Mn–Mn–$(CO)_{eq}$ angles are all acute in contrast to the Mn–Mn–C(ring) angle of 92.2 (1), 92.2 (1)° and of 92.7 (1)°. Final bond lengths for the $Mn_2(CO)_9$ moiety are listed in Table III. The Mn–$(CO)_{ax}$ bond lengths are shorter than the Mn–$(CO)_{eq}$ bond distances; corresponding values for $Mn_2(CO)_{10}$ are 1.811 (3) and 1.856 (7) Å.[24] In a comparison of the structures of **1** and **2**, it appears that the presence of the methyl substituent has little effect, although the methyl group in **2** points toward the second manganese atom, not away from it, as might have been expected on steric grounds. The carbene ring is approximately perpendicular to the Mn–Mn bond direction in **1** but is twisted somewhat further out of this plane in **2**. This configuration may occur to maximize the π back-bonding and may not be a consequence of the cyclic carbene ligands, since it is also observed in *eq*-$[Mn_2(CO)_9(C(OCH_3)Ph)]$.[25] Bond lengths and angles for the Mn-carbene fragments are given in Table IV together with similar values for the Mo-cyclic carbene fragments in $[Cp^*MoI(CO)_2(\overline{CCH_2CH_2CH_2O})]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**5**)[29] and $[CpMoI(CO)_2(\overline{CCH_2CH_2CH_2O})]$ ($Cp = \eta^5\text{-}C_5H_5$) (**6**).[30] The Mn–C(carbene) bond lengths in **1** and **2** of 1.948 (3), 1.952 (3) Å and of 1.948 (3) Å agree with the corresponding distance of 1.950 (5) Å found in the acyclic Fischer-type carbene complex *eq*-$[(CO)_5MnMn(CO)_4(C(OCH_3)Ph)]$,[25] suggesting delocalization of electron density over Mn–C(carbene)–O in all of these complexes.

Thus, the nature of the products from the reactions of $Na[Mn(CO)_5]$ with dibromoalkanes depends on the nature of the dibromoalkane. X-ray crystal structure determinations are underway on the six-membered-ring carbene complexes $[(CO)_5MnMn(CO)_4(\overline{CCH_2CH_2CH_2CH_2O})]$ and $[(CO)_5MnMn(CO)_4(\overline{CCH_2CH_2CH_2CH(CH_3)O})]$.[19]

Acknowledgment. We thank Professor G. E. Jackson for useful discussions, Dr. M. L. Niven for the data collections, and the University of Cape Town and FRD for financial support.

Supplementary Material Available: A listing of mass spectral data for **1**–**4** and listings of fractional atomic coordinates and temperature factors for **1** and **2** (6 pages); listings of observed and calculated structure factors for **1** and **2** (36 pages). Ordering information is given on any current masthead page.

---

[23] Bullock, R. M.; Rappoli, B. J.; Samsal, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261.

[24] Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

[25] Huttner, G.; Regler, D. *Chem. Ber.* **1972**, *105*, 1230.

[26] Guggolz, E.; Layer, K.; Oberdorfer, F.; Ziegler, M. *Z. Naturforsch.* **1985**, *40B*, 77.

[27] Henrick, K.; McPartlin, M.; Iggo, J. A.; Kemball, A. C.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987**, 2669.

[28] Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Rakitin, Yu. V.; Novotovtsev, V. M.; Ellert, O. G.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *214*, 351.

[29] Bailey, N.; Dunn, D. A.; Foxcroft, C. N.; Harrison, G. R.; Winter, M. J.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1988**, 1449.

[30] Bailey, N. A.; Chell, P. L.; Manuel, C. P.; Mukhopadhyay, A.; Rogers, D.; Tabron, H. E.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2397.

