Room temperature controlled potential electrolysis measurements at a platinum basket resulted in a change from green to yellow and consumption of one-electron (n = 0.95 e^-). Voltammograms taken immediately after electrolysis showed mainly the reversible couple for $CpNiCod^{0/+}$ at –0.46 V, but a small reverisible wave was also present at –0.02 V, together with another minor wave (irreversible) at +1.04 V. As time went on, the wave due to CpNiCod diminished and the others grew in. By matching these waves with potentials measured independently for the pure compounds, we have identified the wave at –0.02 V as arising from the oxidation of nickelocene and the wave at +1.04 V as being due to bis(cyclooctadiene)nickel. Therefore, there is good evidence that the ultimate fate of the 19-electron radical is disproportionation into compounds containing metals with 20 valence electrons (Cp_2Ni) and 18 valence electrons (Cod_2Ni) (Scheme II). The reaction appears to be quantitative.

Electrolysis at subambient temperatures slowed down the disproportionation reaction and allowed production of stable solutions of the radical. Thus, electrolysis at –10 °C in CH_2Cl_2 gave only the wave for the neutral radical. By voltammetry at the rotating platinum electrode it was shown that the original reduction wave at –0.46 V had been quantitatively replaced by an oxidation wave at the identical potential. Solutions at this temperature were stable for at least 1 h after electrolysis before any wave for Cp_2Ni was noticed.

The stability of this radical is noteworthy. It is a very rare example of a neutral π-complex radical containing a nonconjugated polyolefin ligand. Previous examples of stable metal π radicals have been generally restricted to "sandwich"-type compounds like Cp_2Co,[7] $CpFe(C_6R_6)$,[8] $(C_6R_6)_2V$,[9] $CpV(C_7H_7)$,[10] $CpCr(C_6H_6)$,[11] and $CpTi(\eta^8$-cyclooctatetraene).[12] The present example suggests that metal–olefin compounds without extensively delocalized orbitals may in certain cases be isolable in free radical form.

Electronic Structure of the Radical. CpNiCod is also of interest because it is isoelectronic with $CpCoCod^-$, in which the cyclooctadiene ligand prefers the 1,3-diene mode of coordination.[1] Electron spin resonance measurements and molecular orbital calculations agree that the half-occupied orbital in the cobalt anion is predominantly metal in character.[13] Because ^{61}Ni is present in low natural abundance (1.2%), no hyperfine splitting is observed from ESR spectra of solutions of CpNiCod, but frozen solution spectra in dichloromethane (163 K) are indicative that, qualitatively, reduction of the cation has again involved a metal-based orbital. An axially symmetric **g** tensor was observed, with $g_{\parallel}$ = 2.182 and $g_{\perp}$ = 2.025. The fact that the unique g value is at low-field is consistent with findings for other d^9 metal π complexes[13,14] and inconsistent with a ligand-based orbital (because of large g value anisotropy) or a d^7 metal configuration. The latter is ruled out because in that case, the unique g value is expected to be the high-field component.[8] Thus, the ESR is consistent with CpNiCod being a formal Ni(I), with appreciable spin density on the metal.

Bonding Mode of the Cod Ligand. In spite of the isoelectronic nature of $CpCoCod^-$ and CpNiCod, the cyclooctadiene ligand prefers the nonconjugated (1,5-diene) mode of coordination in the nickel complex. The electrochemical data clearly supports this conclusion, since changes in the ligand coordination mode would give an electrolysis product with a different $E°$ potential. In the analogous CpCo(diene) complexes, the differences in reduction potentials varied from ca. 200 mV (diene = cyclooctatetraene) to almost 1 V (diene = Cod) when alterations from 1,5 to 1,3 bonding occurred.[1]

The question arises as to why the ligand isomerizes from the nonconjugated to the conjugated form in the cobalt anion but remains as the 1,5 diene in the nickel complex. The obvious difference between the two isoelectronic compounds is the negative charge on the cobalt species, suggesting that delocalization of the excess charge into the Cod ring in $CpCoCod^-$ may be an important factor in dictating the isomerization of the polyolefin ligand to the conjugated isomer.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant CHE80-04242).

Registry No. $CpNiCod^+ PF_6^-$, 42088-01-7; CpNiCod, 80010-11-3.

(6) ΔE_p values of ca. 70 mV were found for 5×10^{-4} M $CpNiCod^+$ in CH_2Cl_2/0.1 M Bu_4NPF_6, virtually identical with those of ferrocene under identical experimental conditions. The increase from the theoretical value of 60 mV is undoubtedly due to uncompensated iR loss common to these weakly polar nonaqueous electrolytes.

