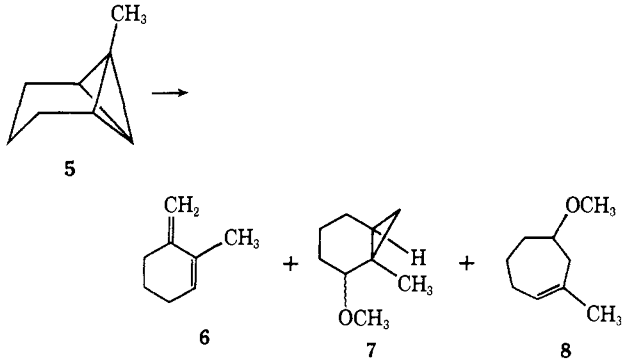
In the presence of sodium bicarbonate, the pH of the solution increases. During this period of pH increase the ability of the complex present in solution to promote the rearrangement of bicyclo[1.1.0]butanes decreases. This is presumably due to the destruction of the active complex by the methanolic sodium bicarbonate.

When 100 μl of **1** was injected into a vigorously stirred solution of 15 mg of rhodium dicarbonyl chloride dimer in 3 ml of dry methanol (containing *no* sodium bicarbonate) an immediate drop in pH from 3.7 to 1.1 was observed.[15] Under these conditions, **1** gave 6% of **4**, 15% of **2**, and 71% of **3**.[16]

When sodium bicarbonate was present, the magnitude of the pH drop was a function of time elapsed between the addition of the rhodium dicarbonyl chloride dimer and the addition of **1**. Rapid injection of 100 μl of **1** *ca.* 50 sec after the addition of the rhodium complex gave a pH drop of 2.8 units, while rapid injection after 3.5 min gave a 2.3-unit drop. This time pH dependence reflected the rate of disapperance of active rhodium complex in methanolic sodium bicarbonate. The rapid addition of **1** within 60 sec after the addition of the rhodium complex gave 15% of **4** and 75% of a 13:87 mixture of **2** and **3**. When 100 μl of **1** was added *dropwise* (neat) to the methanolic sodium bicarbonate solution immediately after the addition of the rhodium complex, only a small decrease in pH was noted for each drop. More importantly, the pH recovered to its original position between each drop. Under these conditions the pH of the solution remained above 5 throughout the period of time required for the isomerization of **1**. This method of dropwise addition resulted in the conversion of **1** into **4** (76% yield) and gave only trace amounts of **2** and **3**. These results clearly show that the formation of **2** and **3** results from an acid-catalyzed process which occurs below pH 5 in methanol, while the formation of **4** is presumably the result of the reaction of **1** with rhodium dicarbonyl chloride dimer or a related species. Thus, these results establish that the formation of **2** and **3** in methanol cannot be used as evidence for the intermediacy of a metal-bonded cyclopropylcarbinyl cation intermediate in the rhodium dicarbonyl chloride dimer promoted conversion of **1** into **4**.[17]

Similar results were obtained with 1-methyltricyclo-$[4.1.0.0^{2,7}]$heptane (**5**). Rapid addition of **5** (neat) to a solution of rhodium dicarbonyl chloride dimer in methanol gave 3% of **6** and 95% of a mixture of the ethers represented by **7** and **8**. Again, pH monitoring showed a large pH drop on addition of **5**. Rapid addition of **5** (neat) to a methanolic solution containing both rhodium dicarbonyl chloride dimer and sodium bicarbonate gave a smaller pH drop, and yielded 22% of **6** and 64% of **7** and **8**. Dropwise addition of **5** (neat), under similar conditions, at a rate sufficient to maintain the pH above 5 gave 61% of **6** and only 3% of **7** and **8**. Thus, pH control, through regulated rate of addition of the bicyclo[1.1.0]butane derivative (**1** or **5**), can provide overwhelming control of the observed products.



Other transition metal complexes were checked to see if they had an acidifying effect in methanol. Rhodium norbornadiene chloride dimer did not produce an acidic solution in methanol, nor did the pH drop on addition of **1**. However, **1** was efficiently isomerized under these conditions to give **4** as the only product. Rhodium dicarbonyl acetylacetonate behaved in a manner similar to rhodium norbornadiene chloride dimer, except that the acetylacetonate complex promoted conversion of **1** to **4** was very slow and small amounts of **2** and **3** could be detected. Palladium chloride, π-allylpalladium chloride dimer, and bis(benzonitrilepalladium) chloride all gave pH profiles similar to rhodium dicarbonyl chloride dimer in methanol. In each case, addition of **1** caused a rapid, substantial decrease in the pH of the methanolic solution.

