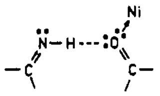
(1127)/1320 (1097) measured (observed with $I > 2.5\sigma(I)$) reflections]. All hydrogen atoms, except that bonded to the imino nitrogen, were localized in the final difference Fourier maps and included in calculations. We used the reported[15a,c] coordinates to evaluate the nonbonding intermolecular distances around the carbonyl oxygen and imino nitrogen atoms in question. For **7a** the shortest distance of 3.045 Å was found between the two particular O and N atoms, which conformed to the $C{=}O\cdots H{-}N{=}C$ hydrogen-bond geometry. This scheme may be realized in **8** as well, assuming the O and N atoms are exchanged.[52]



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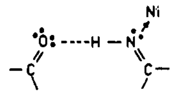

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In the structure of **7b**, the carbonyl oxygen has the shortest intermolecular contact with a cyano nitrogen, at 3.224 Å, and the imino nitrogen points toward two methyl groups, the N···C distances being 3.440 and 3.529 Å, respectively. A more realistic intermolecular linking scheme can be deduced for **8b**, i.e. $N{-}H\cdots N{\equiv}C$ hydrogen-bond and $C{=}O\cdots H_3C$ contacts. The reliability of the formation of a metal–imino nitrogen coordination bond in complexes of type **8** is further supported by diverse structural examples.[53]

The structural misassignments were connected with the uncertain interpretation of the IR spectral data.[15a] The stretching frequency ν_{N-H} at 3200 cm^{-1} for **7a** was reported to be close to that of the solid **4** (3270 cm^{-1}) whereas the existence of a band at 3245 cm^{-1} for **6a** was left without comment. The almost negligible difference in the intensity of the very weak $\nu_{C\equiv N}$ bands at 2220/2235 cm^{-1} for **6a**/**7a**, postulated as being due to the quenching effect of the neighboring oxygen atom in **7a**, can be alternatively explained in terms of the cyano group conjugation with the imino C=N π system perturbed upon coordination, as in **8**.

Finally, the pronounced preference of zinc for oxygen-bearing ligands would make probable the formation of two isomers—**6b** and **7**—if the ligand constitution in **7** were correct. However, the existence of only **6b** was reported.[15d,i]

Conclusions

The above discussion demonstrates in a qualitative manner than the coordination modes of acetylacetonato ligands 3-substituted by polar group(s) are subject to alteration depending on the flexibility and rotation freedom of the ligands themselves, the metal–donor group compliance, and the relative stability of the possible chelates. The conception of ligation competition between the actively coordinating donor groups allows us to suggest an alternative molecular configuration of complexes **7**. 3-(Cyanoiminomethyl)acetylacetone, known for more than 80 years,[15a] is shown to be able to coordinate through the imino nitrogen atom to metal ions preferring N-donor ligands. Two schemes are developed to explain how this could be accomplished.

The 3-cyano-2,4-pentanedionato ligand is not stereochemically allowed to under such changes in its chelation mode but is rigorously forced to act as a bridging ligand. The visible and near-IR electronic spectra of this system and the very low orbital contributions to the observed magnetic moment can be explained only by a very large ground-state splitting of a π type that characterizes the NCacac ligand as an in-plane π donor and an out-of-plane π acceptor. The structure of the $Co(NCacac)_2$ complex is a remarkable example of 3D regular molecular ordering with well-balanced metal–metal distances. The spectral and magnetic data reveal some π back-bonding on the electronic levels of the conjugated chelate system, which could be responsible for the equalization of the intra- and intermolecular interactions.

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Supplementary Material Available: Tables SI and SIII, listing non hydrogen atom anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and AOM expressions for the non-zero matrix elements of the ligand-field and the quartet-state matrices for a *trans*-MO_4N_2 chromophore (2 pages); Table SII, listing observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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[52] The closeness of the X-ray scattering power of O and N is often compensated by their temperature factors in the least-squares refinements.

[53] (a) Hollian, B. L.; Marsh, R. E. *Acta Crystallogr.* **1970**, *B26*, 1049. (b) Matthew, M.; Kunchur, N. R. *Acta Crystallogr.* **1970**, *B26*, 1054. (c) Coghi, L.; Pelizzi, G. *Acta Crystallogr.* **1975**, *B31*, 131. (d) Birker, P. J. M. W. L. *J. Chem. Soc., Chem. Commun.* **1977**, 444. (e) Peng, S.-M.; Wang, Y.; Chiang, C.-K. *Acta Crystallogr.* **1984**, *C40*, 1541.

