The reaction was also monitored by infrared spectroscopy. The 1535-cm^{-1} stretch of the acylate complex decreases at a rate comparable to the rate of increase of acyloin **15** and the rate of change of the ^{7}Li chemical shift. The acyloin carbonyl stretch (1705 cm^{-1}) and alcohol stretch (about 3500 cm^{-1}) also can be observed before workup. In addition, a stretch at 1840 cm^{-1} increases in the IR spectrum. This peak is in the region usually assigned to bridging carbonyls in transition metal dimers and trimers.[15]

Alkylation of the Nickel Acylate Complex by Benzyl Bromide. Unlike the reactions between the nickel acylate complex **1** and either allyl bromide or methyl iodide, which each generate only one product, the reaction with benzyl bromide generates five organic products: 1-phenyl-2-hexanone (**16**), bibenzyl (**17**), 1,3-diphenylacetone (**18**), 5-benzyl-5-hydroxy-6-decanone (**19**), and 1,2-diphenyl-3-heptanone (**20**).



The reaction of the nickel acylate complex with benzyl bromide is much slower than the corresponding reaction with allyl bromide, though faster than the reaction with methyl iodide. This is determined from the observation that the product yield (**16** + **17** + **18** + **19** + **20**), after an oxidative workup, increases with time

---

(13) (a) Kurosawa, H.; Ohnishi, H.; Emoto, M.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1988**, *110*, 6272. (b) For a slow reductive elimination in an analogous iron complex, see: Laurent, P.; Sabo-Etienne, S.; Larsonneur, A.-M.; des Abbayes, H. *J. Chem. Soc., Chem. Commun.* **1988**, 929.

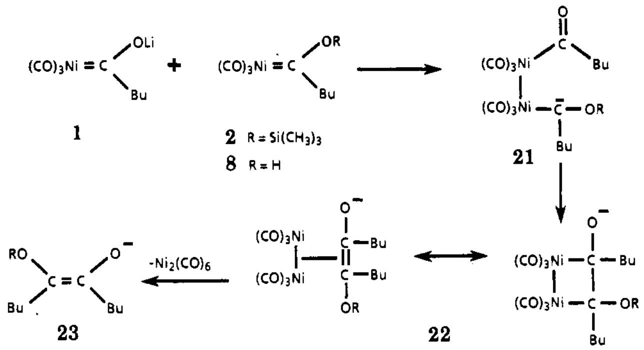
(14) Only a 32% yield of compound **15** can be isolated from this reaction. No other products can be isolated or observed by GC. Thus, much of the methyl iodide and butyllithium are unaccounted for.

(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987, p. 115.

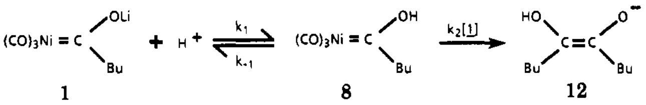
(Table III) and by monitoring the reaction with IR spectroscopy. Specifically, after 30 min at −78 °C, the major peaks for the acylate complex (1935 and 1535 cm^{-1}) are still present with small peaks growing in at 2035 and 1840 cm^{-1}. The spectrum is not much different even after 30 min at room temperature. After a few hours at room temperature, the peaks at 1935 and 1535 cm^{-1} have almost disappeared and new peaks appear at 2035, 1970, 1840, and 1705 cm^{-1}.

Discussion

Mechanism of Acyloin and Enol Ether Formation. On the basis of the facts that (1) in the presence of excess acid the only product observed is the acyloin 5-hydroxy-6-decanone (**10**), (2) in the presence of a proton source the nickel acylate complex generates the acyloin **10** under the reaction conditions and not exclusively in the iodine oxidation, (3) the acyloin generated during the reaction is present in the form of its anion **12**, and (4) the silylated nickel carbene complex is only observed in the presence of excess trimethylsilyl triflate and not in the presence of excess nickel acylate complex, it is reasonably concluded that the observed products are not exclusively formed via carbene coupling of two neutral nickel complexes, i.e., **2** reacting with **2** or **8** reacting with **8**. In fact, on the basis of the chemistry with trimethylsilyl triflate, the carbene coupling reaction must be slow. In a fast reaction, the excess acylate present in the reaction mixture attacks the neutral carbene complex, followed by the elimination of enolate **23**.[16] The resulting enolate, subsequently, either protonates to yield **9** or silylates to produce **13**, depending on the reaction conditions.



To determine if the coupling of the two nickel complexes or the protonation is the rate-determining step, the rate of disappearance of the nickel acylate complex in the presence of added acid was studied.



Assuming that **8** is a steady-state intermediate, the rate expression for the disappearance of **1** is

$$\frac{-\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = \frac{2k_1k_2[\mathbf{1}]^2[\mathrm{H}^+]}{k_{-1} + k_2[\mathbf{1}]}$$

If the protonation is the rate-determining step, then $k_2[\mathbf{1}]$ is significantly greater than k_{-1}, and thus, the rate of disappearance of **1** is first order in acylate complex. If, however, the reaction of two nickel complexes is the rate-determining step, then k_{-1} is significantly greater than $k_2[\mathbf{1}]$, and thus, the rate of disappearance of **1** is second order in acylate complex. As shown in Figure 3, with excess H$^+$, the reaction follows second-order kinetics; therefore, k_{-1} is significantly greater than $k_2[\mathbf{1}]$, and thus, the rate-determining step is the coupling of the two nickel complexes.