The major unanswered questions concern the nature of the acidic material which must account for the pH drop and the mechanism whereby **1** (or **5**) reacts with the transition metal complex in methanol to provide the rapid formation of this unidentified acid. The very transitory nature of these strongly acidic conditions indicates that the acidic material must react rapidly or undergo neutralization under the reaction conditions. It is not known at this time whether this acid is a mineral acid (hydrogen chloride) or a much more complex acid such as a metal hydride. We are continuing to investigate this problem.[18]

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[15] A pH of 1.1 was also measured for a dry methanolic solution which was 5.6 × 10^{-4} *M* in hydrogen chloride.

[16] The ratio of **2**:**3** in the *absence* of added sodium bicarbonate was 17:83. The ratio of **2**:**3** obtained from **1** and dry methanolic hydrochloric acid was 15:85.

[17] It should be noted that these experiments merely rule out the use of certain results as evidence. They do not establish whether or not a metal-bonded cyclopropylcarbinyl cation is involved in the conversion of **1** into **4**.

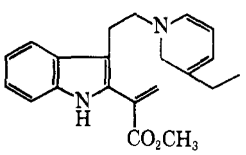
[18] Subsequent to the completion of this study, it was reported that somewhat related behavior can be noted for silver ion [L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Amer. Chem. Soc.*, **94**, 9222 (1972)].

Studies in the Dihydropyridine Series. I. Novel and Stable Complexes of *N*-Methyl-3-ethyl-1,2-dihydropyridine and *N*-Methyl-3-ethyl-1,6-dihydropyridine

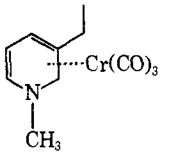
Sir:

Dihydropyridines have been involved as important intermediates in various biological systems. Thus, it is well established that the 1,4-dihydropyridine derivatives play an important role in biological oxidation–reduction reactions involving NADH, and for this as well as other reasons extensive investigations into the chemical and physical properties of this family of compounds have been made.[1] These systems have also been implicated in various areas of plant biosynthesis. For example, numerous investigations in indole alkaloid biosynthesis during recent years[2–7] have revealed the importance of certain dihydropyridines, such as dehydrosecodine (I), in these areas.

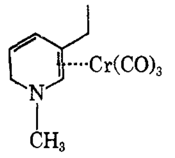
It is well known that electron-withdrawing substituents stabilize the dihydropyridine system, and as the recent review[1] indicates much information is now published on such derivatives. On the other hand, very little data are available on dihydropyridines which lack such substituents although very recent investigations have provided some information in this direction.[8,9] Our own interests demanded that we consider the synthesis of 3-alkyl-substituted dihydropyridines which obviously can exist in the two isomeric 1,2- and 1,6-dihydro forms. It was mandatory that such systems be available in stable form so that they could be subsequently evaluated in biosynthetic studies. We wish to report the preparation of several stable and novel complexes in this series, which, in essence, fulfill our initial objectives.



I



II



III

Metal carbonyls have been applied extensively to the preparation of stable complexes of highly unstable π-electron systems,[10] but it is interesting to note that with the exception of one preliminary report,[11] there are no data on such complexes in which a nitrogen heteroatom is present in the chelating ligand. For our purpose, *N*-methyl-3-ethylpyridinium iodide was reduced *carefully* with sodium borohydride in methanolic sodium hydroxide (helium atmosphere), and the benzene extract containing the mixture of *N*-methyl-3-ethyl-1,2-dihydropyridine (II, without $Cr(CO)_3$) and its corresponding 1,6 isomer (III, without $Cr(CO)_3$) was allowed to react with dry $(CH_3CN)_3Cr(CO)_3$[12] under a helium atmosphere. Careful separation and purification of the resultant product mixture (silica gel column chromatography and tlc) followed by crystallization (benzene–hexane) allowed the isolation of two complexes.

The minor component,[13] mp 97–99°, $\lambda_{max}^{CH_3OH}$ 403 nm, showed three characteristic carbonyl absorptions in the infrared (1830, 1860, and 1942 cm^{-1}), while the nmr spectrum (100 MHz in deuteriobenzene) revealed the following signals: δ 0.7 (CH_3CH_2, t, J = 7 Hz), 1.44 (CH_3N, s), 1.59 (CH_2CH_3, q, J = 7 Hz), 2.4 and 2.24 (C_2H, two doublets, J = 10 Hz), 4.47 (C_4 and C_6H), 4.98 (C_5H, d of d, J = 4.5 and 5.5 Hz). The mass spectrum, apart from a weak molecular ion peak at *m/e* 259, provided fragments which were readily interpreted in terms of a chromium tricarbonyl complex of *N*-methyl-3-ethyldihydropyridine: *m/e* 123 (M − $Cr(CO)_3$), 122 (base peak, $C_8H_{12}N$), 107 (C_7H_9N), 94 (C_6H_8N). In summary, all of the above data provided strong evidence for a 1:1 complex between $Cr(CO)_3$ and *N*-methyl-3-ethyl-1,2-dihydropyridine (II).

