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1,3-Dipolar Cycloadditions to Coordinated Azide in Cobalt Chelate Complexes of the Type LCo(chelate)N_3

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Several electron-poor dipolarophiles (alkynes, alkenes, and nitriles) react with azido cobalt chelate complexes of the type LCo(chelate)N_3 under mild conditions. Coordinated five-membered-ring heterocycles are the initial products of these 1,3-dipolar cycloadditions. Nonterminal alkynes yield triazoles, alkenes yield triazolines, and nitriles yield tetrazoles. The reactivity of the dipolarophile increases with an increase in the electron-withdrawing power of its substituents. The reactivity of the cobalt complexes is influenced by the nature of the neutral trans-coordinated ligand (L, trans effect) and by the nature of the anionic chelating system (cis effect). Other reagents also react with these azido complexes, but the products do not result from 1,3-dipolar cycloadditions. Terminal alkynes behave as C–H acids and produce alkynyl complexes, HCl produces LCo(chelate)Cl, $HClO_4$ produces $[LCo(chelate)]^+ClO_4$, carbon monoxide produces isocyanato complexes, LCo(chelate)NCO, and heterocumulenes generally give ill-defined products but CH_3SCN undergoes ligand substitution and thiocyanate decomposition to produce $CH_3SCNCo(chelate)CN$. Each of the products of these reactions was characterized by elemental analysis and infrared and ^{1}H NMR spectroscopy.

Introduction

Organic azides are synthetically very useful reagents.[1] Among the many and varied transformations that they undergo, perhaps the most important are their 1,3-dipolar cycloaddition reactions to produce heterocycles.[2,3] Thus, alkynes react with organic,[4-6] silyl,[7,8] tin,[9] and lead[10] azides to produce triazoles. But only a few 1,2,3-triazoles with free NH groups have been prepared from explosive HN_3.

Organic azides also react with electron-poor alkenes (enamines and enol ethers[4,11,12]) and strained alkenes[1,4,13] to produce triazolines, but simple alkenes either do not react or react very slowly.

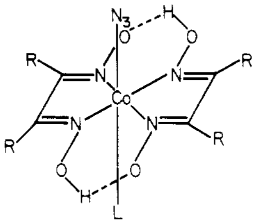
Organic azides,[14,15] binary metal azides,[16-19] silyl azides,[14,20] and complex metal azides[21-36] react with electron-poor nitriles under relatively mild conditions to produce tetrazoles.

In a search for convenient and reactive sources of azides for 1,3-dipolar cycloadditions, we have probed the reactivity of complexes of the type LCo(chelate)N_3.

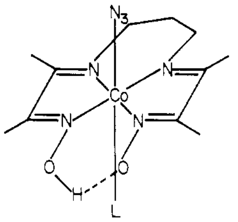
Complexes of the type $LCo^{III}(chelate)X$ have been widely studied because of their resemblance[27-30] to vitamin B_{12}, and a wide variety of these complexes has been synthesized.[31,32] Because the nature of both the anionic chelating ligands and the neutral trans ligand can be widely varied, this affords us the opportunity of simultaneously investigating both the cis and trans effects upon the reactivity of the coordinated azide. We report herein the reactions of a number of LCo(chelate)N_3 complexes I–IV with several representative electron-poor alkynes, alkenes, nitriles, and heterocumulenes.

Results and Discussion

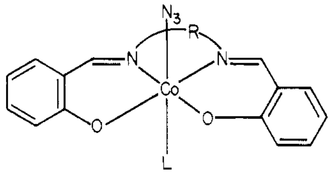
I. Reactions with Alkynes. Complexes I–IV were all found to react with electron-deficient internal alkynes (see Table I) under mild conditions (~20 °C) to produce triazolato complexes similar to what had previously been observed for the $(R_3P)_2M(N_3)_2$[24] (M = Pd,Pt), $[(R_3P)_2MN_3]_2$[23,25] (M = Cu, Ag), $Rh_2(C_5H_5)_2(N_3)_4$,[26] and $CpFe(CO)_2N_3$[33] complexes. The reactions of the cobalt complexes all occur at lower temperatures and usually with shorter reaction times than the analogous reactions of NaN_3[36] and HN_3.[35-39]



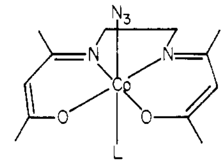
I, R = CH_3, LCo(DH)$_2N_3$
R = Ph, LCo(DPH)$_2N_3$



II, LCo[(DO)(DOH)]N_3



III, R = $(CH_2)_2$, LCo(Salen)N_3
R = o-C_6H_4, LCo(Salphen)N_3



IV, LCo(BAE)N_3

(a) Triazolato Complexes. As was found for the reaction of silyl azides[7] with dimethyl acetylenedicarboxylate, the cobalt complexes react to produce N(2)-bound 4,5-bis(methoxycarbonyl)-1,2,3-triazolates. The structure of the complexes is clearly established as the N(2) isomer from the appearance of their ^{1}H NMR spectra which show a singlet resonance at δ ≃3.7 for the six methoxycarbonyl protons. The ^{1}H NMR