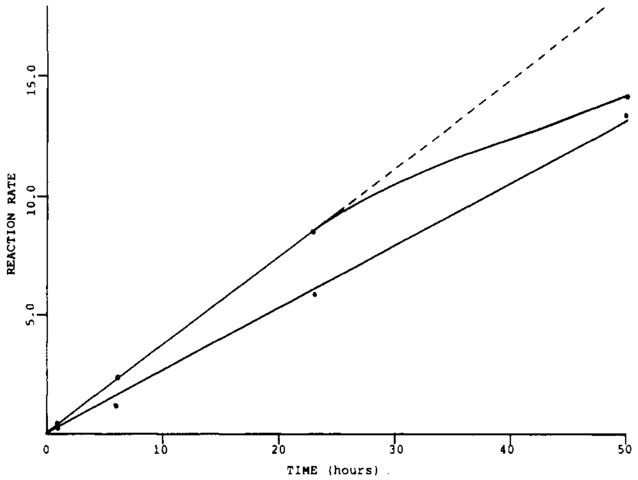
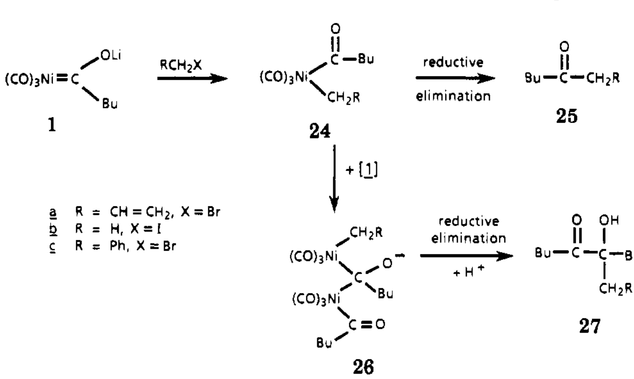


Figure 3. Reaction rate for the disappearance of the nickel acylate complex **1** vs time using 2.86 equiv of 1,3-diphenylacetone as the proton source. The second-order reaction rate (●) is plotted as $(1/[\mathbf{1}] - 1/[\mathbf{1}]_0)$ with units of liters/mole. The first-order reaction (○) is plotted as 10 ln $([\mathbf{1}]_0/[\mathbf{1}])$. The dotted line is an extrapolation of the line generated by the initial points in the first-order plot.

When 1,3-diphenylacetone (2.86 equiv) is the proton source, the slope of the second-order plot is 7.33×10^{-5} M^{-1} s^{-1}, and [H$^+$] is 8.11×10^{-9} mol/L. Thus, the observed rate constant for the acyloin **10** formation is 4.52×10^3 M^{-2} s^{-1}.

Mechanism of Ketone and Substituted-Acyloin Formation. The results for the reaction of **1** with allyl bromide are consistent with a very rapid reaction between allyl bromide and the acylate complex to give **3** (**24a**), followed by a very slow (if unaided by I$_2$) reductive elimination, to give **14** (**25a**). On the other hand, the reaction of **1** with methyl iodide is much slower. It was shown with the oxygen alkylation studies that, in the presence of excess nickel acylate complex, the neutral nickel hydroxy–carbene complex is attacked by anion **1**; thus a reasonable mechanism for the formation of 5-hydroxy-5-methyl-6-decanone (**15** (**27b**)) includes attack of acyl(alkyl)nickel(II) complex **24** by the acylate complex **1**. Complex **26** may possess bridging carbonyls to account for the peak at 1840 cm^{-1} in the IR spectrum. Although the order of the reductive-elimination steps is not known, it is most likely that the acyl–alkyl elimination would occur faster than the alkyl–alkyl elimination by analogy to some cobalt complexes.[17]



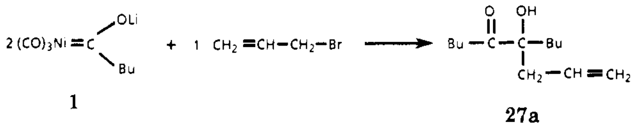
For this mechanism to be correct, an isolated acyl(alkyl)nickel complex must react with acylate complex **1** to give a substituted acyloin derivative after workup. Since the reaction of **1** with allyl bromide generates an isolable acyl(alkyl)nickel complex rapidly, the reaction of 2 equiv of **1** with 1 equiv of allyl bromide should generate an acyloin derivative. When this reaction was performed, no 1-octen-4-one (**14**) was produced; the exclusive product, in 86%

---

[16] A reviewer has suggested that "on the basis of the high electrophilicity of nickel carbenes **2** and **8** (which is evident from the ^{13}C data for the carbene carbon), nucleophilic attack by **1** is expected to occur at the carbene carbon atom." We had, initially proposed this mechanism for the same reason as given by the reviewer; however, we presently favor the mechanism as shown. Our rationale is as follows: if the carbene carbon atom is attacked, a reductive elimination must occur to give **23**, but from our work with allyl bromide, we know these reductive eliminations are slow at room temperature. Thus, we are proposing nickel attack, with no reductive-elimination step, to explain rapid product formation at −100 °C.

[17] Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003.

yield, is 5-hydroxy-5-allyl-6-decanone (**27a**).



In the reaction of **1** with benzyl bromide, it is most likely that compound **16** forms by a mechanism analogous to that for the formation of **14** from allyl bromide, and compound **19** forms by a mechanism analogous to that for the formation of **15** from methyl iodide and **27a** from allyl bromide.