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Facile α/β Diastereomerism in Organocobalt Corrins. Generality of the Phenomenon and Characterization of Additional α-Diastereomers

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Introduction

In a recent publication,[1] we reported that reductive alkylation of cobinamides (Cbi's) with CF_3CH_2I resulted in formation of a mixture of diastereomeric (2,2,2-trifluoroethyl)cobinamides with the α-diastereomer (i.e. the organic ligand in the "lower" axial position) predominating over the β-diastereomer by about 7-fold. This surprising result was in stark contrast to earlier work,[2] which had shown that reductive alkylation of cobinamide with $^{13}CH_3I$ yielded a methylcobinamide product that was at least 95% β-diastereomer. We now report the results of a reexamination of the products of reductive alkylation of cobinamide and cobalamin with CH_3I, as well as the products formed with a variety of other alkylating agents. These results show that formation of pairs of diastereomeric α- and β-alkylcobinamides is a general phenomenon and that similar pairs of diastereomeric α- and β-alkylcobalamins can also be obtained under some conditions.

Experimental Section

Alkylating agents and aquocobalamin (H_2OCbl) were obtained commercially. Factor B[3] was prepared as described previously.[4,5] HPLC was performed with a 4.6 × 75 mm Beckman C_{18} Ultrasphere column using a 50 mM aqueous ammonium phosphate buffer, pH 3.0 (solvent A), and acetonitrile (solvent B).[6] The gradient used was 5% B for 2 min

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[1] Brown, K. L.; Evans, D. R. *Inorg. Chem.* **1990**, *29*, 2559–2561.

[2] Brown, K. L.; Peck-Siler, S. *Inorg. Chem.* **1988**, *27*, 3548–3555.

[3] Factor B is a mixture of the diastereomers of cyanoaquocobinamide, α-CN-β-(H_2O)Cbi and α-H_2O-β-(CN)Cbi.

[4] Renz, P. *Methods Enzymol.* **1971**, *18*, 82–92.

[5] Brown, K. L.; Hakimi, J. M.; Nuss, D. M.; Montejano, Y. D.; Jacobsen, D. W. *Inorg. Chem.* **1984**, *23*, 1463–1471.

[6] Jacobsen, D. W.; Green, R.; Brown, K. L. *Methods Enzymol.* **1986**, *123*, 14–22.

Table I. Yields, Diastereomer Ratios, HPLC Mobilities, and Pyrolysis Products for the Alkylcobamides

alkyl group	alkylating agent	cobamide	tot. yield of RCba's,[a] %	$\alpha:\beta$ ratio[b]	T_R[c]	pyrolysis products[d]
CH_3	CH_3I	α-Cbi	80	4:96	1.20	CH_4, CH_3CH_3 (tr)
		β-Cbi			1.48	
		α-Cbl	71	3:97	1.41	
		β-Cbl			1.53	
$EtOCH_2CH_2$	$EtOCH_2CH_2Br$	α-Cbi	70	20:80	1.16	$(C_2H_5)_2O$, CH_3CH_2OH, $CH_2{=}CHOC_2H_5$, $CH_2{=}CH_2$
		β-Cbi			1.56	
		α-Cbl	84	11:89	1.43	
		β-Cbl			1.64	
CF_3CH_2[e]	CF_3CH_2I	α-Cbi	46	87:13	1.36[f]	CF_3CH_3, $CF_2{=}CH_2$
		β-Cbi			1.70[f]	
		α-Cbl	40	17:83	1.60[f]	
		β-Cbl			1.68[f]	
$NCCH_2$	$NCCH_2Br$	α-Cbi	65	73:27	1.01	CH_3CN
		β-Cbi			1.27	
		α-Cbl	45	21:79	1.31	
		β-Cbl			1.24	
CF_3	CF_3I	α-Cbi	85[g]	93:7	1.25	CF_3H
		β-Cbi			1.64	
		α-Cbl	40[g]	15:85	1.45	
		β-Cbl			1.53	
CF_2H	CF_3I[g]	α-Cbi	85[g]	98:2	1.15	CF_2H_2
		β-Cbi			1.50	
		α-Cbl	40[g]	52:48	1.39	
		β-Cbl			1.48	

[a] Products were converted to the dicyanocobamides by aerobic photolysis in excess cyanide and quantitated by using the known molar absorptivity at 368 nm.[7,8] [b] From integration of high-performance liquid chromatograms. The areas were corrected for the differences in molar absorptivities of the products at the observation wavelength (254 or 350 nm). [c] Mobilities are quoted as retention times relative to that of CNCbl (7.0 min). [d] Identified by mass spectrometry. All alkylcobamides with the same alkyl group gave the same pyrolysis products. [e] Reference 1. [f] HPLC retention times were 1.23, 1.48, 1.35, and 1.41, respectively, on a 4.6 mm × 25 cm Beckman C_8 Ultrasphere column.[1,6] [g] (Difluoromethyl)cobamides are formed in situ by reductive defluorination or (trifluoromethyl)cobamides.[5] The relative proportion of CF_3Cba's and CF_2HCba's was time-dependent with the former predominating at short alkylation times.

followed by a linear increase to 25% B over 10 min. After a hold at 25% B for 2 min, a linear gradient to 5% B over 2 min reestablished starting conditions. Retention times are given relative to that of CNCbl (7.0 min). UV–visible spectra were obtained on a Cary 219 recording spectrophotometer, and all cobamides were quantitated by conversion to their dicyano derivatives ($\epsilon = 3.04 \times 10^4$ M^{-1} cm^{-1})[7,8] by aerobic photolysis in excess cyanide. Anaerobic pyrolysis of solid RCba's was performed as described previously,[5] and the products were identified by GC/MS on a Finnigan 4500 GC/MS instrument equipped with a 6 in. × 2 mm ID Carbopak B/1% SP1000 column.