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(1) "The Chemistry of the Azido Group", S. Patai, Ed., Interscience, New York, 1971.
(2) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961).
(3) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963).
(4) G. L'abbe, *Chem. Rev.*, **69**, 345 (1969); E. Lieber, R. L. Minnis, and C. N. R. Rao, *Chem. Rev.*, **65**, 377 (1965).
(5) A. Michael, *J. Prakt. Chem.*, **48**, 94 (1893).
(6) R. Huisgen, R. Knorr, L. Möbius, and G. Szeimies, *Chem. Ber.*, **98**, 4014 (1964); R. Huisgen, G. Szeimies, and L. Möbius, *ibid.*, **100**, 2494 (1967); R. Huisgen and R. Knorr, *Naturwissenschaften*, **48**, 716 (1962).
(7) L. Birkhofer and P. Wegner, *Chem. Ber.*, **99**, 2512 (1966).
(8) J. S. Thayer, *Organomet. Chem. Rev.*, **1**, 157 (1966).
(9) T. Itano, N. Mikara, K. Sisido, and T. Isida, *J. Organomet. Chem.*, **44**, 117 (1972).
(10) H. Gorth and M. C. Henry, *J. Organomet. Chem.*, **9**, 117 (1967).
(11) R. Huisgen, L. Möbius, and G. Szeimies, *Chem. Ber.*, **98**, 1138 (1965).
(12) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Chem. Ber.*, **96**, 802 (1963).
(13) R. Huisgen, L. Möbius, G. Müller, H. Stangl, G. Szeimis, and J. M. Vernon, *Chem. Ber.*, **98**, 3992 (1965).
(14) L. A. Lazukina and V. P. Kukhar, *Zh. Org. Khim.*, **15**, 2216 (1979).
(15) A. A. Melnikov, M. M. Sokolova, M. A. Pervozvanskaya, and V. V. Melnikov, *Zh. Org. Khim.*, **15**, 1861 (1979).
(16) E. Wiberg and H. Michaud, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, **9B**, 496 (1954); H. Behringer and K. Kohl, *Chem. Ber.*, **89**, 2648 (1956).
(17) R. Huisgen, J. Sauer, H. J. Sturm, and J. H. Markgraf, *Chem. Ber.*, **93**, 2106 (1960).
(18) L. A. Lester, E. V. Crabtree, J. V. Lowe, M. J. Cziesla, and R. Evans, *Tetrahedron Lett.*, **33**, 2885 (1965).
(19) W. G. Finnegan, R. A. Henry and R. Loftquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).

0020-1669/82/1321-1226$01.25/0

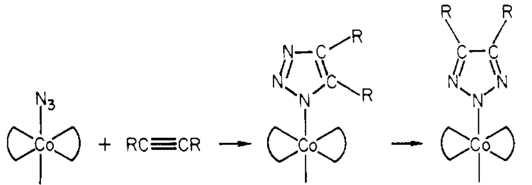
Table I. Triazolato Complexes Formed from the Reaction of Alkynes with Cobalt Azido Chelate Complexes