In these three reactions, the ratio of ketone **25** to substituted acyloin **27** is determined by the rate of formation of **24**. If **24** is generated very rapidly, as with allyl bromide, there is no acylate **1** present to react with **24**, and thus, **25** is observed. If **24** is generated very slowly, as with methyl iodide, the reaction between **1** and **24** by comparison is fast, and thus, only **27** is observed. Finally, if the rate of formation of **24** is intermediate between these two extremes, as it is with benzyl bromide, both products **25** and **27** are generated.

Mechanism of Formation of 17, 18, and 20. As shown in Table III, there is little benzyl bromide remaining after 1 h as judged by GC monitoring of the reaction, yet a great deal of benzyl halide (mostly as benzyl iodide) can be isolated after an I_2 workup. Secondly, the amount of bibenzyl (**17**) observed by GC monitoring is much greater than that obtained after an I_2 workup. Control experiments show that benzyl bromide and benzyl iodide are stable to the GC conditions and that radical traps, such as diphenylethylene,[18] have no effect on this reaction. Thus, the data in Table III indicate that, in solution, a metal complex must be present which (1) reductively eliminates to bibenzyl in the hot injection port of the GC, (2) yields benzyl iodide upon reaction with I_2 or I^-, and (3) inserts a carbonyl, given enough time, to eventually give diphenylacetone (**18**).

By analogy to the mechanism proposed for the dimerization of aryl halides to give biaryls,[19] a dibenzylnickel(II) or -nickel(III) species is the likely intermediate. The formation of this complex cannot come from the reaction of benzyl bromide with nickel tetra- or tricarbonyl because the reaction of benzyl bromide with nickel tetracarbonyl generates benzyl bromide and benzyl iodide, but no bibenzyl, after an I_2 workup, even when the reaction is heated. Since acylate complex **1** is stable in the absence of an electrophile, complex **24c** must be the precursor to the bibenzyl complex.

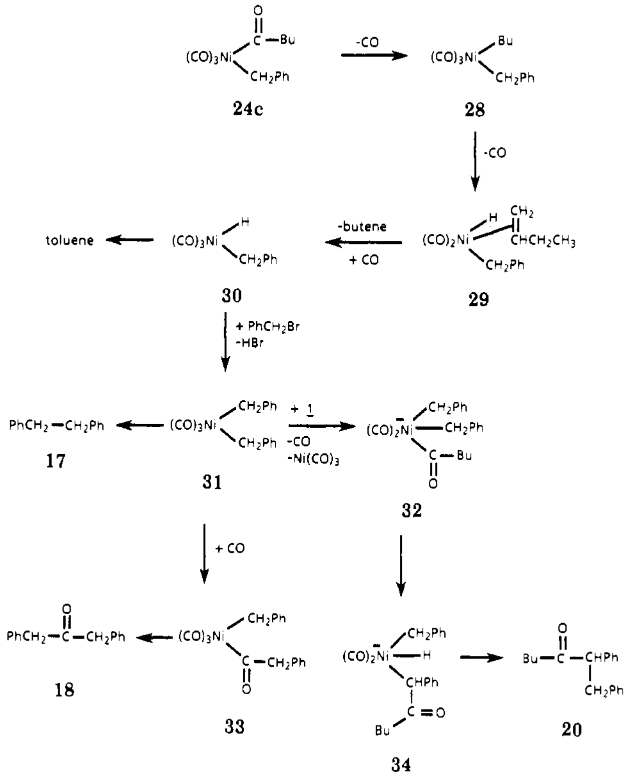
Three other points must be noted before a mechanism is proposed: (1) acyloin derivative **19** is formed in the reaction and not in the workup so there must be a proton source in the reaction mixture, (2) 1-butene and no butane is present in the gas phase above the reaction mixture, and (3) small amounts of toluene are observed by GC monitoring before workup. A proposed mechanism is shown in Scheme I.

The intermediates shown in Scheme I are nickel(0) and nickel(II) complexes. However, by strict analogy to the aryl coupling reaction, they should be nickel(I) and nickel(III) complexes. This change can easily be accomplished by replacing a CO in each complex by a bromine. Compounds similar to many of these intermediates are known.[3,13,20,21]

Summary

The nickel acylate complex **1**, generated by reaction of butyllithium and nickel tetracarbonyl in THF, is monomeric.[1] Unlike the analogous iron complex,[21] the nickel complex is unaffected by the addition of a crown ether. In addition, unlike the iron complex, protonation of the nickel complex generates no aldehyde; only an acyloin is formed.

Scheme I



It is known that chromium acylate complexes exclusively oxygen alkylate.[22] There is mainly indirect evidence, through organic product isolation, that iron acylate complexes either metal or oxygen alkylate depending on the nature of the electrophile.[13b,21,23] In this paper, direct and indirect support is provided for oxygen alkylation of the nickel acylate complex with hard acids and metal alkylation with soft acids.

Finally, it has been shown that, in those cases in which the acylate complex nickel alkylates, if the reaction is fast, a single acyl transfer occurs to give a simple ketone after workup, and if the reaction is slow, a second acyl transfer occurs to give an acyloin derivative after workup. In those cases in which the acylate complex oxygen alkylates, a nickel carbene complex is formed, which in turn generates an enol ether derivative.

Experimental Section

General Data. All reactions were carried out by using oven dried glassware that was cooled under an argon atmosphere or in a desiccator. All reactions were conducted under an argon atmosphere.