In a typical reductive alkylation, factor B or H_2OCbl (10–11 mg, ca. 0.01 mmol) in 1.0 mL of 10% acetic acid was purged with argon for 1 h. Zinc wool (0.01 mol), quickly freshened with 1.0 N HCl, was added, and the reduction was allowed to proceed for 30 min. Alkylating agent (ca. 1.0 mmol) was introduced, and the reaction was allowed to proceed for 10–60 min. For reduction with $NaBH_4$, acetic acid was omitted, and a solution (in deaerated water) containing 0.10 mmol of $NaBH_4$ was added by syringe in place of zinc wool. Reaction mixtures were desalted by chromatography on Amberlite XAD-2[5] and the isomeric RCba's were separated by HPLC. Product yields and isomer ratios were determined from integration of high-performance liquid chromatograms at 254 and 350 nm, using molar absorptivities determined from the isolated compounds.

Results and Discussion

Careful inspection of high-performance liquid chromatograms of the organocobinamide product obtained by reduction of factor B[3,4] with zinc/acetic acid, followed by alkylation with CH_3I, revealed a small peak (4% of the total RCbi) when a shorter retention time ($T_R = 1.20$) than the major product, β-CH_3Cbi ($T_R = 1.48$, Table I). Comparison of the UV–visible spectra of the two products (Figure 1A) shows that, as with the diastereomeric CF_3CH_2Cbi's,[1] all of the spectral transitions occur at the same wavelength (although with different molar absorptivities) except the longest wavelength (or α) band, which is red-shifted by 32 nm in the minor product (Table II), slightly more than the 27-nm red shift seen in the CF_3CH_2Cbi's. Comparison of the spectrum of the major product (Figure 1A, solid line) to that of the base-off species of β-CH_3Cbl[2] (Figure 1B, solid line) shows that they are identical above 300 nm. Furthermore, when the reductive alkylation of factor B was performed with ^{13}C-enriched methyl iodide, the ^{13}C resonance of the major product, as shown previously,[2] had the same chemical shift (1.67 ppm, relative to TSP) and H–C coupling constant (143.5 Hz) as observed for the base-off species of β-CH_3Cbl, while the minor product had a ^{13}C resonance at 3.19 ppm ($J_{HC} = 142.2$ Hz, Table II), which is about 1.5 ppm downfield from that of the well-characterized β-CH_3Cbi and base-off β-CH_3Cbl (Table II). In addition, both products from alkylation with CH_3I gave methane (and small amounts of ethane) on anaerobic pyrolysis, while the ^{13}C-enriched products both gave $^{13}CH_4$. We conclude that the faster migrating, minor product is the α-diastereomer of CH_3Cbi. Hence, reductive alkylation of cobinamide with CH_3I *does* yield a mixture of diastereomers, but in contrast to the case of CF_3CH_2I, the β-diastereomer predominates by almost 25:1. This is consistent with our earlier estimate that the major product obtained by reductive alkylation of factor B with CH_3I was at least 95% β-CH_3Cbi.[2]

Similar results have now been obtained upon reductive alkylation of factor B with ethoxyethyl bromide, bromoacetonitrile, and trifluoromethyl iodide (Table I). Only ethyl iodide[2] failed to yield any detectable (i.e. <2%) α-diastereomer. As was previously found for CF_3Cbl,[5] reductive defluorination of the (trifluoromethyl)cobamides produced difluoromethyl species, so that reductive alkylation of factor B with CF_3I produced four organocobinamides that were readily separable by HPLC. The relative proportions of CF_3Cbi's and CF_2HCbi's varied with alkylation time, the CF_3Cbi's predominating at shorter alkylation times and the CF_2HCbi's at longer alkylation times.

The results of the alkylation of cobinamide with the various alkylating agents are summarized in Table I. Total yields of RCbi's varied from 40% to 85%, while the $\alpha:\beta$ ratio of diastereomers varied widely from 4:96 for R = CH_3 to 93:7 for R = CF_3. For all the compounds, the products formed upon anaerobic pyrolysis of both diastereomers of the RCbi were the same as those

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(7) Barker, H. A.; Smyth, R. D.; Weissbach, H.; Toohey, J. I.; Ladd, J. N.; Volcani, B. E. *J. Biol. Chem.* **1960**, *235*, 480–488.

(8) The molar absorptivity of $(CN)_2Cbi$ is assumed to be the same as that of $(CN)_2Cbl$[7] at 368 nm.