Redox Behavior of Nickel Acylate Complexes

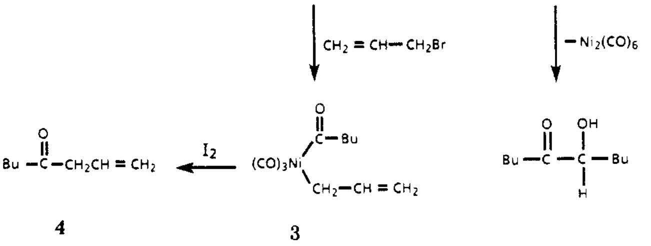
Allan R. Pinhas*,[1a] and James W. Hershberger*,[1b]

Departments of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172,
and Miami University, Oxford, Ohio 45056

Received March 20, 1990

Summary: **The cyclic voltammetry and bulk oxidation with ferrocenium ion and molecular iodine of three nickel complexes were studied. The results are most consistent with both Cp_2Fe^+ and I_2 acting as single-electron oxidants.**

Recently, we have been investigating the reactivity of the monomeric nickel acylate complex **1**, generated from the reaction of butyllithium and nickel tetracarbonyl in tetrahydrofuran, with a variety of acids and electrophiles.[2]



When the acylate complex is treated with water, a mineral acid, or a ketone that has a pK_a less than 17, an acyloin derivative is formed. When acylate complex **1** is treated with allyl bromide, a stable acyl(allyl)nickel complex, **3**, is formed. This complex converts to a ketone upon oxidation with iodine (I_2).[3,4]

In addition, the I_2 oxidation of nickel acylate complex **1** itself has been investigated.[2] This reaction generates a variety of acyl coupling products, which appear to be due to radical coupling reactions; however, the exact mechanism of formation of these products is unknown.

---

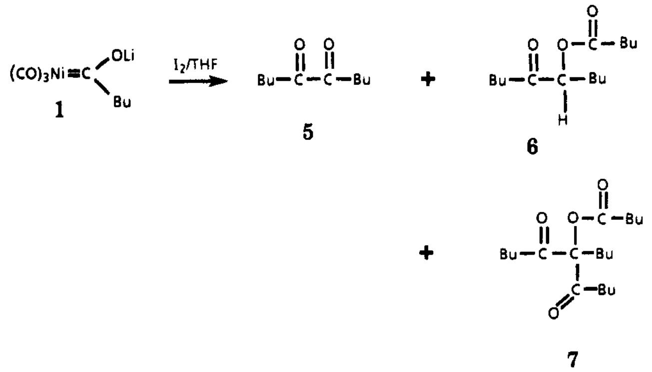
[1] (a) University of Cincinnati. (b) Miami University.

[2] Simunic, J. L.; Pinhas, A. R. *Inorg. Chem.* **1989**, *28*, 2400.

[3] For a variety of examples of oxidation-induced reductive eliminations, see for example: (a) 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; pp 324–333. (b) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547. (c) Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68.

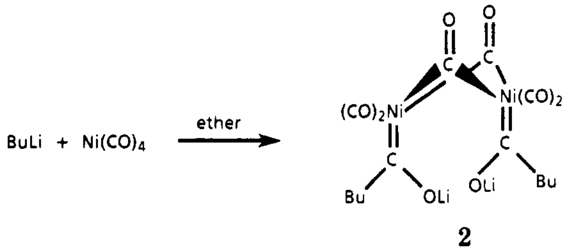
[4] Many oxidation-induced reductive eliminations of iron complexes have been reported, although the role of the metal-centered radical generally has not been elucidated. See for example: (a) Yamamoto, A.; Morifuji, K.; Ikeda, S.; Saito, T.; Uchida, Y.; Misono, A. *J. Am. Chem. Soc.* **1968**, *90*, 1878. (b) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *Ibid.* **1986**, *108*, 6328.

0276-7333/90/2309-2840$02.50/0



The mechanism of reaction of transition-metal acyls and alkyls with halogens (X_2) has been an area of active research in the past decade. The electrophilic cleavage of iron complexes of the type $CpFe(CO)_2R$ has received the most attention.[5] For these substrates the final products (RX and $CpFe(CO)_2X$) may arise by initial single-electron transfer from the metal complex to the halogen or by a two-electron process. The reaction of iodine with aqueous alkylcobalamin to give R–I and oxidized cobalt appears to proceed by an initial single-electron transfer.[6,7]

The role of the iodine oxidation in the foregoing nickel reactions is intriguing, in that none of the products contain a halogen. To our knowledge, the mechanism of halogenolysis of metal acylate complexes has not been studied previously. In this note, we take a closer look at the redox behavior of the nickel acylate complex generated in THF, **1**, and the proposed dimeric acylate complex generated in diethyl ether, **2**,[8,9] as well as the neutral nickel complex **3**.