The major product from the above reaction, mp 68°, $\lambda_{max}^{CH_3OH}$ 399 nm, also portrayed carbonyl bands in the infrared (1825, 1860, and 1942 cm^{-1}) and exhibited an instructive nmr spectrum. In this case, however, the spectrum had to be obtained in two solvents (C_6D_6 and $CDCl_3$) before a complete analysis could be made. Thus, in C_6D_6 the following signals were observed: δ 1.12 (CH_3CH_2, t, J = 7 Hz), 1.45 (CH_3N, s), complex pattern of lines in region 2.3–2.7 (CH_2CH_3 and C_6H), 3.09 (C_5H, octet, $J_{4,5}$ = 7 Hz, $J_{5,6}$ = 5.5 and 1.5 Hz), 4.58 (C_2H, s), 4.83 (C_4H, d, $J_{4,5}$ = 7 Hz). The complex set of signals mentioned could be somewhat resolved in $CDCl_3$: δ 2.73 (CH_2CH_3, apparent octet, J = 7 and 15 Hz), 3.1–3.5 (C_6H, complex multiplet). It should be noted that there was a general solvent shift observed for *all* protons and the latter values, in comparison to those in C_6D_6, should be considered in those terms. As in the case of the above mentioned isomer, the mass spectrum revealed the following characteristic fragments: *m/e* 259, 123, 122, 107, and 94. All of these data are in support of a 1:1 complex between $Cr(CO)_3$ and *N*-methyl-3-ethyl-1,6-dihydropyridine (III).

In order to confirm the above assignments and to obtain more precise information about the nature of the bonding in these novel systems, both complexes were subjected to X-ray analysis. Crystals of *N*-methyl-3-ethyl-1,2-dihydropyridinetricarbonylchromium (IIa) are orthorhombic, a = 14.999 (7), b = 13.263 (5), and c = 12.164 (9) Å, Z = 8, space group *Pbca*. Those of *N*-methyl-3-ethyl-1,6-dihydropyridinetricarbonylchromium (IIIa) are monoclinic, a = 10.700 (3), b = 14.280 (6), and c = 7.926 (6) Å, β = 97.83 (4)°, Z = 4, space group $P2_1/n$. The structures were determined with Mo Kα scintillation counter data by heavy atom methods, and refined by full-matrix least-squares techniques. The final R of the 1,2-dihydropyridine complex was 0.039 for 916 observed reflections, that of the 1,6-dihydropyridine complex

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(1) For an excellent and recent review, see U. Eisner and J. Kuthan, *Chem. Rev.*, **72**, 1 (1972).

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(8) F. W. Fowler, *J. Org. Chem.*, 37, 1321 (1972).

(9) F. W. Fowler, *J. Amer. Chem. Soc.*, **94**, 5926 (1972).

(10) For extensive reviews, see, "Organic Synthesis via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968; G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. II, Methuen and Co., London, 1968, Chapter 3; R. B. King, *Accounts Chem. Res.*, **3**, 417 (1970).

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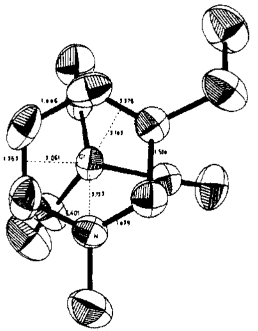
(13) Satisfactory elemental analyses and detailed spectroscopic data were obtained for both complexes. The nmr signals reported in δ values are based on detailed decoupling studies on these and related compounds in this series.

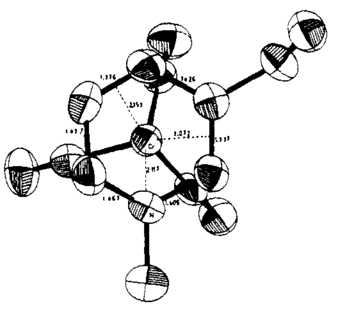
Table I. Atomic Positional Parameters (×10⁴)