			IR data (KBr), cm^{-1}			^1H NMR data, $CDCl_3$ vs. Me_4Si	
complex	starting azide complex	alkyne	triazolato ring vib	ν(C=O)	ν(C–O)	δ	rel intens
1a	$PPh_3Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	827, 798, 773	1737	1296	7.42, 3.79,[b] 2.42[a]	15:6:12
1b	$MePPh_2Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	829, 804, 780	1720	1243	7.55, 3.70,[b] 1.99,[c] 1.95[a]	10:6:3:12
1c	$Me_2PPhCo(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	823, 801, 791, 778	1738, 1717	1238	7.35, 3.71,[b] 2.09,[a] 1.53[c]	5:6:12:6
1d	$PBu_3Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	828, 801, 770	1730	1290	3.68,[b] 2.26,[a] 1.1	6:12:27
1e	$P(Bzl)_3Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	826, 794, 773	1748, 1720	1295	6.8. 3.65,[b] 2.95,[c] 2.13[a]	15:6:6:12
1f	$P(OCH_3)_3Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	827, 792, 780	1732	1285	3.74,[b] 3.65, 2.31[a]	6:9:12
1g	$P(OPh)_3Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	828, 798, 775	1737	1295	7.08, 3.74,[b] 2.08[a]	15:6:12
1h	$PhNH_2Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	838, 823, 803	1727, 1692	1298		
1i	$pyCo(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	825, 805, 779	1725	1245	3.78,[b] 2.37[a]	6:12
1j	$NH_3Co(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	832, 805, 776	1729	1243		
1k	$1\text{-MeImCo}(DH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	834, 800, 779	1720	1295	7.1, 3.74,[b] 3.58, 2.30[a]	3:6:3:12
1l	$AsPh_4[Co(DH)_2(N_3)_2]$	$CH_3CO_2C\equiv CCO_2CH_3$	828, 799, 792, 771	1709, 1734	1295		
1m	$PBu_3Co(DPH)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	826, 801, 779	1743, 1722	1288	7.25, 3.72,[b] 1.45	20:6:27
1n	$[Co[(DO)(DOH)pn](N_3)_2]$	$CH_3CO_2C\equiv CCO_2CH_3$	829, 798, 772	1740	1293		
1o	$PPh_3Co(Salen)N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	828, 798, 775	1730		7.28, 3.69	8:6
1p	$PPh_3Co(Salphen)N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	822, 798, 775	1712, 1732		7.37, 3.57	26.9:6
1q	*cis*-$PPh_3Co(acac)_2N_3$	$CH_3CO_2C\equiv CCO_2CH_3$	830, 804, 780	1720, 1750	1295	7.37, 4.58, 3.70,[b] 1.65	15:2:6:11.65
2a	$PhNH_2Co(DH)_2N_3$	$HC\equiv CCO_2Et$	850, 779	1712	1241, 1091	7.18, 4.16, 3.44, 2.22,[a] 1.26	5:2:2:12:3
2b	$pyCo(DH)_2N_3$	$HC\equiv CCO_2Et$	830, 775	1730	1236, 1090	7.25, 4.25, 2.22,[a] 1.30	5:2:12:3
2c	$NH_3Co(DH)_2N_3$	$HC\equiv CCO_2Et$	829, 745	1705	1242, 1092		
2d	$AsPh_4[Co(DH)_2(N_3)_2]$	$HC\equiv CCO_2Et$	842, 831, 777	1723 sh, 1709	1242, 1231, 1092, 1078		
2e	$PPh_3Co(Salphen)N_3$	$HC\equiv CCO_2Et$	808, 778	1720	1227, 1090		
2f	$pyCo(Salphen)N_3$	$HC\equiv CCO_2Et$	808, 778	1720	1227, 1090	7.50, 4.17, 1.16	17.8:2.08:3

[a] Oxime CH_3, doublet, $J_{PH} = 1$ Hz. [b] CO_2CH_3. [c] P-CH_3 or P-CH_2, doublet, $J_{PH} = 11$ Hz.

spectrum of an N(1)-bound isomer would exhibit two proton resonances for its anisochronous methoxycarbonyl groups. Each of the triazolato complexes also possesses very characteristic infrared spectra that clearly show the absence of $\nu(N_3)$ and the presence of ν(C=O), ν(C—O), and triazolato ring frequencies (see Table I).

Changing the electron-donor ability of the other ligands coordinated to the cobalt (III) center brings about a change in the rate constant for the cycloaddition reaction by 2 orders of magnitude.[40]



V VI (1)

For example, the pseudo-first-order rate constants for the reactions of $LCo(DH)_2N_3$ with dimethyl acetylenedicarboxylate are $\sim 10^{-3}$ s^{-1} when L = PPh_3 and $\sim 10^{-5}$ s^{-1} when L = Bzl_3P at 27 °C in $CHCl_3$. Though the N(1) isomer (V) (reaction 1) is surely the kinetic product of these reactions, the isolated thermodynamically stable product is the N(2) isomer (VI). Isomerization from N(1)- to N(2)-bound triazole is most likely sterically promoted as has been found for the analogous tetrazolato complexes.[41]

Following the cycloaddition reaction, the base B = PPh_3, is partially liberated and produces an equilibrium mixture of five-and-six coordinate complexes as depicted in reaction 2.

$$\mathrm{XCo(chelate)PPh_3} \xrightleftharpoons[+\mathrm{PPh_3}]{-\mathrm{PPh_3}} \mathrm{XCo(chelate)} \qquad (2)$$

$$\mathrm{X = triazolate}$$

By additon of triphenylphosphine to the reaction solution, one

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(20) S. S. Washburne and W. R. Peterson, Jr., *J. Organomet. Chem.*, **21**, 427 (1970).

(21) W. Beck and W. P. Fehlhammer, *Angew. Chem.*, **79**, 146 (1967); W. Beck, W. P. Fehlhammer, P. Pöllman, and H. Schächl, *Chem. Ber.*, **102**, 1976 (1969).

(22) W. Beck, W. P. Fehlhammer, H. Bock, and M. Bauder, *Chem. Ber.*, **102**, 3637 (1969); W. Beck, M. Bauder, W. P. Fehlhammer, P. Pöllman, and H. Schächl, *Inorg. Nucl. Chem. Lett.*, **4**, 143 (1968).