(7) Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 209.
(8) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.
(9) Henrici-Olive, G.; Olive, S. *Z. Phys. Chem. (Wiesbaden)* **1967**, *56*, 223 and references therein.
(10) Engelbretson, G.; Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 481.
(11) Evans, S.; Green, J. C.; Jackson, S. E. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 249 and references therein.
(12) Van Oven, H. O.; de Leifde Meijer, H. J. *J. Organomet. Chem.* **1969**, *19*, 373.
(13) Albright, T. A.; Geiger, W. E.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* **1981**, *103*, 4787.
(14) Van Willigen, H.; Geiger, W. E.; Rausch, M. D. *Inorg. Chem.* **1977**, *16*, 581.

(15) Notes Added in Proof: Dr. Ulrich Koelle and co-workers have recently prepared the title compound (*J. Organomet. Chem.*, in press). We thank Dr. Koelle for informing us of this prior to publication of his data. A series of related $CpNiL_2$ compounds (L = phosphines or other Lewis bases) has also been reported recently by Barefield and co-workers (*J. Am. Chem. Soc.*, **1981**, *103*, 6219).

Umpolung with Rhodium Iminoacyls. The Use of Metal Oxidation State To Control the Nucleophilicity or Electrophilicity of Acyl Carbons

J. William Suggs* and Sherman D. Cox
Bell Laboratories
Murry Hill, New Jersey 07974

Received September 28, 1981

Summary: Rhodium(III) iminoacyl hydrides are reduced with dimethylcadmium to give rhodium(I) iminoacyl compounds. These show acyl anion-like reactivity. The same functional group can exhibit acyl anion or acyl cation reactivity depending upon the oxidation state of the attached transition metal.

Hydroacylation, the addition of an aldehyde's C–H bond across an olefin to give a ketone, can be achieved with stable acylrhodium(III) hydrides, or their derivatives, (iminoacyl)rhodium(III) hydrides, and unhindered olefins.[1] However, this methodology cannot be used to append several classes of carbon groups to aldehydes. Methyl groups cannot be appended, since this requires insertion of methylene between the aldehyde C–H bond. Similarly,

*To whom correspondence should be addressed at the Department of Chemistry, Brown University, Providence, Rhode Island 02912.

(1) Suggs, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 489.

0276-7333/82/2301-0402$01.25/0 © 1982 American Chemical Society

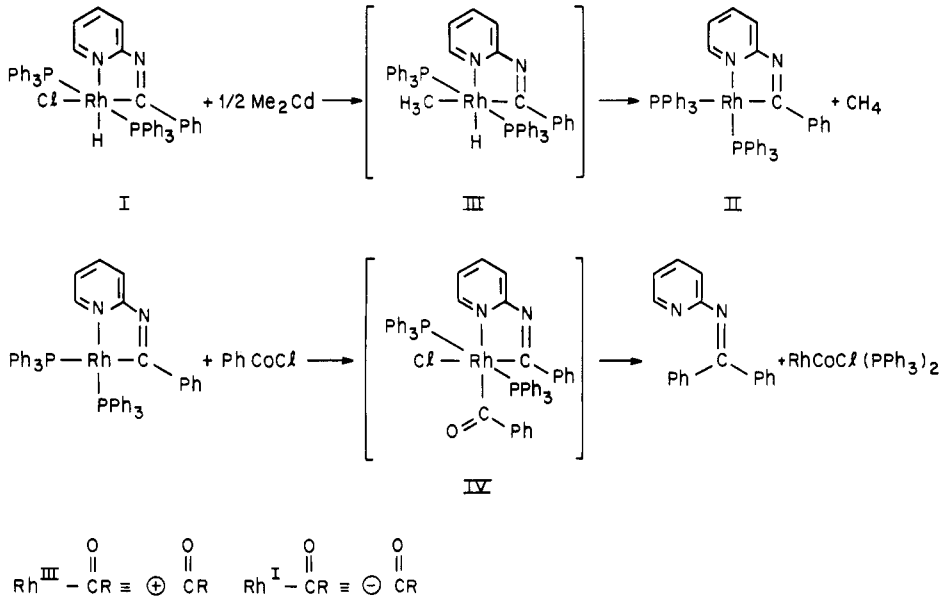

Figure 1. Formation and reaction of the rhodium(I) iminoacyl.

phenyl groups cannot be added, since this corresponds to addition of benzyne. We have developed a way to overcome this limitation which, although stoichiometric in rhodium, does permit efficient recovery of the metal. This new method also illustrates the use of a metal's oxidation state to switch reactivity of a bound acyl derivative between nucleophilicity and electrophilicity.