2

Specifically, we wanted to test the hypothesis that iodine is a one-electron oxidant and that the organic products of iodinolysis arise from a labile 17-electron complex. This study was done by using cyclic voltammetry to evaluate the energetics of the redox processes and by using ferrocenium ion (Cp_2Fe^+) as a bulk oxidant for comparison with the I_2 oxidations.

Results

Cyclic Voltammetry. The cyclic voltammetry of the nickel complexes was performed in THF under rigorously maintained air- and water-free conditions. In each case, a satisfactory response was obtained with a Pt-disk working electrode when the concentration of the nickel complex was less than 10^{-3} M. 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. It is interesting to note that the passivated working electrode *did* respond almost normally to ferrocene or decamethylferrocene.

Table I. Cyclic Voltammetry Data[a]

	E_p^{ox}, V	E_p^{red}, V	$E°'$, V
1	−0.62		
2	−0.49		
3	0.52		
Cp_2Fe[b]	0.352	0.267	0.310
Cp^*_2Fe	−0.078	−0.152	−0.12
I_2	0.49	0.34	0.42

[a] Conditions: solvent, THF/0.15 M tetrabutylammonium perchlorate; scan rate, 100 mV/s; working electrode, Pt; reference electrode, saturated NaCl-SCE. [b] The value of $E°'$ for the Cp_2Fe/Cp_2Fe^+ couple is taken to be 0.31 V.[11]

Acylate complex **1** and acylate complex **2** exhibit well-defined irreversible oxidation processes at −0.62 and −0.49 V, respectively (Table I). The neutral acyl(allyl)nickel complex **3** exhibits an irreversible oxidation process at +0.52 V (Table I). The results in Table I are for a scan rate of 100 mV/s; however, the values of the peak potentials are nearly constant at scan rates ranging from 50 to 200 mV/s. The difference of about 1 V between the oxidation potentials of the anionic complexes and that of the neutral species is consistent with the difference in ionic charge. 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.

The nickel complexes all exhibit a single, broad, cathodic wave at about −1.5 V. This apparently corresponds to the reduction of Li^+ present as the counterion for complexes **1** and **2** or as LiBr, which is a side product in the synthesis of complex **3**. (In a control experiment $LiClO_4$ has a broad cathodic wave at −1.64 V.)

In a THF solution, I_2 exhibits a reduction process at +0.34 V, corresponding to reduction of I_2 to I_3^-, and an oxidation process on the return scan at +0.49 V, corresponding to the oxidation of I_3^- back to I_2.[10]

The values of the peak potentials were ascertained by their positions relative to the Cp_2Fe/Cp_2Fe^+ redox couple or, when more convenient, the decamethylferrocene/decamethylferrocenium ($Cp^*_2Fe/Cp^*_2Fe^+$) redox couple. A typical protocol involved addition of Cp_2Fe or Cp^*_2Fe to the analyte after the measurement of the nickel complex was complete, in order to scale the voltage axis with a scan of the reference complex. This procedure guarded against errors arising from variations in the response of the reference electrode, which was rendered somewhat unreliable by variable junction potentials. Cp_2Fe/Cp_2Fe^+ is taken as having $E°' = +0.31$ V,[11] and thus, $Cp^*_2Fe/Cp^*_2Fe^+$ is fixed at $E°' = -0.12$ V.

As discussed earlier, at concentrations of nickel complex above 10^{-3} M, the Pt electrode was passivated toward the complex but responded to the ferrocene or decamethylferrocene. Under these conditions, the oxidation wave of the iron complex was enhanced and displaced toward

---

[5] (a) Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521. (b) Dong, D.; Slack, D. A.; Baird, M. C. *Ibid.* **1979**, *18*, 188. (c) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539. (d) Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33. (e) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57. (f) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619. (g) De Luca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359. (h) Moss, J. R.; Scott, L. G. *Ibid.* **1989**, *363*, 351.

[6] Fanchiang, Y.-T. *Organometallics* **1985**, *4*, 1515.

[7] For a recent review of the chemistry of 17-electron metal complexes see: Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

[8] Simunic, J. L. Ph.D. Thesis, University of Cincinnati, 1987.

[9] Sawa, Y.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 4183.

[10] For a discussion of the complex equilibria arising from the reduction of molecular iodine see: Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 45.