(23) Z. Dori and R. F. Ziolo, *Chem. Rev.*, **73**, 247 (1973).

(24) P. Kreutzer, Ch. Weis, H. Böhme, T. Kemmerich, W. Beck, C. Spencer, and R. Mason, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, **27B**, 745 (1972).

(25) L. Busetto, A. Pallazzi, and R. Ros, *Inorg. Chim. Acta*, **13**, 233 (1975).

(26) W. Rigby, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* 371 (1979).

(27) G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968).

(28) R. H. Abeles and D. Dolphin, *Acc. Chem. Res.*, **9**, 114 (1976).

(29) R. B. Silverman and D. Dolphin, *J. Am. Chem. Soc.*, **98**, 4626 (1976).

(30) A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzer, *Inorg. Chim. Acta, Rev.*, **4**, 41 (1970).

(31) W. Beck, T. Kemmerich, and H. Böhme, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **34B**, 200 (1979), and references contained therein; T. Kemmerich, Dissertation, Universität München, 1975.

(32) D. Dodd and M. D. Johnson, *Organomet. Chem. Rev.*, **52**, 1 (1973).

(33) A. Rosan and M. Rosenblum, *J. Organomet. Chem.*, **80**, 103 (1974).

(34) S. Yamaha, *Chem. Abstr.*, **51**, 14697*e* (1957).

(35) O. Dimroth and G. Fester, *Ber. Dtsch. Chem. Ges.*, **43**, 2219 (1910).

(36) E. Oliveri-Mandala and A. Coppola, *Gazz. Chim. Ital.*, **40** II, 436 (1910); *Chem. Abstr.*, **4**, 2455 (1910).

(37) L. W. Hartzel and F. R. Benson, *J. Am. Chem. Soc.*, **76**, 667 (1954).

(38) R. Hüttel, *Ber. Dtsch. Chem. Ges.*, **74**, 1680 (1941).

(39) J. C. Sheehan and C. A. Robinson, *J. Am. Chem. Soc.*, **73**, 1208 (1951).

(40) The kinetics and mechanism of these reactions will be further discussed in a future publication.

(41) N. E. Takach, E. M. Holt, N. W. Alcock, R. A. Henry, and J. H. Nelson, *J. Am. Chem. Soc.*, **102**, 2968 (1980).

Table II. Alkynyl Complexes Formed by Reaction of Terminal Alkynes with Cobalt Azido Chelate Complexes

complex	starting azide complex	alkyne	ν(C≡C)	ν(C=O)	ν(C–O)
6a	$pyCo(DH)_2N_3$	HC≡CC(O)H			
6b	$PPh_3Co(Salphen)N_3$	HC≡CC(O)H			
6c	$[Co[(DO)(DOH)pn](N_3)_2]$	HC≡CC(O)H	2108	1682	
7a	$N_3Co(DH)_2py$	$HC≡CCH(O_2CH_3)_2$			
7b	$PPh_3Co(Salphen)N_3$	$HC≡CCH(O_2CH_3)_2$	2101	1754, 1737	
8a	$PPh_3Co(Salen)N_3$	$HC≡CCO_2Et$	2114	1712	1197, 1105?

can isolate the corresponding complex which loses triphenylphosphine upon washing with diethyl ether. The tendency for formation of the five-coordinate complex is a function of the chelating ligand system and increases in the order[28] $(DH)_2 \sim$ Salphen $<$ $(PH)_2$ $<$ (NH_2) $<$ Salen $<$ BAE (cis effect). These equilibria also occur for the bases L = $AsPh_3$, $SbPh_3$, $P(OPh_3)_3$, and $P(OEt)_3$ but not with the more tightly bound base pyridine. These observations lead to the conclusion that the triazolate has a greater trans-labilizing ability than azide. When the chelate is Salen or BAE, both the PPh_3Co(chelate)triazolate and Co(chelate)triazolate complexes may be isolated. Loss of triphenylphosphine from the former upon washing with ether is visually evident by the formation of crystalline triphenylphosphine in the ether wash solutions.

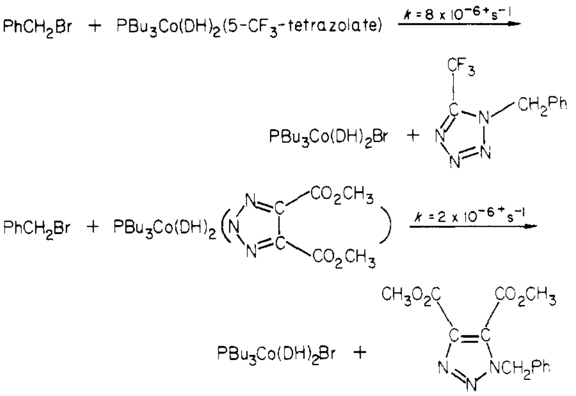
Similar to these reactions, the diazido cobalt complexes react with dimethyl acetylenedicarboxylate to produce bis(triazolate) complexes (compounds **1l** and **1n** of Table I).