When a solution of the (iminoacyl)rhodium(III) hydride I is dissolved in a 1:1 mixture of CH_2Cl_2 and THF at −20 °C (0.05 M solution) under argon and a solution of $(CH_3)_2Cd$ in THF (0.5 equiv) added dropwise over 10 min, the initial yellow color is replaced over 15 min by a deep red color, characteristic of Rh(I). Methane is evolved as detected by mass spectrometry, corresponding to 0.75 equiv/mol of rhodium, and the hydride resonance at δ −11.1 disappears. Apparently, chloride–methyl exchange occurs, followed by reductive elimination of methane (expected to be fast) to give the (iminoacyl)rhodium(I) compound II.[2] Although we have not been able to isolate II in crystalline form, ^{31}P NMR spectroscopy (as well as the chemical reactions described below) provides strong evidence for its formation.[3] The ^{31}P resonance of I at δ −32.5 (J_{Rh-P} = 117 Hz) is cleanly replaced with two doublets of doublets at δ −42.2 and −38.8 (downfield from 85% H_3PO_4), with J_{P-P} = 32.6 Hz and J_{Rh-P} = 144 Hz for both phosphines.[4]

The iminoacyl group of II could be alkylated by addition of CH_3I or $C_6H_5CH_2Br$ and heating the solution at reflux for 30 min. Bubbling CO through the warm solution and addition of ether precipitates the rhodium as $RhCOCl(PPh_3)_2$, with greater than 90% recovery of the metal. The ketimine, which remains in solution, can be hydrolyzed over wet silica gel, and thin-layer chromatography gives acetophenone and desoxybenzoin, respectively, in 70–80% yield. No ketone formation occurs if the dimethylcadmium reduction step is omitted.

Of the two products (diketone or monoketone), which could arise from II and benzoyl chloride, only one is formed. Although oxidative addition apparently forms the bisacyl IV, the two acyl carbons do not couple to give (after hydrolysis) any 1,2 diketone. Instead decarbonylation intervenes, followed by reductive elimination to give benzophenone (72% yield after hydrolysis and chromatography).[5] In this case, the rhodium can be recovered as $RhCOCl(PPh_3)_2$ without adding additional CO. Reaction of II with secondary bromides or branched acid chlorides gives no branched ketones. Instead, the intermediate *sec*-alkylrhodium(III) iminoacyl compounds undergo β elimination rather than coupling. This is consistent with the observation that I catalyzes olefin isomerization in internal olefins but gives no branched ketone products.

Several other rhodium-based procedures for ketone synthesis are presently in the literature.[8] Each may be useful for preparing small amounts of valuable ketones under mild conditions. The most useful feature of this work is, however, the illustration of how changes in a metal's oxidation state can be used to switch the reactivity of its ligands between two states. In the sense complex I, with the iminoacyl group bound to rhodium in the metal's higher oxidation state, reacts with olefins to give ketones, the masked acyl has the reactivity of an acyl cation.[9] With the iminoacyl bound to rhodium in a lower oxidation state, the reactivity pattern is that of an acyl anion.[10] Thus the same functional group can exhibit opposite reactivities, controlled by the charge density of the metal to which it is bound.

Registry No. I, 80399-45-7; II, 80409-35-4; $(CH_3)_2Cd$, 506-82-1; CH_3I, 71-88-4; $C_6H_5CH_2Br$, 100-39-0; $RhCOCl(PPh_3)_2$, 13938-94-8.

(2) Dimethylcadmium was chosen since it is a mild alkylating agent and will not attack the carbon–nitrogen double bond in I. Even under the above conditions, however, small amounts of methyl ketones are formed by the reaction of II with dimethylcadmium.

(3) Purification of II was apparently hampered by the presence of $CdCl_2$.

(4) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*.

(5) In the hydroacylation procedure of Schwartz and Cannon,[6] an intermediate acylmetal alkyl couples to give a ketone rather than first decarbonylating. Our result may reflect the reluctance of acyl groups to couple[7] as well as perhaps a barrier to reductive elimination due to one of the carbons being constrained by chelation.

(6) Schwartz, J.; Cannon, J. B. *J. Am. Chem. Soc.* **1974**, *96*, 4721.

(7) Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436.

(8) (a) Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190. (b) Hegedus, L. S.; Kendall, P. M.; Lo, S. M.; Sheats, J. R. *Ibid.* **1975**, *97*, 5448. (c) Reference 6.

(9) The mechanism of insertion involves addition of a rhodium hydride to a double bond, followed by carbon–carbon coupling. Since two anionic groups are on the metal, it must be in at least the +2 state.

(10) Acylcarbonylferrates provide an interesting example of a species which reacts with both electrophiles (alkyl halides)[11] and nucleophiles (olefins)[12] without a change in metal oxidation state.

(11) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

(12) McMurry, J. E.; Andrus, A. *Tetrahedron Lett.* **1980**, *21*, 4687.