[11] Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

Table II. Product Yields (%) from the Oxidation of Acylate Complexes 1 and 2

	complex 1		complex 2	
	I_2 oxidn	Cp_2Fe^+ oxidn	I_2 oxidn	Cp_2Fe^+ oxidn
5	22	13	57	63
6	35	66	9	6
7	32	8	2	0

positive voltage; the reduction wave was diminished in size or, at very high nickel complex concentrations, nearly absent. This appears to be a classic example of a "catalytic wave" phenomenon[12] due to regeneration of the electroactive ferrocene from ferrocenium ion by a rapid nonelectrochemical process. The most likely explanation is that Cp_2Fe^+ is being reduced back to Cp_2Fe by a nickel complex.

$$Cp_2Fe \xrightleftharpoons{\text{electrode}} Cp_2Fe^+ \xrightarrow[\text{fast}]{\text{Ni complex}} Cp_2Fe$$

Bulk Oxidation with Cp_2Fe^+. Bulk electrolytic oxidation of the nickel complexes was not practical because of the passivation of the working electrode at high concentrations. However, electrochemically generated ferrocenium ion provided an attractive alternative as a one-electron oxidant. Therefore, $Cp_2Fe^+BF_4^-$ was synthesized and employed as an oxidant of the nickel complexes in a manner similar to the procedure used for the iodine oxidations.[2]

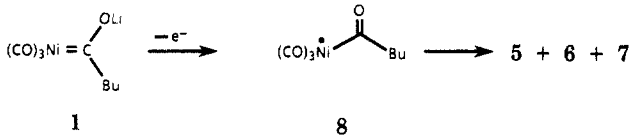
When complex **1** or complex **2** is oxidized by ferrocenium ion, organic products **5**, **6**, and **7** are generated. These are the same products formed from an iodine oxidation, and they are produced in about the same overall yield (Table II). However, the ratio of products, particularly in the case of complex **1**, is quite dependent on the choice of I_2 or Cp_2Fe^+ as the oxidant. The results reported in Table II are the average of multiple runs; no significant change in product yield or distribution was observed for Cp_2Fe^+:Ni ratios varying from 1.2:1.0 to 2.2:1.0. When complex **3** is oxidized with Cp_2Fe^+ or with I_2, the same products (1-octen-4-one (**4**) with a small amount of the conjugated isomer and of an acyloin derivative) in the same yields were obtained. In each of the Cp_2Fe^+ oxidation reactions, the ferrocenium ion was converted to ferrocene and no new organic products were formed as determined by gas chromatography.

Discussion

These results are most simply interpreted in terms of product formation ensuing from initial out-sphere, single-electron oxidation of nickel comlexes **1**, **2**, and **3** by molecular iodine or by ferrocenium ion. The observation of the catalytic wave phenomenon during the cyclic voltammetry of ferrocene in the presence of excess nickel complex and the results of the bulk oxidations of the nickel complexes with ferrocenium ion demonstrate that Cp_2Fe^+ is serving as a simple one-electron oxidant. The striking similarity in product yields and distributions for the bulk oxidations with either iodine or ferrocenium suggests that molecular iodine behaves in a similar fashion. Thus, mechanisms involving any initial metal–halogen or ligand–halogen bonding seem to be eliminated.

Barring a substantial overpotential owing to poor electrode kinetics (and this seems unlikely in view of the small dependence of the peak potentials upon the scan rate[13]), the peak potential for the irreversible oxidation of a nickel complex will be at least an approximate measure of the thermodynamic oxidation potentials. Thus, a hypothetical electron transfer from nickel complex **1** or **2** is energetically favorable by more than 1 V. In contrast, the putative single-electron transfer for complex **3** to iodine is approximately nonergonic.

The organic products **5**, **6**, and **7** from the oxidation of complex **1** probably arise from the reaction of a nickel-centered radical, such as **8**, with other nickel complexes.



1 **8**

The intermediacy of acyl radicals can be discounted because only trace amounts of products from pentanoyl decarbonylation (such as octane) are observed. Furthermore, when iodine is present, trapping of the pentanoyl radical to give the acyl iodide followed by hydrolysis to pentanoic acid would be expected but is not observed. The relative yields of the organic products may be sensitive to the rate of formation of the 17-electron complex **8** as it affects the rate at which the radicals couple to give the different products. The rate of oxidation of **1** by I_2, a completely homogeneous reaction, is certainly more repid than the oxidation of **1** by Cp_2Fe^+, which is partially heterogeneous, owing to the limited solubility of Cp_2Fe^+ in THF.