(b) Alkynyl Complexes. Terminal alkynes react as CH acids and undergo a ligand substitution reaction rather than a 1,3-dipolar cycloaddition with the cobalt azide complexes to produce alkynyl complexes with liberation of HN_3 according to reaction 3 (see Table II). The more electron withdrawing

$$LCo(chelate)N_3 + RC{\equiv}CH \rightarrow RC{\equiv}CCo(chelate)L + HN_3 \quad (3)$$

the R group, the more stable is the alkynyl complex. Propynal and (more slowly) propynal diacetate produced only the alkynyl substitution product independent of the nature of the cobalt azide complex, whereas ethyl propiolate produced predominantly the triazolate complex. But ethyl propiolate reacted with $PPh_3Co(Salen)N_3$ to produce the alkynyl complex, suggesting that there is little difference in the stability of the triazolate and alkynyl complexes. The alkynyl complexes have also been obtained by reaction of the corresponding chlorocomplexes with the sodium or silver acetylide.[42,43] The velocity[40] of the cycloaddition or ligand substitution as well as the nature of the product formed (alkynyl or triazolate complex) is related to the acidity of the alkyne. By comparison, trimethylsilyl azide gave no cycloaddition products in these reactions, only HN_3 liberation occurred.[44]

(c) Cleavage of the Coordinated Triazole. We have recently shown[41] that the complexes $PBu_3Co(DH)_2$(5-R-tetrazolate) react with alkyl halides such as benzyl bromide and methyl iodide to alkylate the tetrazole ring regiospecifically at the N(1) nitrogen. Since all the triazolate complexes contain N(2)-bound triazolate, it was of interest to determine if they would react similarly to produce N(1)-alkylated triazoles. Accordingly, seven of the $LCo(DH)_2$(triazolate) complexes were reacted with benzyl bromide in $CDCl_3$ at room temperature in a 5-mm NMR tube, and the progress of the reaction was followed by ^1H NMR spectroscopy for 3 months. The complexes with L = PBu_3, CH_3PPh_2, and $(CH_3)_2PPh$ were all found to react whereas when L = 1-methylimidazole, pyridine, $P(OCH_3)_3$, or PPh_3, either no reaction or decomposition occurred. The results were determined by comparing the ^1H NMR spectra of the reaction solutions to that of an independently prepared sample of 1-benzyl-4,5-bis(methoxycarbonyl)-1,2,3-triazole. The latter shows singlets at δ 7.22, 5.75, 3.90, and 3.83 in the ratio 5:2:3:3. The 2-benzyl-1,2,3-triazole isomer was not available, but it should be readily distinguishable from the 1-benzyl isomer by having a benzyl CH_2 resonance at a value different from δ 5.75 and having isochronous methoxycarbonyl methyl resonances. In each of the three cases where alkylation occurred, it occurred regiospecifically at the N(1) nitrogen and at approximately the same rate as for the alkylation of coordinated tetrazole[45] (compare reactions 4 and 5). Both reactions were run under



(4)

(5)

pseudo-first-order conditions at 36 °C in $CDCl_3$. The complex $PPh_3Co(DH)_2$(triazolate) also reacted with benzyl bromide, but alkylation of PPh_3[46] to form $[BzlPPh_3]^+Br^-$ occurred rather than alkylation of triazolate; this is consistent with the previous conclusions that PPh_3 dissociation occurs for this complex.

Most attempts at liberating and isolating the triazole from these complexes have been unsuccessful. Typically, the chelate system also reacts with the liberating reagents to produce oily decomposition products, making isolation of the free triazole difficult. However, treatment of the complexes with HCl in acetone liberates the triazole in low yield and reaction with acetyl chloride produces the N(1) acetyltriazole which can be hydrolyzed to the triazole (see Experimental Section).

II. Reactions with Alkenes. Most of the alkenes investigated did not produce pure products, probably due to the general thermal instability and base sensitivity of Δ^2-triazoline.[47] The progress of the reactions of alkenes with azido cobalt complexes can be followed by the loss of $\nu(N_3)$ in the infrared spectrum. Generally, these reactions occur over a long period of time as with the corresponding alkyne reactions.[40] A uniform, well-characterized product was isolated from the reaction of diethyl maleate with the azido cobalt complex $N_3Co(DH)_2NH_3$ in $Me_2SO/CHCl_3$ as shown in reaction 6. This product exhibits ν(C=O) at 1742 cm^{-1}, ν(NN) at 1634 cm^{-1}, and ν(CO) at 1203 and 1044 cm^{-1}. The complex contains $CHCl_3$ of solvation. Similar reactions with maleic anhydride, acrolein, ethyl

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(42) T. Kemmerich, Dissertation, Universität München, 1975.