Tetrahydrofuran was freshly distilled from potassium benzophenone ketyl. Nickel tetracarbonyl was transferred from a 1-lb lecture bottle into a 10-mL sidearm flask, maintaining a strong argon flow, and stored under argon until used. Transfers were made via syringe, and excess $Ni(CO)_4$ was quenched in an iodine/CCl_4 bath. (*Caution*! $Ni(CO)_4$ is toxic and extremely flammable when exposed to air. All work with this complex should be conducted in a well-ventilated hood. Maintaining an argon atmosphere during all transfers and using nonflammable solvents in the iodine bath minimizes the probability of fire.)

Butyllithium (1.6 M) was stored under argon and titrated before use with diphenylacetic acid. Water and aqueous NH_4Cl were deaerated

---

(18) See, for example: Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific and Technical: Essex, England, 1987, pp 740–741.

(19) (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547. (b) Reference 15; p 313.

(20) Miller, R. G.; Pinke, P. A.; Stauffer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211.

(21) (a) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342. (b) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766.

(22) (a) Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Fischer, E. O.; Kalbfus, W. *J. Organomet. Chem.* **1972**, *46*, C15. (c) Fischer, E. O.; Kreis, G.; Kreissl, F. R. *J. Organomet. Chem.* **1973**, *56*, C37. (d) Fischer, E. O.; Selmayr, T.; Kreissl, F. R.; Schubert, U. *Chem. Ber.* **1977**, *110*, 2574. (e) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *12*, P1.

(23) (a) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099. (b) Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Muller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162. (c) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325. (d) Laurent, P.; Tanguy, G.; des Abbayes, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1754.

with argon immediately prior to use.

Instrumentation. A Varian Model 3300 gas chromatograph was used for all GC analyses with a flash vaporization injector at 225 °C, a flame ionization detector at 325 °C, and a 12 ft × $^{1}/_{8}$ in. 5% SP-2100 on 100/120 Supelcoport column. Temperature programming was used: initial temperature of 50 °C for 1 min; increase by 10 °C/min to 250 °C; increase by 20 °C/min to 300 °C; held at 300 °C for 4 min.

A Kratos high-pressure liquid chromatograph was used for all separations with a Kratos Spectroflow 783 detector, two Spectroflow 400 pumps, a Spectroflow 591 static mixer/injector, a 250 × 7.0 mm reverse-phase C_{18} column, gradient programming, and a 3 mL/min flow rate. The solvents were deaerated HPLC grade CH_3CN and H_2O filtered with the Nanopure II system.

All infrared spectra were recorded on a Perkin-Elmer Model 599 infrared spectrophotometer with CaF_2 or KBr cells and a scan range of 4000–1000 or 2500–1000 cm^{-1}.

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

All GC/mass spectra were recorded on a Hewlett-Packard Model 9133 spectrometer using a 0.25 mm × 15 m fused silica capillary SPB-1 column and temperature programming.

General Procedure. A solution of the pentanoyl nickelate was prepared by allowing 1.2 mL (10 mmol) of nickel tetracarbonyl to react under argon with 1.6 M butyllithium (6.2 mL; 10 mmol) in 30 mL of THF for 15 min at −78 °C, followed by 1 h at ambient temperature. 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 23 h, excess nickel carbonyl was quenched by quickly pouring the reaction mixture into a flask containing 2.5 g (10 mmol) of solid iodine and stirring for 15 min. The mixture was washed with aqueous sodium bisulfite until the aqueous layer was colorless. The combined aqueous layers were then washed with approximately 50 mL of ether. The ether layer was added to the organic solution and dried with potassium carbonate.

Electrophiles. H_2O, 1.0 mL (55.5 mmol); NH_4Cl, 1.0 mL saturated aqueous solution; HI, 1.5 mL 47% aqueous solution; HBF_4, 0.9 mL 55% ethereal solution; trimethylsilyl triflate, 1.9 mL (10 mmol); 1,3-diphenylacetone, 2.1 mL (10 mmol); 1,3-diphenylacetone, 6.0 mL (28.6 mmol); acetophenone, 1.2 mL (10 mmol); 2-hexanone, 1.2 mL (10 mmol); 4-heptanone, 1.4 mL (10 mmol); H_2O, 0.18 mL (10 mmol); H_2O, 0.045 mL (2.5 mmol); benzyl bromide, 1.2 mL (10 mmol); allyl bromide, 0.9 mL (10 mmol); methyl iodide, 0.6 mL (10 mmol).

12-Crown-4 Addition. The acylate anion was generated as in the general procedure. It was monitored by ^{13}C NMR spectroscopy with the terminal carbonyl peak and acyl carbonyl peak at δ 205.323 and 317.531, respectively. Then 1.72 g (10 mmol) of 12-crown-4 was added. After 1 hour a ^{13}C NMR spectrum and an IR spectrum were obtained with the carbonyl peaks at δ 205.603 and 316.260 and at 1990 (w), 1940 (s), and 1535 (m) cm^{-1}. It was also monitored after 23 h: δ 205.518 and 316.116; 1980 (w), 1950 (s), and 1540 (m) cm^{-1}.

Oxidation by I_2. This was performed as in the general procedure, except no additional electrophile was added. Yields (%) at 1 h: 5-nonanone, 3; **4**, 22; **5a**, 31; **5b**, 4; **6**, 32. Yields (%) at 23 h: 5-nonanone, 4; **4**, 21; **5a**, 29; **5b**, 4; **6**, 33. (If the reaction is performed such that nickel tetracarbonyl is added to a cold solution of butyllithium in THF, after 1 h the following yields (%) are obtained: 5-nonanone, 8; **4**, 26; **5a**, 11; **5b**, 12; **6**, 37.)