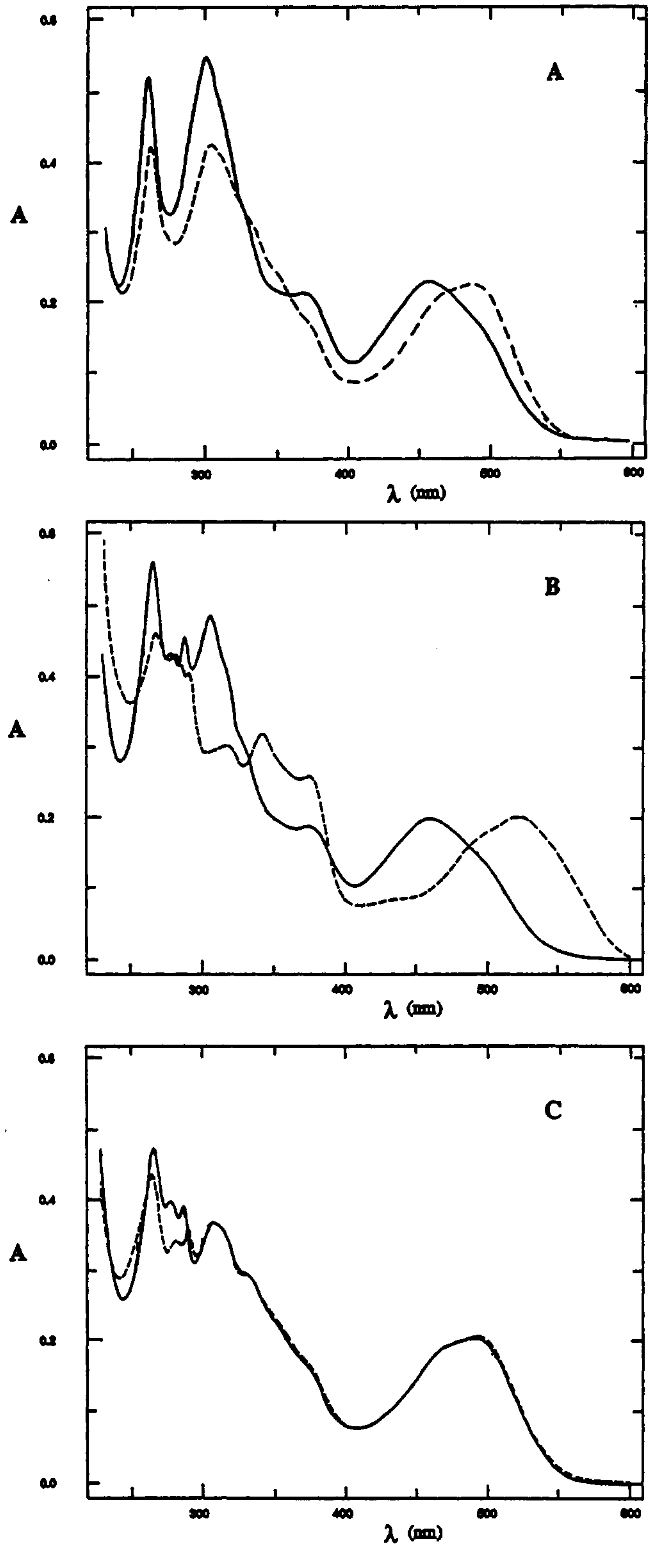

Figure 1. (A) Electronic spectra of the methylcobinamides, 2.19×10^{-5} M in 0.2 M potassium phosphate buffer (pH 7.1): (dashed line) α-CH_3Cbi; (solid line) β-CH_3Cbi. (B) Electronic spectra of β-methylcobalamin, 2.31×10^{-5} M: (solid line) base-off β-CH_3Cbl in 0.5 M HCl; (dashed line) base-on β-CH_3Cbl in 0.2 M potassium phosphate buffer (pH 7.1). (C) Electronic spectra of α-methylcobalamin, 1.98×10^{-5} M: (solid line) in 0.5 M HCl; (dashed line) in 0.2 M potassium phosphate buffer (pH 7.1).