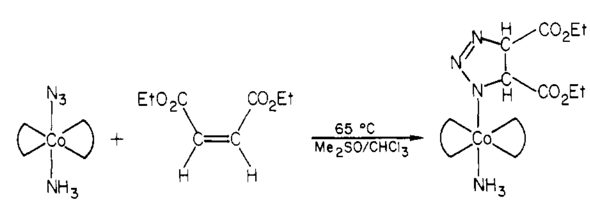
(43) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964); for other acetylide cobalt(III) complexes, see ref 30 and 32.

(44) W. Schwab and F. Wille, to be submitted for publication.

(45) N. E. Takach and J. H. Nelson, *Inorg. Chem.*, **20**, 1258 (1981).

(46) W. C. Trogler, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, **14**, 2708 (1975).

(47) R. Huisgen, G. Szeimies, and L. Möbius, *Chem. Ber.*, **99**, 475, 491 (1966).



(6)

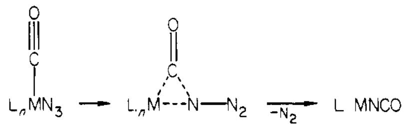
acrylate, acrylonitrile, and cyclopentadiene dimer did not produce analyzable products, but in each case $\nu_{as}(N_3)$ completely disappeared indicating that a reaction had occurred.

III. Reaction with Nitriles. These azido cobalt chelate complexes undergo 1,3-dipolar cycloadditions only with very electron-deficient nitriles. In the reaction of a coordinatively unsaturated azido complex, partial activation of the nitrile by prior coordination to the metal through formation of a σ-donor bond may occur as previously discussed.[22,48] A similar catalytic effect by the central metal in the coordinatively saturated cobalt chelate complexes is not likely. An increase in coordination number is also prohibited on steric grounds, and substitution of the trans ligand is not anticipated as in each case the coordinated bases are all stronger donors than nitriles.[49,50]

Both N(1)- and N(2)-bound tetrazoles may be formed by the reaction of azido complexes with nitriles. Molecular orbital calculations[51-57] indicate that these two bonding modes are essentially electronically and energetically equivalent, and for Pd and Pt both isomers are obtained.[24,50,52] However, we have recently shown[41] that in the $R_3PCo(DH)_2$(tetrazolate) complexes, N(2) coordination of the tetrazole is sterically promoted. It is therefore likely that the products listed in Table III contain N(2)-bound tetrazolates.[41] The relative rates of these reactions are a strong function of the nature of the nitrile (*o*-phthalodinitrile, benzonitrile, and acetonitrile did not react), the trans base, and the chelate ring system.[40] Both of the diazido complexes $[Co[(DO)(DOH)pn](N_3)_2]$ and $Ph_4As[Co(DH)_2(N_3)_2]$ did not react, and the complex $PPh_3Co(DH)_2N_3$ reacted much more slowly[40] than the more electron-rich Schiff-base complexes $PPh_3Co(Salen)N_3$ and $PPh_3Co(Salphen)N_3$.

As was found for triazolates, the tetrazolates are also better trans-labilizing ligands than azide and the tetrazolate complexes are isolated as base free complexes.

IV. Reactions with Carbon Monoxide. Azide complexes react with carbon monoxide in solution to produce isocyanato complexes and the mechanism in reaction 7 has been proposed for these reactions.[21,58]



(7)

Table III. Tetrazole Complexes Formed from the Reaction of Nitriles with Cobalt Azido Chelate Complexes

complex	starting azide complex	nitrile
9a	$PPh_3Co(Salphen)N_3$	$NCCF_3$
10a[a]	$PPh_3Co(Salen)N_3$	$NCCO_2C_2H_5$
10b	$PPh_3Co(Salphen)N_3$	$NCCO_2C_2H_5$
11a[a, b]	$PPh_3Co(Salphen)N_3$	$NCCH_2CN$

[a] The product does not contain PPh_3. [b] Only one nitrile group reacts.

The high velocity of these reactions for coordinatively unsaturated complexes supports the proposal of coordination to and activation of CO by the central metal atom. In contrast the reaction of the azido cobalt oximes with CO probably occurs by direct interaction to form the isocyanato complexes $PPh_3Co(DH)_2NCO$(**12a**) and $pyCO(DH)_2NCO$(**12b**). More drastic conditions are necessary to cause these reactions (5 days at 50 °C and 40 atm of CO), and a catalytic effect of the cobalt atom is precluded by the steric bulk of the other ligands. These same complexes may be prepared by metathesis of the chloro complexes with NaNCO.