5,6-Decanedione (4). ^{1}H NMR (CD_2Cl_2), δ: 2.695 (t, J = 7.2 Hz, 4 H), 1.520 (quintet, J = 7.5 Hz, 4 H), 1.40–1.25 (m, 4 H), 0.888 (t, J = 7.2 Hz, 6 H). ^{13}C NMR (THF), δ: 199.937, 36.245, 26.366, 23.495, 14.604. IR ($CDCl_3$), cm^{-1}: 2960 (s), 2940 (m), 2880 (m), 1710 (vs), 1705 (vs). MS, *m/e*: 170 (15.8%), 85 (100%), 57 (49.7%), 41 (17.1%). Retention times: GC, 9.7 min; HPLC, 22 min.

BuC(O)CH(Bu)(OC(O)Bu) (5a). ^{1}H NMR ($CDCl_3$), δ: 4.993 (dd, J = 8.1, 4.5 Hz, 1 H), 2.444 (dt, J = 18.0, 7.5 Hz, 2 H), 2.443 (dt, J = 22.5, 7.2 Hz, 2 H), 1.70–1.25 (m, 14 H), 0.904 (t, J = 7.5 Hz, 6 H), 0.884 (t, J = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$), δ: 207.784, 173.487, 78.234, 38.373, 36.302, 33.778, 30.154, 27.437, 25.420, 25.236, 22.304, 13.840. IR ($CDCl_3$), cm^{-1}: 2960 (vs), 2940 (vs), 2880 (s), 1740 (vs), 1725 (vs), 1170 (m). MS, *m/e*: 256 (0.6%), 171 (5.0%), 170 (5.1%), 86 (6.1%), 85 (100%), 57 (15.1%). Retention times: GC, 16.2 min; HPLC, 29 min.

(BuC(O))$_2$C(OH)(Bu) (5b). (**5b** could not be isolated from **5a**; ^{1}H and ^{13}C NMR and IR data presented are the difference spectra for a mixture of **5a** and **5b** and isolated **5a**.) ^{1}H NMR ($CDCl_3$), δ: 4.694 (s, 1 H), 2.680 (dt, J = 18.3, 7.2 Hz, 4 H), 1.70–1.25 (m, 14 H), 0.929 (t, J = 7.5 Hz, 9 H). ^{13}C NMR ($CDCl_3$), δ: 209.725, 90.982, 36.939, 26.918, 22.713, 13.718. IR ($CDCl_3$), cm^{-1}: 3500–3380 (w), 2960 (s), 2940 (s), 2880 (s), 1695 (s). MS, *m/e*: 256 (0.7%), 173 (10.9%), 172 (100%), 129 (22.5%), 85 (19.1%), 57 (15.4%). Retention time: GC, 16.8 min.

(BuC(O))$_2$C(OC(O)Bu)(Bu) (6). ^{1}H NMR ($CDCl_3$), δ: 2.523 (dt, J = 34.2, 7.2 Hz, 2 H), 2.315 (dt, J = 24.6, 7.2 Hz, 4 H), 1.629 (quintet, J = 7.5 Hz, 4 H), 1.56–1.45 (m, 4 H), 1.45–1.28 (m, 10 H) (0.923 (t, J = 7.5 Hz), 0.892 (t, J = 7.5 Hz), and 0.877 (t, J = 7.5 Hz, 12 H)). ^{13}C NMR ($CDCl_3$), δ: 204.599, 171.289, 138.206, 94.980, 38.423, 34.168, 29.040, 27.229, 27.126, 25.999, 25.355, 22.828, 22.433, 22.320, 14.074, 13.898. IR ($CDCl_3$), cm^{-1}: 2970 (vs), 2940 (s), 2880 (s), 1760 (s), 1745 (s). MS, *m/e*: 340 (2.1%), 256 (4.6%), 172 (100%), 85 (37.7%), 57 (23.1%). Retention times: GC 20.1 min; HPLC, 39 min.

Unidentified Tetramers. MS, *m/e*: 340 (2.9%), 256 (6.8%), 173 (12.5%), 172 (100%), 85 (16.4%), 57 (13.1%). Retention time: GC, 19.1 min. MS, *m/e*: 340 (3.9%), 256 (4.6%), 173 (10.4%), 172 (100%), 85 (14.8%), 57 (11.9%). Retention time: GC, 19.7 min.

$BuCOOCH_2CH_2CH_2CH_2I$ (7). This reaction was performed as above except the anionic solution was added dropwise to the I_2 over 15–20 min. After the mixture was stirred for an additional 15 min, the usual workup was continued. ^{1}H NMR ($CDCl_3$), δ: 4.094 (t, J = 6.3 Hz, 2 H), 3.214 (t, J = 6.7 Hz, 2 H), 2.305 (t, J = 7.5 Hz, 2 H), 1.907 (dt, J = 14.7, 6.6 Hz, 2 H), 1.747 (quint, J = 6.0 Hz, 2 H), 1.610 (quint, J = 7.5 Hz, 2 H), 1.348 (sextet, J = 7.2 Hz, 2 H), 0.920 (t, J = 7.5 Hz, 3 H). ^{13}C NMR ($CDCl_3$), δ: 173.802, 62.968, 34.028, 30.081, 29.626, 27.030, 22.525, 13.709, 5.750. IR ($CDCl_3$), cm^{-1}: 2960 (s), 1725 (s), 1460 (s), 1380 (s), 1245 (s), 1170 (s). MS, *m/e*: 284 (0.3%), 183 (19.7%), 182 5.8%), 158 (9.6%), 157 (100%), 155 (13.7%), 154 (15.1%), 141 (5.1%), 128 (4.4%), 127 (9.0%), 103 (15.1%), 86 (3.0%), 85 (42.2%), 57 (15.5%), 55 (28.9%). Retention times: GC, 15.8 min; HPLC, 24 min.