For acylate complex **2**, the major product of the oxidation is diketone **5** and the yields with the two oxidants are quite similar. Thus, the dimeric structure of **2** influences the course of the reaction. This seems to indicate that the reaction proceeds by a unimolecular pathway with a small bimolecular component.

For the acyl(allyl)nickel complex **3**, product formation probably proceeds by a reductive elimination of the allyl ketone from a nickel(III) complex. There is evidence that bis(aryl)nickel(III) complexes readily reductively eliminate biaryl, and there are many other cases of oxidation inducing a reductive elimination.[3,4] As with complex **2**, this reductive-elimination reaction is unimolecular, and the two single-electron oxidants generate the exact same ratio of products.

Conclusion

We have shown that the iodinolyses of complexes **1**, **2**, and **3** proceed by an initial one-electron oxidation to afford a labile 17-electron nickel complex. This is the first mechanistic study of the halogenolysis of metal acylate complexes. These results provide insight into the halogenolysis reactions of other, easily oxidized, organometallic complexes.

Experimental Section

General Considerations. The synthesis of the nickel acylate complex in THF, the synthesis of the acyl(allyl)nickel complex, the spectroscopic data, and the chromatographic conditions have been reported previously.[2] The nickel acylate complex in ether was synthesized exactly like that in THF except diethyl ether was used as the solvent and the solution of the anion was stirred for 23 h.[8] The ether then was removed from this anion by a strong flow of argon and the remaining solid dissolved in THF. All subsequent experiments with complexes **1**, **2**, and **3** were performed in THF solutions. Tetrahydrofuran was freshly distilled from benzophenone ketyl. Anhydrous acetonitrile was used as received from Aldrich. Tetrabutylammonium perchlorate, employed as the electrolyte for the cyclic voltammetry, was dried at 60 °C/0.1 Torr for 12 h prior to use. Tetrabutylammonium tetrafluoroborate was used as received from Aldrich. Ferrocene

---

[12] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

[13] For a detailed discussion of the application of cyclic voltammetry to irreversible electrochemical processes see: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790.

and decamethylferrocene were purchased from Aldrich and Strem, respectively, and were used without further purification.

Cyclic Voltammetry. Cyclic voltammetry was performed with a BAS-100 electrochemical analyzer employing a Pt-disk working electrode and, in the same compartment, a Pt-wire counter electrode. The solvent was THF with 0.15 M tetrabutylammonium perchlorate. The reference electrode (saturated NaCl–SCE) was immersed in a reservoir of solvent and electrolyte that 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 the iR drop error inherent in a low-conductivity nonaqueous medium. Low substrate concentrations were required to minimize fouling of the working electrode. All peak potentials are reported relative to ferrocene (the Cp_2Fe/Cp_2Fe^+ couple is taken to have $E^{\circ\prime}$ equal to +0.31 V).[11]

Preparation of $Cp_2Fe^+BF_4^-$. Preparative electrochemistry was performed with a Princeton Applied Research Model 173 potentiostat equipped with a PAR model 179 digital coulometer. The cell was a three-compartment design with a low-porosity frit separating the working solution from the counter electrode compartment. The working electrode was Pt mesh, the counter electrode was nichrome wire, and the reference was saturated NaCl–SCE. An argon atmosphere was maintained over the working solution.

In a typical experiment, 1.0 mmol of ferrocene (0.19 g) in 35 mL of acetonitrile/0.2 M tetrabutylammonium tetrafluoroborate was oxidized until 48.0 C had passed to afford, in theory, 0.50 mmol of ferrocenium tetrafluoroborate. The acetonitrile was removed in vacuo at room temperature to leave a mixture containing $Cp_2Fe^+BF_4^-$, unoxidized ferrocene, and $Bu_4N^+BF^-$.