V. Reactions with Heterocumulenes. A variety of simple heterocumulenes such as carbon disulfide, isocyanates (RN=C=O), isothiocyanates (RN=C=S), and thiocyanates (RSC≡N) react with organic azides[59] as well as metal azide complexes[31,23-26,60] to produce five-membered heterocyclic rings. Upon reaction of the oxime complex $PPh_3CO(DH)_2N_3$ with methyl thiocyanate, the first thing which occurs is ligand substitution of PPh_3 by CH_3SCN. Subsequently, the azide group is replaced by cyanide so that one eventually isolates the complex $NCCo(DH)_2NCSCH_3$ as depicted in reaction 8.

$$\underset{\substack{\nu_{as}(N_3) = \\ 2007\ cm^{-1}}}{N_3Co(DH)_2PPh_3} \xrightarrow[-PPh_3]{+NCSCH_3}$$

$$\underset{\substack{\nu_{as}(N_3) = 2023\ cm^{-1} \\ \nu_{as}(NCS) = 2189\ cm^{-1}}}{N_3Co(DH)_2NCSCH_3} \xrightarrow[-N_3]{+NCSCH_3} \underset{\substack{\nu(CN) = 2138, \\ 2110\ cm^{-1}}}{NCCo(DH)_2NCSCH_3} \qquad (8)$$

This is not too surprising since several organic reagents are known to decompose thiocyanates to cyanides.[61] One can follow the reactions of other heterocumulenes with the $LCo(chelate)N_3$ complexes by observing the disappearance of the $\nu_{as}(N_3)$ stretching frequency in the infrared. Though the azide complexes completely reacted in each case no definitive well-characterizeable products could be isolated from these reactions. Surprisingly, whereas CS_2 reacted with[21,25] platinum,[24] copper,[62,63] and rhodium[26] azide complexes to produce thiocyanates, the azido cobalt complexes did not react with CS_2 either thermally or photochemically; in each case the azido complexes were recovered unchanged from these reactions.

VI. Reactions with Acids. Protonation of the azide ligand of $LCo(chelate)N_3$ complexes with acids leads to HN_3 elimination. Treatment with HCl solutions produces the analogous chloride complexes $LCo(chelate)Cl$. Similarly noncoordinating acids react to produce salts of the type $[Co(chelate)L]^+X^-$ (L = PPh_3, py; X = ClO_4^- and HSO_4^-).

Experimental Section

A. Reagents and Physical Measurements. Chemicals were reagent grade and were used as received or synthesized as described below.

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(48) P. H. Kreutzer, Dissertation Universität München, 1971; J. Erbe, Dissertation, Universität München, 1978.
(49) W. P. Ferlhammer, T. Kemmerich, and W. Beck, *Chem. Ber.*, **112**, 468 (1979).
(50) D. G. Batyr, M. P. Starysh, V. N. Shafranskii, and Yu. Ya. Kharitonov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **19**, 704 (1974).
(51) J. H. Nelson, D. L. Schmitt, R. A. Henry, D. W. Moore, and H. B. Jonassen, *Inorg. Chem.*, **9**, 2678 (1970).
(52) D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Am. Chem. Soc.*, **96**, 6928 (1974).
(53) R. L. Kieft, W. M. Peterson, G. L. Blundell, S. Horton, R. A. Henry, and H. B. Jonassen, *Inorg. Chem.*, **15** 1721 (1976).
(54) W. Woznicki and B. Zurawoski, *Acta Phys. Pol.*, **31**, 95 (1967).
(55) A. V. Moskvin, V. A. Ostrovskii, I. Yu. Shirobokov, G. I. Koldobskii, and B. C. Gidaspov, *Zhur. Org. Khim.*, **14**, 2440 (1978).
(56) E. S. Krougauz, D. A. Bochvar, I. V. Stankevich, and V. V. Korshak, *Dokl. Akad. Nauk SSSR*, **179**, 94 (1968).
(57) M. A. Schroeder, R. C. Mukino, and W. M. Tolles, *Tetrahedron*, **29**, 3463 (1973).
(58) J. P. Collman, M. Kubota, and J. W. Hoshing, *J. Am. Chem. Soc.*, **89**, 4809 (1967).
(59) M. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, 1967.
(60) P. H. Kreutzer, Dissertation Universität München, 1971.
(61) "The Chemistry of Cyanates and their Thio Derivatives", Part 2, S. Patai, Ed., Interscience, New York, 1977, p 866 ff.
(62) R. F. Ziolo and Z. Dori, *J. Am. Chem. Soc.*, **90**, 6560 (1968).
(63) R. F. Ziolo, Ph.D. Dissertation, Temple University, Philadelphia, Pa., 1970.