$BuCOOCD_2CD_2CD_2CD_2I$ (7-d_8). This reaction was performed in THF-d_8 on one-tenth the normal scale. ^{1}H NMR ($CDCl_3$), δ: 2.305 (t, J = 7.5 Hz, 2 H), 1.609 (quint, J = 7.5 Hz, 2 H), 1.348 (sextet, J = 7.5 Hz, 2 H), 0.920 (t, J = 7.5 Hz, 3 H). Small peaks can be observed just above the base-line noise at δ 4.1, 3.2, 1.9, 1.8.

Protonation. This was performed as in the general procedure. Yields: H_2O (1.0 mL), 81%; NH_4Cl, 77%; HI, 91%; HBF_4, 66%; HBF_4/H_2O, 80%; H_2O (0.18 and 0.045 mL), yields as indicated in text.

5-Hydroxy-6-decanone (10). ^{1}H NMR ($CDCl_3$), δ: 4.174 (dd, J = 7.2, 3.9 Hz, 1 H), 3.6–3.4 (s, 1 H), 2.464 (td, J = 7.5, 5.4 Hz, 2 H), 1.90–1.75 (m, 1 H), 1.602 (d quint, J = 15.3, 7.5 Hz, 2 H), 1.55–1.40 (m, 3 H), 1.336 (sextet, J = 7.5 Hz, 4 H), 0.920 (t, J = 7.5 Hz, 6 H). ^{13}C NMR (THF), δ: 212.733 (s), 76.583 (d), 37.774 (t), 33.696 (t), 27.196 (t), 25.939 (t), 22.741 (t), 22.565 (t), 14.116 (q), 14.029 (q). IR ($CDCl_3$), cm^{-1}: 3600–3400 (m), 2960 (m), 2935 (m), 2870 (m), 1710 (s). MS, *m/e*: 172 (1.7%), 116 (13.2%), 87 (49.9%), 86 (19.6%), 85 (27.6%), 69 (100%), 57 (26.8%), 41 (26.7%). Retention times: GC, 11.2 min; HPLC, 12 min.

1,3-Diphenylacetone Quench. This reaction was performed as in the general procedure with yields and times given in the text. Values used for Figure 3 are as follows. For 10 ln ([**1**]$_0$/[**1**]): 0 h, 0; 1 h, 0.5; 6 h, 2.3; 23 h, 8.5; 50 h, 14.1. For 1/[**1**] − 1/[**1**]$_0$: 0 h, 0 L/mol; 1 h, 0.2 L/mol; 6 h, 1.1 L/mol; 23 h, 5.9 L/mol; 50 h, 13.4 L/mol. The correlation coefficient for the second-order reaction is 0.9991.

Silylation Reaction. This was performed as in the general procedure except the workup was modified due to the water sensitivity of the product. After being stirred for 23 h at room temperature, the reaction mixture was filtered under argon and the solvent was removed to give a dark oil with solids. Then 20 mL of petroleum ether was added, and the solution was again filtered and concentrated. This petroleum ether wash was repeated once more with 10 mL to give a pale yellow oil, which proved to be a 59% yield of a cis and trans mixture of compound **13**.

***cis*- and *trans*-5,6-Bis(trimethylsiloxy)-5-decene (13).** ^{1} NMR ($CDCl_3$), δ: 2.131 (t, J 7.5 Hz, 2.5 H), 2.018 (t, J = 7.8 Hz, 1.5 H), 1.65–1.20 (m, 8 H), 0.900 (t, J = 7.2 Hz, 6 H), 0.163 (s) and 0.145 (s) (18 H). ^{13}C NMR ($CDCl_3$), δ: 137.780, 134.367, 31.284, 29.862, 29.679, 29.025, 22.608, 22.299, 13.942, 0.813, 0.616. IR (CH_2Cl_2), cm^{-1}: 3050 (s), 2980 (s), 2960 (s), 1420 (s), 1260 (vs).

Formation of the Siloxy–Carbene Complex 2. The nickel acylate complex was synthesized as in the general procedure. To a second three-necked flask was added 3.8 mL (20 mmol) of trimethylsilyl triflate. This flask was cooled to −78 °C and the THF solution of the anion was added with a syringe over 10 min. After 1 min, 2.0 mL (14 mmol) of triethylamine was added to remove excess trimethylsilyl triflate. After 1 min more, the cold bath was removed and samples were taken, via syringe, for spectroscopic analysis.

$(CO)_3NiC(OSi(CH_3)_3)Bu$ (2). ^{13}C NMR (THF), δ: 386.895, 192.852, 37.601, 35.335, 23.576, 14.842, 2.692. IR (THF), cm^{-1}: 1990 (vs).

Allyl Bromide Reactions. These reactions were performed as in the general procedure with yields[11] and times as indicated in the text. Samples for monitoring by IR and NMR spectroscopy were removed via syringe, with results given in the text.

