84°[10] but **10** gave a mixture melting point with this substance of 64–68°.

The methyl ester was prepared by treatment of **10** with diazomethane. This in turn was converted to the diphenylcarbinol **11** and dehydrated with *p*-toluenesulfonic acid in benzene to yield 6-diphenylmethylenebicyclo[3.2.1]octane (**12**), mp 105–106°, in 100% yield. Cleavage of **12** with RuO_2–$NaIO_4$ in carbon tetrachloride yielded bicyclo[3.2.1]octan-6-one (**13**) in 40% yield, mp 153–155°, semicarbazone 180–182° (lit.[4] 150–153°), semicarbazone 190–192° (lit.[5] 155–157°), semicarbazone 187–190° (lit.[6] 155–157°), ir (CCl_4) 1745 cm^{-1} (lit.[7] 1745 cm^{-1}), ir ($CHCl_3$) 1725 cm^{-1} (lit.[5] 1726 cm^{-1}), mass spectrum: *m/e* 124, 81, 80, 67, 54, 41 (lit.[7] *m/e* 124, 81, 80, 67, 54, 41). An authentic sample[11] showed the same tlc (10% ether–pentane on silica gel), glc retention time (15% SE-30°, 80°) and ir spectrum as **13**.

These data alone do not rule out **14** as a possible structure; however, ester **8** was found to incorporate four atoms of deuterium.[12] The ketonic carbonyl of ester **8** occurs at 1710 cm^{-1} which is the same frequency as that reported for bicyclo[3.2.1]octan-3-one.[13] The mechanism of the acid-catalyzed lactonization will be discussed in the full paper.[14]

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(10) K. D. Gundermann and H. Schulze, *Chem. Ber.*, **94**, 3254 (1961).

(11) We thank Professor H. Goering, University of Wisconsin, Madison, for kindly providing a sample of **13**.

(12) The M + 4 peak at *m/e* 186 of deuterated **8** has intensity 48% of the base peak occurring at *m/e* 98. The parent molecular ion of **8** itself is at *m/e* 182 (44% of the base peak at *m/e* 96). Under the conditions used (CH_3OD, and a catalytic amount of $NaOCH_3$ at room temperature for 24 hr) the proton bond to the carbon bearing the carbomethoxy group does not exchange, as indicated in the nmr by no change in the methyl resonance at δ 3.7.

(13) W. R. Moore, W. R. Moser, and J. E. La Prade, *J. Org. Chem.* **28**, 2200 (1963).

(14) Acid-catalyzed cyclization of *exo*- or *endo*-2-methylbicyclo-[2.2.2]oct-5-ene-2-carboxylic acid yielded a γ-lactone, mp 131–132° (lit.[1] 131–132°), ir (γ-lactone C=O) 1770 cm^{-1} and a δ-lactone, mp 128–129° (lit.[1] 123–123°), ir (δ-lactone C=O) 1735 cm^{-1}. Raney-nickel reduction of 5-*exo*-iodo-6-*endo*-hydroxy-2-*exo*-methylbicyclo[2.2.2]octane-2-*endo*-carboxylic acid γ-lactone yielded the γ-lactone mp 131–132°. A complete chemical degradation of the δ-lactone was not carried out but the keto acid (RuO_2–HIO_4–NaOH) showed a carbonyl stretching frequency at 1730 cm^{-1} (six-membered ketone.) By analogy with results in the present system it appears likely that the above δ-lactone possesses the [3.2.1]octyl structure.