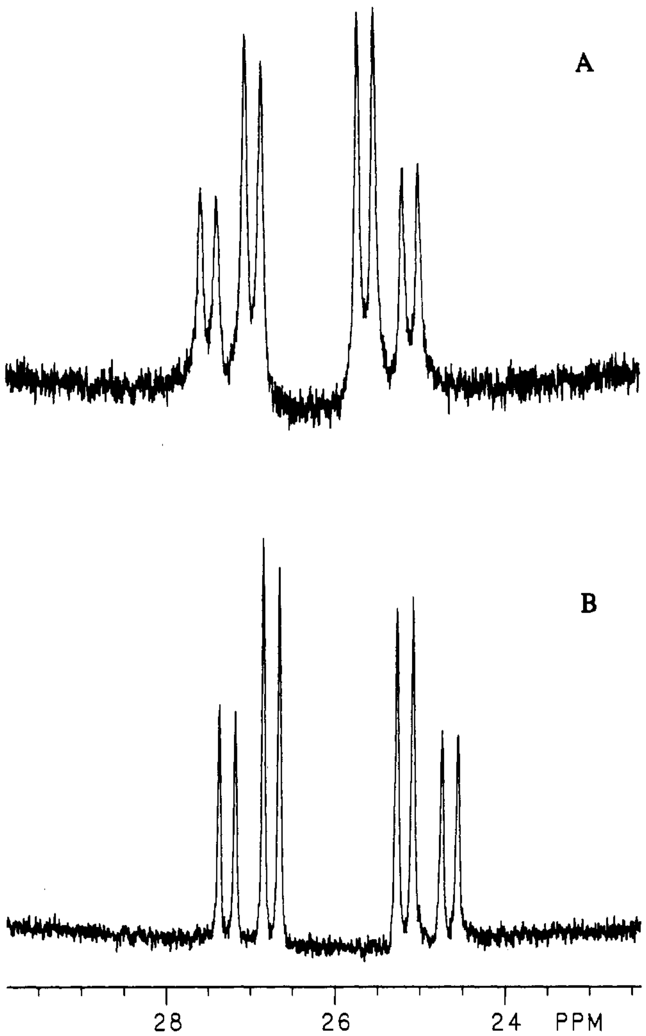

Figure 2. (A) ^{19}F NMR spectrum (282.9 MHz) of base-off β-CF_2HCbl in 1.0 M HCl, 10% D_2O. (B) ^{19}F NMR spectrum (282.9 MHz) of β-CF_2HCbi in 10% D_2O. Chemical shifts are relative to external fluorobenzene.

from the analogous β-RCbl (Table I). All of the compounds were photolabile, and readily produced $(H_2O)_2Cbi$ upon aerobic photolysis or $(CN)_2Cbi$ upon aerobic photolysis in excess cyanide. In addition, in every case, the slower migrating RCbi diastereomer had a UV–visible spectrum identical (above 300 nm) with that of the base-off species of the analogous β-RCbl.[5] The faster migrating RCbi diastereomers, however, showed the typical red shift of the α-band, which varied from 8 to 40 nm, depending on the organic ligand (Table II). The only exception was the diastereomeric CF_3Cbi's, whose spectra were nearly identical except for differences in molar absorptivities. For these compounds, the ^{19}F NMR resonance of the slower migrating diastereomer had the same chemical shift as that of the base-off species of β-CF_3Cbl (Table II). We consequently conclude that the fast-migrating member of each pair of RCbi diastereomers is the α-diastereomer. As was the case with the ^{13}C resonances of the diastereomeric $^{13}CH_3Cbi$'s and the ^{19}F resonance of α-CF_3CH_2Cbi,[1] the ^{19}F resonance of α-CF_3Cbi is downfield from that of the β-diastereomer (Table II). However, the ^{19}F NMR spectra of the CF_2HCba's show a puzzling anomaly (Figure 2). The ^{19}F resonances of base-off β-CF_2HCbl (Figure 2A) and β-CF_2HCbi (Figure 2B) are quite similar to each other and are clearly AB quartets of doublets. Apparently, the diastereotopic fluorine atoms differ in chemical shift by about 2 ppm, have a geminal homonuclear coupling constant of about 149 Hz, and are each coupled to the CF_2H proton with a coupling constant of about 54 Hz (Table II). In the α-CF_2HCbi diastereomer, a similar nonequivalence of the two fluorines occurs, with a fluorine chemical shift difference of about 3 ppm, but the resonances are shifted slightly upfield from those of the β-diastereomer. In contrast, in the ^{19}F NMR spectrum of base-on β-CF_2HCbl, the fluorines are equivalent and appear as a doublet with a geminal H–F coupling constant of 53 Hz (Table II). This interesting anomaly is currently under further investigation.

Table II. UV–Visible and NMR Spectroscopic Data for the Diastereomeric Alkylcobamides

alkyl group	cobamide	λ_{max}, nm ($10^{-4}\epsilon$, M^{-1} cm^{-1})[a]	δ, ppm	J, Hz
CH_3	α-Cbi	490 (1.05)	3.19[b]	142.2[c]
	β-Cbi	458 (1.06)	1.67[b,d]	143.5[c,d]
	α-Cbl	493 (1.05)	3.26[b]	142.1[c]
	β-Cbl, base-on	520 (0.895)	9.52[b,d]	138.6[c,d]
	β-Cbl, base-off	460 (0.886)[e]	1.75[b,d,f]	143.7[c,d,f]
$EtOCH_2CH_2$	α-Cbi	482 (1.01)		
	β-Cbi	461 (0.895)		
	α-Cbl	479 (1.04)		
	β-Cbl, base-on	525 (0.832)		
	β-Cbl, base-off	458 (0.924)[e]		
CF_3CH_2[g]	α-Cbi	482 (1.00)	59.52[h]	14.7[i]
	β-Cbi	455 (0.890)	57.38[h]	13.9[i]
	α-Cbl	482 (1.04)	59.53[h]	14.5[i]
	β-Cbl base-on	530 (0.952)	58.97[h]	14.4[i]
	β-Cbl, base-off	454 (0.878)[e]	57.40[f,h]	13.5[f,i]
$NCCH_2$	α-Cbi	490 (0.927)		
	β-Cbi	482 (0.890)		
	α-Cbl	490 (0.923)		
	β-Cbl, base-on	530 (0.868)		
	β-Cbl, base-off	478 (0.851)[e]		
CF_3	α-Cbi	511 (1.02)	90.71[h]	
	β-Cbi	512 (0.895)	86.64[h]	
	α-Cbl	512 (1.01)	90.72[h]	
	β-Cbl, base-on	541 (1.04)	81.73[h,j]	
	β-Cbl, base-off	513 (0.934)[e]	86.81[f,h]	
CF_2H	α-Cbi	490 (1.09)	23.63, 26.62[h,k]	156.5,[l] 53.6[m]
	β-Cbi	451 (0.855)	24.96, 26.99[h,k]	149.1,[l] 54.0[m]
	α-Cbl	492 (1.13)	23.13, 26.40[h,k]	155.3,[l] 48.0[m]
	β-Cbl, base-on	516 (1.01)	18.26[h]	53.2[m]
	β-Cbl, base-off	450 (0.973)[e]	25.40, 27.17[f,h,k]	148.4,[l] 53.5[m]