	x/a	y/b	z/c
(A) *N*-Methyl-3-ethyl-1,2-dihydropyridinetricarbonylchromium			
Cr	1267 (1)	1215 (1)	2523 (1)
O(10)	3114 (3)	979 (4)	1632 (4)
O(11)	1487 (4)	3458 (4)	2295 (5)
O(12)	472 (4)	1275 (5)	279 (5)
N(1)	948 (3)	−291 (4)	3004 (4)
C(2)	1619 (4)	−388 (4)	3889 (5)
C(3)	1867 (4)	687 (5)	4174 (5)
C(4)	1179 (5)	1359 (5)	4323 (5)
C(5)	305 (4)	1128 (5)	3890 (6)
C(6)	200 (4)	309 (6)	3224 (6)
C(7)	813 (5)	−1207 (6)	2347 (6)
C(8)	2820 (5)	860 (5)	4578 (6)
C(9)	3104 (5)	1963 (6)	4645 (7)
C(10)	2393 (5)	1062 (5)	1960 (5)
C(11)	1392 (4)	2589 (5)	2399 (6)
C(12)	770 (5)	1227 (6)	1141 (6)
H(2a)	2135	−763	3566
H(2b)	1385	−737	4569
H(4)	1243	1960	4654
H(5)	−181	1543	4009
H(6)	−282	167	2919
H(7a)	484	−987	1736
H(7b)	1221	−1284	2068
H(7c)	634	−1737	2648
H(8a)	3199	513	4043
H(8b)	2825	452	5251
H(9a)	2728	2175	5113
H(9b)	3747	1891	4926
H(9c)	3057	2382	3823
(B) *N*-Methyl-3-ethyl-1,6-dihydropyridinetricarbonylchromium			
Cr	1612 (1)	2502 (1)	1992 (2)
O(10)	1134 (7)	2010 (6)	−1712 (9)
O(11)	−148 (8)	913 (6)	2357 (10)
O(12)	3876 (7)	1245 (5)	2628 (10)
N(1)	2475 (6)	3828 (5)	1841 (9)
C(2)	1165 (8)	3954 (6)	1444 (12)
C(3)	411 (9)	3671 (6)	2658 (12)
C(4)	1008 (9)	3244 (6)	4184 (12)
C(5)	2303 (9)	3245 (7)	4543 (12)
C(6)	3031 (9)	3929 (8)	3628 (12)
C(7)	3257 (9)	4156 (8)	571 (14)
C(8)	−1007 (9)	3797 (7)	2311 (13)
C(9)	−1424 (8)	4670 (7)	3274 (12)
C(10)	1338 (8)	2202 (7)	−293 (12)
C(11)	535 (10)	1525 (8)	2266 (13)
C(12)	3013 (9)	1721 (7)	2368 (11)
H(2)	785	4260	383
H(4)	500	2987	4764
H(5)	2692	3027	5510
H(6a)	2986	4598	3770
H(6b)	3839	3865	3365
H(7a)	2878	3939	−349
H(7b)	3333	4828	625
H(7c)	4153	3746	1194
H(8a)	−1296	3347	2760
H(8b)	−1199	3806	1020
H(9a)	−1162	5024	2415
H(9b)	−2299	4678	2972
H(9c)	−1291	4549	4643

being 0.067 for the 907 observed reflections. Table I lists the atomic positional parameters.

The bond lengths as shown in IIa and IIIa are intermediate between those normally expected for simple alkene and aromatic systems. In each compound the chromium atom interacts with the double bonds and the lone-pair electrons of the nitrogen to give a distorted octahedral coordination. In both compounds the tetrahedral carbon atom and the carbon atom next to it deviate significantly from the plane of the other four ring atoms. Intermolecular contacts correspond to van der Waals interactions.


IIa


IIIa

In summary, the above complexes provide stable representatives of the isomeric 1,2- and 1,6-dihydropyridine series, and we hope that they will be useful as convenient sources of these reactive dienamine systems. Further results in this direction will form the subject of forthcoming publications.

Acknowledgment. Financial aid from the National Research Council of Canada is gratefully acknowledged. One of us (V. E. R.) is grateful for a fellowship from Consejo Nacional de Ciencia y Tecnologia, Mexico, and A. Z. is indebted to the Politecnico di Milano for the leave from this institution to allow him to participate in these investigations.

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Metal Assisted Cycloaddition Reactions of Dicarbonyl(*pentahapto*cyclopentadienyl)(allenyl)iron. Mechanism and Synthetic Applications. Stereospecificity of Protonation of Dicarbonyl(*pentahapto*cyclopentadienyl)(propargyl)iron

Sir:

A number of cycloaddition reactions of *monohapto*allyl,[1] *monohapto*cyclopropyl,[2] *monohapto*cyclopropylmethyl,[1a] and *monohapto*propargyl[1c,d,3] metal complexes with a variety of electrophiles have been reported. We now wish to report the extension of these processes to the *monohapto*allenyl complex (**1**) and to provide evidence for the intermediacy of a cationic iron–acetylene complex in these reactions.

The allenyl complex is readily prepared in 52% yield by the metallation of propargyl benzenesulfonate with

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