The integrity of the ferrocenium salt was verified by dissolving the $Cp_2Fe^+BF_4^-/Cp_2Fe/Bu_4N^+BF_4^-$ mixture in 35 mL of acetonitrile and reducing the solution at 0.00 V vs NaCl–SCE until the current ceased to flow. In each of three trials, more than 90% of the calculated charge passed, indicating that most of the expected ferrocenium ion had been present.

Bulk Oxidations with Cp_2Fe^+. To the solid mixture of ferrocenium tetrafluoroborate, ferrocene, and electrolyte salt was added 4 mL of THF, and the solution was stirred under an argon atmosphere until most of the solids had dissolved. Then 1 mL of a THF solution containing the metal complex (0.25 M based on nickel) was added dropwise at room temperature. This solution was stirred for 15 min before being quenched with 2 mL of water. The organic layer and the water layer were then separated, and the organic layer was analyzed for products. For the oxidation of the two acylate complexes, products and yields are given in Table II. For the I_2 oxidation of the acyl(allyl)nickel complex **3**, the yields are as follows: 1-octen-4-one (**4**), 81%; 2-octen-4-one, 8%; 5-hydroxy-5-allyl-6-decanone, 11%. For the Cp_2Fe^+ oxidation of the acyl(allyl)nickel complex **3**, the yields are as follows: 1-octen-4-one (**4**), 80%; 2-octen-4-one, 7%; 5-hydroxy-5-allyl-6-decanone, 13%.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. CHE-8603898 to A.R.P.) for financial support of this work and the donors of the Petroleum Research Fund, administered by the American Chemical Society (to J.W.H.), and the Research Corp. (to J.W.H.) for the purchase of the electrochemical instrumentation. We also thank Ms. Elaine Cudmore for the drawings and typing in this paper.

Note Added in Proof. After this manuscript was accepted, a paper appeared (Mitsudo, T.; Ishihara, A.; Suzuki, T.; Watanabe, Y. *Organometallics* **1990**, *9*, 1357) which showed that the reaction between I_2 and the corresponding iron acylate complex generates an anionic acyldiiodotricarbonyliron complex.

Structure of a Trinuclear Zr_2Al μ-Ketone Complex with a Bridging Trigonal-Bipyramidal Methyl Group[†]

Robert W. Waymouth, Kristine S. Potter, William P. Schaefer, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, 164-30, California Institute of Technology, Pasadena, California 91125

Received January 23, 1990

Summary: The reaction of a zirconocene acyl chloride with 0.5 equiv of trimethylaluminum results in the formation of the trinuclear Zr_2Al complex $[Cp_2Zr(\eta^2(C,O)\text{-}OC(CH_3)_2]_2(\mu\text{-}AlMe_2)(\mu\text{-}Me)$, which contains a trigonal-bipyramidal bridging methyl group. The complex crystallizes in the monoclinic system, in space group $P2_1/n$ (C^5_{2h}, No. 14), with a = 10.574 (1) Å, b = 16.456 (2) Å, c = 16.763 (2) Å, β = 103.71 (1)°, V = 2833.6 (9) Å^3, and Z = 4. This is one of the few structures that contains a bridging methyl group with a near-trigonal-bipyramidal structure in which the metals occupy the axial positions and the three hydrogen atoms are in the equatorial plane.

Bridging ligands serve as structural models for intermediates in ligand-transfer processes.[1] The structural features of such ligands are useful in interpreting the stereochemistry of related transmetalation reactions. We recently reported the structure of a complex that contained a novel trigonal-bipyramidal methyl group bridging two zirconium centers.[2] This structure, the first example of this type of coordination between transition-metal centers, is of considerable interest as a model for transmetalation reactions that proceed with inversion of configuration.[3] Since our initial report, several other structures of complexes exhibiting a linear methyl bridge have been published.[4] In only one of these cases were the hydrogens of

---

[†] Contribution No. 8060.

[1] Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. *Chem. Rev.* **1983**, *83*, 135.

[2] (a) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427. (b) Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050.

[3] A number of SE_2 reactions have been observed to proceed with inversion of stereochemistry at the carbon center: Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177.

[4] (a) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423. (b) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853. (c) Busch, M. A.; Harlow, R.; Watson, P. L. *Inorg. Chim. Acta* **1987**, *140*, 15. (d) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (e) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1989**, 369. (f) Stults, S. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1989**, *111*, 4507.

0276-7333/90/2309-2843$02.50/0