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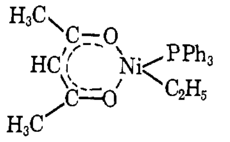
Preparation and Properties of a Nonrigid Ethyl Nickel Complex, $NiC_2H_5(acac)(PPh_3)$, and Its Methyl Analog, $NiCH_3(acac)(PPh_3)_2$

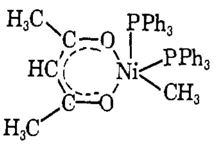
Sir:

Processes involving an olefin insertion into a metal–hydrogen bond and a reverse β-hydrogen elimination from the transition metal alkyl have been widely assumed as a mechanism explaining the hydrogen exchange and isomerization reactions of olefins catalyzed by transition metals and their compounds.[1] However, the examples of appropriate model compounds which show the interconversion are quite limited.[2–4] We wish to report here the syntheses and properties of ethyl(acetylacetonato)(triphenylphosphine)-nickel(II), $NiEt(acac)(PPh_3)$ (**1**), whose nmr shows the rapid hydrogen interchange in the ethyl group and of a related methyl complex, methyl(acetylacetonato)-bis(triphenylphosphine)nickel(II), $NiCH_3(acac)(PPh_3)_2$ (**2**).

These nickel complexes with alkyl, acetylacetonato, and triphenylphosphine ligands[5,6] have been isolated as intermediates in the alkylation reactions of nickel acetylacetonate in the presence of triphenylphosphine to give unstable dialkyl nickel complexes and their dealkylated zerovalent nickel complexes.[7,8] **1** and **2** have been obtained as yellow crystals in good yields by the reactions of nickel acetylacetonate with dimethyl- and diethylaluminum monoethoxide in the presence of triphenylphosphine in toluene below −30° for 40 hr. The complexes can be recrystallized from toluene, benzene, acetone or ether. *Anal.* Calcd for **1**: C, 66.9; H, 6.0; mol wt, 449. Found: C, 66.9; H, 6.1; mol wt (cryoscopic in benzene), 450. Calcd for **2**: C, 72.3; H, 5.8. Found: C, 72.5; H, 6.0.



1



2

The ir spectra of **1** and **2** indicate the presence of the alkyl, acetylacetonato, and triphenylphosphine ligands. Acid hydrolysis of the methyl and ethyl complexes gave methane and ethane quantitatively, and deuteriolysis afforded CH_3D and C_2H_5D, respectively. Thermolysis of **1** (mp 93°) at 100° released ethylene, hydrogen, and a small amount of ethane, whereas from **2** (mp 102–103°) methane and ethane were liberated at 120° in a ratio of 1:2.

The proton and ^{31}P nmr spectra of **1** and **2** in various solvents and at various temperatures reveal complicated fluxional behaviors of these complexes in solutions. Table I summarizes the proton nmr data of the ethyl and methyl complexes. The two methyl groups in the acetylacetonato ligand in **2** are magnetically nonequivalent in benzene whereas they are equivalent in pyridine. The methyl groups of the acetylacetonato ligand in **1** also behave similarly; they are nonequivalent in acetone, benzene, and toluene while equivalent in pyridine at room temperature and nonequivalent

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(4) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

(5) Jolly, *et al.*,[6] have recently isolated the similar complexes with tricyclohexylphosphine ligand, $NiCH_3(acac)[P(C_6H_{11})_3]$ and $NiC_2H_5(acac)[P(C_6H_{11})_3]$, without mentioning the fluxional behavior of the ethyl complex.

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Table I. Nmr Data of the Methyl and Nickel Complexes[a]

Complex	Solvent	Temp, °C	δ, chemical shifts in ppm[b]		
			CH_3-Ni	CH_3(acac)	CH(acac)
$CH_3Ni(acac)(PPh_3)_2$	Benzene	25	0.09 (3, s)	1.39 (3, s) 1.89 (3, s)	5.30 (1, s)
	Pyridine	25	0.04 (3, s)	1.78 (6, s)	5.40 (1, s)
			CH_3CH_2Ni	CH_3(acac)	CH(acac)
$CH_3CH_2Ni(acac)(PPh_3)$	Acetone-d_6	25	0.18 (5, s)	1.42 (3, s) 1.89 (3, s)	5.37 (1, s)
	Benzene	25	0.77 (5, s)	1.43 (3, s) 1.93 (3, s)	5.30 (1, s)
	Pyridine[c] (220 MHz)	64	0.60 (3, t)[d] 0.89 (2, q)[d]	1.76 (6, s)	5.40 (1, s)
		−36	0.6 (3, br, s) 0.9 (2, br, s)	1.62 (3, br, s) 1.82 (3, br, s)	