1-Octen-4-one (14). ^{1}H NMR (CDCl$_3$), δ: 6.20–5.80 (m, 1 H), 5.178 (dd, J = 9.3, 1.2 Hz) and 5.134 (dd, J = 16.8, 1.2 Hz) (2 H), 3.167 (d, J = 6.6 Hz, 2 H), 2.440 (t, J = 7.5 Hz, 2 H), 1.561 (quintet, J = 7.5 Hz, 2 H), 1.325 (quintet, J = 7.5 Hz, 2 H), 0.904 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (CDCl$_3$), δ: 211.628, 130.744, 118.615, 47.730, 42.089, 25.828, 22.322, 13.821. IR (CDCl$_3$), cm^{-1}: 3160 nw), 3080 (w), 2960 (s), 2940 (s), 2880 (s), 1710 (s), 1635 (m), 1460 (m), 1380 (m). Retention time: GC, 7.8 min.

2-Octen-4-one. ^{1}H NMR (CDCl$_3$), δ: 6.95–6.75 (m, 1 H), 6.123 (dq, J = 15.9, 1.5 Hz, 1 H), 2.518 (t, J = 7.5 Hz, 2 H), 1.890 (dd, J = 6.6, 1.5 Hz, 3 H), 1.70–1.45 (m, 2 H), 1.321 (quintet, J = 7.2 Hz, 2 H), 0.913 (t, J = 7.2 Hz, 3 H). IR (CDCl$_3$), cm^{-1}: 3150 (w), 2950 (s), 2920 (s), 2860 (m), 1680 (s), 1660 (s), 1620 (s), 1450 (s), 1370 (s). Retention time: GC, 8.7 min.

Methyl Iodide Reaction. These reactions were performed as in the general procedure. Samples for monitoring by GC and IR and NMR spectroscopy were removed via syringe.

5-Hydroxy-5-methyl-6-decanone (15). ^{1}H NMR (CDCl$_3$), δ: 3.95–3.85 (broad, 1 H), 2.500 (dt, J = 11.1, 7.2 Hz, 2 H), 1.72–1.55 (m, 4 H), 1.40–1.20 (m, 6 H), 1.345 (s, 3 H), 0.926 (t, J = 7.5 Hz, 3 H), 0.881 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (CDCl$_3$), δ: 214.630, 78.708, 39.350, 35.433, 25.757, 25.548, 22.927, 22.398, 13.887. IR (CDCl$_3$), cm^{-1}: 3600–3400 (br, m), 2960 (s), 2940 (s), 2880 (s), 2870 (s), 1705 (s). MS, *m*/*e*: 187 (0.1%), 186 (0.2%), 102 (6.8%), 101 (100%), 83 (13.8%), 59 (9.1%), 57 (13.9%), 55 (18.6%), 45 (29.8%), 43 (26.3%), 41 (18.7%). Retention times: GC, 12.2 min; HPLC, 21 min.

Benzyl Bromide Reactions. These reactions were performed as in the General Procedure with the yields and times as indicated in the text. Samples for monitoring by GC and IR spectroscopy were removed via syringe.

1-Phenyl-2-hexanone (16). ^{1}H NMR (CD$_2$Cl$_2$), δ: 7.35–7.10 (m, 5 H), 3.660 (s, 2 H), 2.436 (t, J = 7.4 Hz, 2 H), 1.501 (quintet, J = 7.4 Hz, 2 H), 1.251 (sextet, J = 7.4 Hz, 2 H), 0.853 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (THF), δ: 207.115, 136.442, 130.578, 129.458, 127.643, 50.695, 42.318, 23.358, 14.617. IR (CDCl$_3$), cm^{-1}: 3100 (w), 3070 (w), 3040 (w), 2960 (m), 2940 (m), 2900 (w), 2880 (w), 1710 (s). MS, *m*/*e*: 176 (21.6%), 92 (12.4%), 91 (76.1%), 89 (14.4%), 85 (100%), 65 (32.6%), 63 (11.5%), 57 (77.3%), 44 (13.2%). Retention times: GC 13.0, min; HPLC, 17 min.

Bibenzyl (17). ^{1}H NMR (CDCl$_3$), δ: 7.35–7.10 (m, 10 H), 2.924 (s, 4 H). ^{13}C NMR (THF), δ: 143.009, 129.436, 129.297, 126.938, 39.209. MS, *m*/*e*: 182 (25.8%), 91 (100%), 65 (17.3%), 44 (12.6%). Retention times: GC, 14.5 min; HPLC, 9 min.

1,3-Diphenylacetone (18). ^{1}H NMR (CDCl$_3$), δ: 7.40–7.10 (m, 10 H), 3.719 (s, 4 H). IR (CDCl$_3$), cm^{-1}: 3090, 3070, 3030, 1710. MS, *m*/*e*: 210 (20.8%), 118 (10.0%), 91 (100%), 65 (20.1%), 44 (20.0%). Retention times: GC, 17.4 min; HPLC, 10 min.

5-Benzyl-5-hydroxy-6-decanone (19). ^{1}H NMR (CDCl$_3$), δ: 7.30–7.15 (m, 5 H), 3.698 (s, 1 H), 2.980 (dd, J = 17.1, 14.1 Hz, 2 H), 2.488 (ddd, J = 22.2, 8.7, 6.3 Hz, 1 H), 1.92–1.20 (m, 11 H), 0.895 (t, J = 7.2 Hz, 3 H), 0.878 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (THF), δ: 214.921, 138.133, 131.561, 130.752, 129.539, 128.831, 127.415, 83.078, 49.760, 46.502, 40.322, 38.591, 26.458, 24.335, 23.444, 14.736. IR (CDCl$_3$), cm^{-1}: 3600–3400 (w), 3090 (w), 3070 (w), 3030 (w), 2960 (s), 2940 (s), 2880 (m), 1710 (s). MS, *m*/*e*: 262 (0.3%), 177 (100%), 91 (29.2%), 85 (17.7%), 57 (17.7%). Retention times: GC, 18.6 min; HPLC, 27 min.