[a] Wavelength and molar absorptivity of the lowest energy (α) band in water at neutral pH, unless otherwise noted. [b] ^{13}C chemical shifts reported downfield from external TSP. [c] $^{1}J_{HC}$. [d] Reference 2. [e] In 0.5 M HCl. [f] In 1.0 M HCl. [g] Reference 1. [h] ^{19}F chemical shifts reported downfield from external fluorobenzene. [i] $^{3}J_{HF}$. [j] Reference 7. [k] The ^{19}F NMR spectrum is an AB quartet of doublets. [l] $J_{F_AF_B}$. [m] $^{2}J_{HF}$.

We have also investigated the possibility of the occurrence of the α-diastereomers of methyl- and other alkylcobalamins, since our previous work showed that α-CF_3CH_2Cbl could be obtained under the appropriate conditions. When aquocobalamin was reduced with zinc/acetic acid (but *not* when it was reduced with sodium borohydride) and then alkylated with CH_3I (or $^{13}CH_3I$), the alkylcobalamin fraction (about 70% of the total material) contained, in addition to the well-characterized β-CH_3Cbl (T_R = 1.53, Table I), a very small amount (ca. 3%) of a yellow material with a shorter retention time (T_R = 1.41). The UV–visible spectrum of this material (Figure 1C) was identical, above 300 nm, with that of the α-diastereomer of CH_3Cbi. Unlike β-CH_3Cbl (Figure 1B), it failed to show a typical base-on/base-off spectral shift of a β-RCbl, instead showing minor spectral changes in the UV region (Figure 1C), attributable to protonation of a pendent, but uncoordinated, dimethylbenzimidazole nucleotide.[5] In addition, this material produced methane (or $^{13}CH_4$) upon anaerobic pyrolysis, and its ^{13}C NMR resonance was 1.5 ppm downfield from that of β-$^{13}CH_3Cbi$ and base-off β-$^{13}CH_3Cbl$ but was essentially identical with that of α-$^{13}CH_3Cbi$ (Table II). We conclude that this material is the α-diastereomer of CH_3Cbl, in which coordination of the pendent nucleotide is prevented by the α organic ligand.

Similar results were obtained with all the other alkylating agents. In each case (except for the $NCCH_2Cbl$'s), the α-diastereomer had a shorter HPLC retention time than the β-RCbl and the α:β ratio was lower for the RCbl's than that for the analogous RCbi's (Table I). Again, alkylation with CF_3I produced pairs of diastereomeric CF_3Cbl's and CF_2HCbl's. All of the RCbl's were convertible to H_2OCbl upon aerobic photolysis and yielded $(CN)_2Cbl$ upon aerobic photolysis in excess cyanide. In every case, the α-RCbl had a UV–visible spectrum identical, above 300 nm, with that of the α-RCbi, and the spectrum of each α-RCbl showed only minor changes in the UV region upon acidification, attributable to protonation of the uncoordinated benzimidazole nucleotide. All of the α-RCbl's gave the same products, upon anaerobic pyrolysis, as the analogous β-RCbl's and RCbi's. The ^{19}F NMR resonances of the α-diastereomers of CF_3Cbl and CF_2HCbl were identical with those of the α-diastereomers of the respective alkylcobinamides, with α-CF_2HCbl again showing the ^{19}F AB quartet of doublets (Table II). In no case could α-RCbl's be obtained when H_2OCbl was reduced with borohydride, consistent with an earlier report.[5] This does not appear to be an effect of the reducing agent itself, as α-RCbi's were readily obtained when factor B was reduced with borohydride and alkylated. The failure to obtain α-RCbl's with borohydride as opposed to zinc/acetic acid reduction may be a pH effect involving the acid/base chemistry of the benzimidazole nucleotide in cobalamins. This question is currently under investigation.