[a] Chemical shifts are referenced to internal TMS. When TMS interferes with the sample peaks, an appropriate peak of the known chemical shift relative to TMS was used as the standard. The chemical shift values with an external TMS varied depending on the concentration of the sample. [b] Figures in parentheses mean peak intensity and the multiplicity: s, singlet; t, triplet; q, quartet; br, broad. [c] Peaks due to ethane and the coordinated ethylene which were formed by decomposition of **1** are observed at δ 0.72 and 2.5–2.8, respectively. [d] $J = 7.4$ Hz.

at −36°. The peaks due to the ethyl protons in **1** show striking variation depending on solvent. The ethyl peaks are observed as a singlet in benzene, acetone, toluene, and tetrahydrofuran whereas in more basic solvents such as pyridine and triethylamine they are observed as a multiplet at 100 MHz and as a pair of a triplet and a quartet at 220 MHz. The singlet ethyl peak of **1** in toluene is broadened by lowering the temperature, but neither the splitting of the peak nor the appearance of a hydride peak was observed at −100°. Examination of the ^{31}P nmr spectrum of **1** revealed that the coordinated triphenylphosphine ligand exchanges quite rapidly with the added triphenylphosphine in pyridine even at −40° where the methyl protons in the acetylacetonato ligand are observed as nonequivalent. On the other hand the exchange of the triphenylphosphine ligand in benzene or toluene is much slower. These results suggest that a partial dissociation of the acetylacetonato ligand (bidentate → monodentate) and recoordination may be operative as a mechanism to make the methyl protons of the acetylacetonato ligand equivalent. Lewis bases enhance the ligands dissociation whereas they suppress the proton interchange of the ethyl group bonded to nickel. Although the β elimination is considered as a possible mechanism to explain the rapid interconversion in less basic solvents, the ethylene-coordinated nickel hydride which is assumed as the intermediate may not be present as a separate entity of a measurable lifetime, since no hydride peak was observed and attempts to cause the isomerization of butene-1 with **1** failed.

By enhancing the ligand exchange rate, Lewis bases cause another complication; pyridine (py) causes the disproportionation of **1** as follows

$$2NiC_2H_5(acac)(PPh_3) + 2py \longrightarrow Ni(acac)_2 \cdot 2py + (PPh_3)_2Ni(C_2H_4) + C_2H_6 \quad (1)$$

$Ni(acac)_2 \cdot 2py$ was isolated and identified after leaving the pyridine solution of **1** at room temperature for 2 weeks or after heating the solution at 70° for 2 hr. The presence of ethane formed by the disproportionation reaction is observed as a singlet peak at δ 0.72 and the peak of the coordinated ethylene, which is present in the equilibrium $(PPh_3)_2NiC_2H_4 \rightleftarrows (PPh_3)_2Ni + C_2H_4$, is observed in the range δ 2.5–2.8.[7,9] Methane is formed by treating **2** in pyridine, and a similar disproportionation of **2** to eq 1 appears to be taking place.

The thermal stability of the present ethyl complex **1** which has an ethyl group having β hydrogens readily abstractable by transition metal is noteworthy in discussing the theory to explain the stability of the transition metal alkyls.[10]

Acknowledgment. The authors are grateful to Professor I. Morishima of Kyoto University for the measurement of the 220-MHz nmr spectrum.

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Nucleic Acid Related Compounds. VII. Conversion of Ribonucleoside 2′,3′-Ortho Esters into Deoxy, Epoxy, and Unsaturated Nucleosides[1,2]

Sir:

We wish to report the conversion of nucleoside 2′,3′-ortho esters into the corresponding 3′-halo-3′-deoxy-*xylo* ester intermediates which are versatile precursors of epoxy, deoxy, and unsaturated nucleosides.[3]

Usual means of access to these modified nucleosides involve prior construction of a suitable carbohydrate derivative followed by coupling with a blocked and/or

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(2) For the previous paper in this series see: M. J. Robins and E. M. Trip, *Biochemistry*, 12, 2179 (1973).

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