1,2-Diphenyl-3-heptanone (20). ^{1}H NMR (CDCl$_3$), δ: 7.32–7.00 (m, 10 H), 3.919 (t, J = 7.5 Hz, 1 H), 3.420 (dd, J = 13.8, 7.8 Hz, 1 H), 2.895 (dd, J = 13.5, 6.9 Hz, 1 H), 2.295 (dd, J = 17.7, 7.5 Hz, 1 H), 2.271 (dd, J = 17.1, 7.5 Hz, 1 H), 1.44–1.30 (m, 2 H), 1.101 (sextet, J = 7.2 Hz, 2 H), 0.751 (t, J = 7.2 Hz, 3 H). ^{13}C (CD$_2$Cl$_2$), δ: 210.486, 140.858, 139.693, 129.857, 129.640, 129.339, 129.080, 128.110, 126.945, 43.264, 42.887, 39.392, 26.903, 26.593, 23.279, 22.958, 14.573, 14.414. IR (CDCl$_3$), cm^{-1}: 3090 (w), 3070 (w), 3030 (w), 2960 (s), 2940 (m), 2880 (w), 1710 (s). MS, *m*/*e*: 266 (74.0%), 209 (25.1%), 181 (71.6%), 85 (100%), 57 (46.6%). Retention times: GC, 20.0 min; HPLC, 29 min.

5-Hydroxy-5-allyl-6-decanone (27a). ^{1}H NMR (CDCl$_3$), δ: 5.62–5.76 (m, 1 H), 5.078 (d, J = 16.5 Hz) and 5.068 (d, J = 10.8 Hz) (2 H), 3.80–4.00 (broad, 1 H), 2.38–2.52 (m, 4 H), 1.702 (dd, J = 8.7, 7.8 Hz) and 1.577 (quintet, J = 7.5 Hz) (4 H), 1.30–1.50 (m, 6 H), 0.896 (dt, J = 12.6, 7.2 Hz, 6 H). ^{13}C NMR (CDCl$_3$), δ: 213.758, 132,482, 118.376, 81.361, 43.506, 38.329, 36.129, 35.819, 25.452, 22.952, 22.418, 13.886. IR (CDCl$_3$), cm^{-1}: 3400–3600 (br, m), 2950 (s), 2930 (s), 2860 (s), 1700 (s), 1635 (m). MS, *m*/*e*: 213 (0.2%), 171 (10.0%), 127 (18.1%), 86 (5.7%), 85 (100%), 57 (32.2%), 55 (4.8%), 43 (4.7%), 41 (13.5%).

Acknowledgment. We wish to thank the Research Corp. and the National Science Foundation (Grant CHE-8603898) for financial support of this work. In addition, we wish to thank the University Research Council of the University of Cincinnati for a summer fellowship to J.L.S. and Elaine Cudmore for the typing and drawings in this manuscript. The NMR spectrometer used in this study was purchased with the aid of an NSF instrumentation grant (CHE-8102974).

Contribution from the Departments of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW, U.K., and University of Reading, Whiteknights, Reading RG6 2AD, U.K.

Preparation and Spectral Properties of a Series of Bis(phosphite) Alkyne Complexes and X-ray Crystal Structure of $[\mathrm{WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)}]$

Paul K. Baker,*,[†] Elaine M. Armstrong,[†] and Michael G. B. Drew*,[‡]

Received April 12, 1988

The complexes $[\mathrm{WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2}]$ (R = Me, Ph) react with 2 equiv of $\mathrm{P(OR')_3}$ (R′ = Me, Et, ^{i}Pr, ^{n}Bu) in CH$_2$Cl$_2$ at room temperature to give the four-electron alkyne compounds $[\mathrm{WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}RC_2R)}]$ (**1**–**8**) via displacement of acetonitrile and an alkyne ligand, respectively. X-ray single-crystal crystallographic studies were carried out on the complex $[\mathrm{WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)}]$ (**1**). Crystals of **1** are orthorhombic, space group *Pnab*, in a unit cell of dimensions a = 14.214 (12), b = 15.332 (12), and c = 20.350 (25) Å. The structure was refined to R = 0.062 for 2164 reflections with $I > 3\sigma(I)$. The coordination geometry around tungsten in **1** may be considered in terms of a pseudooctahedral structure. The complex has cis-iodide ligands, which are trans to a P(OMe)$_3$ and a but-2-yne ligand. The other two sites are occupied by carbonyl and P(OMe)$_3$ ligands. ^{31}P NMR studies are interpreted in order to suggest the geometry of complexes **1**–**8** in solution. The barrier to but-2-yne rotation of **1** is 55.3 kJ mol^{-1}. ^{13}C NMR chemical shifts of the alkyne contact carbons above 200 ppm in these complexes indicate that the alkyne ligand is acting as a four-electron donor in these compounds.

Introduction

Alkyne complexes of molybdenum and tungsten have become increasingly important in recent years, mainly due to their ability to act as two- and four-electron donors in a variety of complexes.[1] Molybdenum(II) and tungsten(II) alkyne complexes containing cyclopentadienyl or indenyl[2] and dithiocarbamates[3] as attached

---

[†] University College of North Wales.

[‡] University of Reading.

(1) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466. Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

0020-1669/89/1328-2406$01.50/0