As seen in Table I, the diastereomeric outcome of the reductive alkylation of factor B and aquocobalamin varies widely with the nature of the organic group of the alkylating agent. Due to the downwardly projecting b, d, and e propionamide side chains and the f secondary amide side chain, the α-face of Cbi's is clearly more congested than the β-face, which is bracketed by the a, g, and c acetamide side chains. Nevertheless, the bulkiest of the organic ligands studied here [CF_3, E_s (Taft steric substituent constant[9,10]) = −2.4;[11] CF_3CH_2, E_s = −2.5[12]] substantially prefer the α-position, while the smallest (CH_3, E_s = −1.24;[11] CH_3CH_2, E_s = −1.31[11]) overwhelmingly prefer the β-position. It remains unclear whether the products of reductive alkylation of these cobamides are under kinetic or thermodynamic control, although evidence of time dependence of the diastereomer ratio for some alkyl groups suggests the latter. The time-dependent defluorination of CF_3Cba's to CF_2HCba's further complicates such observations. Further experiments to answer the question of thermodynamic vs kinetic control are currently in progress.

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(9) Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

(10) Taft, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 3120–3128; **1953**, *75*, 4538–4539.

(11) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91–118.

(12) Estimated from data in ref 11.

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Synthesis and Reactivity of Ruthenium Hydride Complexes Containing Chelating Triphosphines. 6. Reactions of Ruthenium Hydride Complexes with CO$_2$-like Molecules[1]

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Introduction

Activation of CO$_2$ by transition-metal complexes has been attracting increasing attention, presumably due to the interest in utilizing inexpensive and abundant CO$_2$ as a feedstock for organic compounds.[2] Insertion of CO$_2$ into M–H or M–C bonds constitutes one of the important steps in the production of carbon-containing compounds from CO$_2$.[2] In this connection, ruthenium hydride complexes such as RuH$_2$(PPh$_3$)$_4$ and RuHCl(PPh$_3$)$_3$ are active for the catalytic production of formates or formic acid from CO$_2$.[3-6] The formate complex RuH(O$_2$CH)(PPh$_3$)$_3$ could be synthesized by the insertion of CO$_2$ into a Ru–H bond in RuH$_2$(L)(PPh$_3$)$_3$ (L = H$_2$, N$_2$, PPh$_3$).[7,8] Insertion of CO$_2$-like molecules, such as CS$_2$,[7,8b,9-13] carbodiimides,[14,15] isothiocyanates,[16] and isocyanates[17] into Ru–H bonds in several monophosphine ruthenium hydride complexes has also been reported. We herein report the reactions of CO$_2$ and CO$_2$-like molecules with the chelating triphosphine complexes RuH$_2$(H$_2$)(Cyttp) and RuHCl(Cyttp) (Cyttp = PhP(CH$_2$CH$_2$CH$_2$P(C$_6$H$_{11}$)$_2$)$_2$).

Experimental Section

All manipulations were performed under an argon atmosphere by using standard Schlenk techniques, unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Solutions were transferred by use of syringes that were flushed with argon before use. Air-sensitive solids were handled and transferred in a Vacuum Atmospheres HE43 inert-atmosphere box equipped with a Mo-40 catalyst system. Minute traces of oxygen and water were removed from commercially available argon by passing the gas through two columns packed with hot (180 °C) BASF active copper catalyst and Drierite, respectively.

Reagent grade chemicals were used as purchased from Aldrich Chemical Co., Inc., unless stated otherwise. Ruthenium trichloride hydrate was loaned by Johnson Matthey Inc. RuCl$_2$(Cyttp) and RuHCl(Cyttp)[18] were prepared by literature methods.

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 4000 to 200 cm^{-1}, as pressed potassium bromide pellets, as Nujol mulls, or in solution. Spectra were calibrated against the sharp 1601-cm^{-1} peak of polystyrene film. A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz) and phosphorus-31 (101.25 MHz) NMR spectra in 5-mm tubes. Residual solvent proton resonances were used as internal standards for the ^{1}H spectra. Phosphorus chemical shifts were determined relative to 85% H$_3$PO$_4$ as an external standard. The ^{31}P NMR and selected ^{1}H NMR data are collected in Tables I and II, respectively. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

RuH$_2$(H$_2$)(Cyttp). In a typical experiment, a mixture of 0.30 g of RuCl$_2$(Cyttp) (0.40 mmol) and 0.20 g of NaH (8.3 mmol) in 30 mL of THF was stirred overnight at ca. 40–50 °C under H$_2$ atmosphere to give a light yellow solution. The solvent was then removed completely, and the residue was extracted with ca. 40 mL of benzene, which was removed subsequently to give a light yellow solid. The reactivity of the compound was studied by adding appropriate amounts of other reagents to the extract.

Table I. ^{31}P NMR Data for the Ru(Cyttp) Complexes from Reactions of CO$_2$ and CO$_2$-like Molecules[a]

compd	δ_{P_1}	δ_{P_2}	$^2J(P_1P_2)$
RuH(O$_2$CH)(Cyttp) (**1**)	52.1	25.7	38.7
RuH(*p*-TolNCHN-*p*-Tol)(Cyttp) (**2**)	36.2	19.6	40.5
RuH(CyNCHNCy)(Cyttp) (**3**)	39.6	24.0	40.4
RuH(S$_2$CH)(Cyttp) (**4A**)	39.8	22.4	41.4
RuH(S$_2$CH)(Cyttp) (**4B**)	28.6	28.2	38.7
"Ru(S$_2$CH$_2$)(Cyttp)" (**4C**)	46.0		49.8
RuCl(S$_2$CH)(Cyttp) (**5**)	15.4	4.4	37.6

[a] Spectra were obtained in benzene. Chemical shifts are in δ with respect to external 85% H$_3$PO$_4$ (δ 0.0); positive values are downfield; coupling constants are in hertz. P$_1$ is the central phosphorus atom, and P$_2$, the two terminal phosphorus atoms in Cyttp.

Table II. Selected ^{1}H NMR Data for the Ru(Cyttp) Complexes from the Reactions of CO$_2$ and CO$_2$-like Molecules[a]

compd	δ_{Ru-H}	$^2J(P_1H)$	$^2J(P_2H)$	δ_{X_2CH}
RuH(O$_2$CH)(Cyttp) (**1**)	−23.02 (dt)	39.1	20.1	8.57
RuH(*p*-TolNCHN-*p*-Tol)(Cyttp) (**2**)	−21.32 (dt)	33.0	21.3	8.90
RuH(CyNCHNCy)(Cyttp) (**3**)	−20.30	29.4	24.6	8.20
RuH(S$_2$CH)(Cyttp) (**4A**)	−13.91 ("q")	18	23	11.85
RuH(S$_2$CH)(Cyttp) (**4B**)	−15.69 ("q")	23.8	23.8	11.60
"Ru(S$_2$CH$_2$)(Cyttp)" (**4C**)				6.08
RuCl(S$_2$CH)(Cyttp) (**5**)				11.45 (dt)[b]

[a] Spectra were obtained in benzene. Chemical shifts are in δ with respect to Me$_4$Si (δ 0.0); coupling constants are in hertz. P$_1$ is the central phosphorus atom, and P$_2$, the two terminal phosphorus atoms in Cyttp. d = doublet; q = quartet; t = triplet. [b] $J(P_1H)$ = 5.4 Hz; $J(P_2H)$ = 3.4 Hz.

RuH(O$_2$CH)(Cyttp). A mixture of 1 g of dry ice (CO$_2$) and RuH$_2$(H$_2$)(Cyttp) (ca. 0.26 mmol, prepared from 0.20 g of RuCl$_2$(Cyttp) with

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(1) Part 5: Jia, G.; Meek, D. W. Submitted for publication in Organometallics.

(2) For example: (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135.

(3) Inoue, Y.; Sasaki, Y.; Hasimoto, H. *J. Chem. Soc., Chem. Commun.* **1975**, 718.

(4) Kokomnikov, I. S.; Lobeeva, T. S.; Vol'pin, M. E. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1972**, 2263.

(5) Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, 863.

(6) Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc., Chem. Commun.* **1981**, 213.

(7) Kolomnikov, I. S.; Gusev, A. I.; Alesksandrov, G. G.; Lobeeva, T. S.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1973**, *59*, 349.

(8) (a) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58. (b) Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 784.

(9) Harris, R. O.; Hota, N. K.; Sadvoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259.

(10) (a) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1975**, *99*, C65. (b) Robinson, S. D.; Sahajpal, A. *Inorg. Chem.* **1977**, *16*, 2718.

(11) (a) Kalinin, A. E.; Gusev, A. I.; Struchkov, Yu. T. *J. Struct. Chem.* (*Engl. Transl.*) **1973**, *14*, 804. (b) Harris, R. O.; Sadavoy, L. S.; Nyburg, S. C.; Pickard, F. H. *J. Chem. Soc., Dalton Trans.* **1973**, 2646.

(12) (a) Mores, F. G.; Tenhoedt, R. W. M.; Langhout, J. P. *J. Organomet. Chem.* **1974**, *63*, 93. (b) Mores, F. G.; Ten Hoedt, R. M. H.; Langhout, J. P. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2279.

(13) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 875.

(14) (a) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1975**, *117*, C111. (b) Brown, L. D.; Robinson, S. D.; Sahajpal, A.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 2728.

(15) (a) Harris, A. D.; Robinson, S. D.; Sahajpal, A.; Hursthouse, M. B. *J. Organomet. Chem.* **1979**, *174*, C11. (b) Harris, A. D.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1327.

(16) (a) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1976**, *111*, C26. (b) Robinson, S. D.; Sahajpal, A. *Inorg. Chem.* **1977**, *16*, 2722.

(17) (a) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1979**, *164*, C9. (b) Sahajpal, A.; Robinson, S. D. *Inorg. Chem.* **1979**, *18*, 3572.

(18) Jia, G.; Gallucci, J. C.; Meek, D. W. *Inorg. Chem.* **1991**, *30*, 403.

0020-1669/91/1330-1953$02.50/0