Table IV. Reaction Conditions and Physical Properties of the Triazolato Products from the Reaction of Cobalt Azido Chelate Complexes with Alkynes

complex	react conditions	% yield	pptng solvent	dec pt. °C	recrystn solvent	color	elemental anal. % C calcd	% C found	% H calcd	% H found	% N calcd	% N found
1a	3 h, RT,[f] $CHCl_3$	69	C_2H_5OH	220	$CHCl_3/C_2H_5OH$	brown metallic plates	52.25[a]	52.49	4.80	4.89	13.33	12.82
1b	5 h, RT, CH_2Cl_2	95	pet. ether[g]	228	$CHCl_3$/pet. ether	yellow powder	48.17	48.11	4.90	4.64	14.56	14.34
1c	5 h, RT, CH_2Cl_2	90	pet. ether	224	$CHCl_3$/pet. ether	yellow powder	43.24	43.52	5.07	4.92	16.04	15.89
1d	5 h, RT, CH_2Cl_2	75	pet. ether	168	$CHCl_3$/pet. ether	yellow crystals	46.25	46.42	6.96	6.33	14.51	14.62
1e	5 h, RT, CH_2Cl_2	68	pet. ether	180–182	C_2H_5OH/H_2O	brown crystals	51.85	51.56	5.53	5.61	13.22	13.04
1f	5 h, RT, CH_2Cl_2	94	pet. ether	122	$CHCl_3$/pet. ether	brown crystals	34.20	34.02	4.86	4.65	16.41	16.28
1g	10 days, RT, $CHCl_3$	50	ether	168	$CHCl_3$/pet. ether	ocher crystals	49.03[b]	47.53	4.62	4.50	12.52	12.59
1h	65 days, RT, Me_2SO	63	2 years in refrigerator			long red brown needles	41.00	40.76	5.16	5.13	17.38	17.58
1i	24 h, RT, CH_2Cl_2	25	pet. ether	217	C_2H_5OH (ΔT)	orange plates	41.29[c]	41.29	4.56	4.89	20.29	19.55
1j	25 days, RT, Me_2SO	54	C_2H_5OH			yellow powder	33.77	33.79	5.15	5.14	19.71	19.23
1j′[e]	25 days, RT, Me_2SO	66	C_2H_5OH	238	$CHCl_3$	yellow gold plates	30.59	30.76	4.66	4.51	17.84	18.31
1k	5 h, RT, CH_2Cl_2	65	pet. ether	228	$CHCl_3$/pet. ether	yellow crystals	38.95	38.77	4.68	4.46	22.70	22.18
1l	RT, Me_2SO				Me_2SO/-, $CHCl_3$/pet. ether	yellow crystals	46.59	45.84	4.08	4.30	12.07	12.04
1m	10 h, RT, CH_2Cl_2	70	pet. ether	186	$CHCl_3$/pet. ether	red-brown crystals	59.83	59.54	5.96	5.63	10.61	10.21
1n	1 h, 80 °C, Me_2SO	78	H_2O	217	$CHCl_3$/ether	beige powder	41.45	41.53	4.69	4.28	21.02	19.17
1o	0.25 h, RT, CH_2Cl_2	44	pet. ether	241	CH_2Cl_2/pet. ether	yellow powder	51.87[d]	49.68	3.96	3.90	13.75	13.31
1p	10 min, RT, CH_2Cl_2	61	ether with PPh_3	224	CH_2Cl_2/ether with PPh_3	dark red	64.47	63.98	4.27	4.50	8.55	8.17
1q	24 h, RT, $CHCl_3$	59	pet. ether	159–161	$CHCl_3/CH_3OH$	brown needles	58.07	57.96	4.98	4.67	5.97	5.54
2a[h]	90 days, RT, $CHCl_3$	67	pet. ether	225	twice from acetone/pet. ether	light beige powder	40.22	40.87	4.77	5.02	19.25	19.61
2b	29 days, RT, $CHCl_3$	25	ether	215	$CHCl_3$/py/ether	red-beige	42.52	40.15[i]	4.56	4.80[i]	22.04	20.55[i]
2b′[j]	5 days, 65 °C, $CHCl_3$	83	pet. ether			light red	36.35	37.96	4.18	4.59	17.85	17.58
2c[k]	35 days, RT, Me_2SO	72	$CHCl_3$/pet. ether	214		beige	34.35	33.63	5.57	5.74	21.37	22.88
2d	11 days, RT, C_2H_5OH	69	pet. ether			yellow	52.95	52.24	4.87	5.05	14.70	14.21
2e	12 days, RT, CH_2Cl_2	71	ether	160		red-brown	66.57	62.80[l]	4.56	4.85	9.03	8.93
2f[h]	*m*	85	pet. ether	186		light orange	52.22	54.10	3.83	4.09	11.78	12.31

[a] Mol wt: calcd, 735.6; found, 832. [b] Mol wt: calcd, 783.2; found, 774. [c] Mol wt: calcd, 552.2; found, 576.0. [d] Incomplete combustion–burns with a residue. [e] $CHCl_3$ adduct. [f] RT = room temperature. [g] pet. ether = petroleum ether. [h] $CHCl_3$ adduct. [i] Containing $CHCl_3$. [j] Mol wt: calcd, 627.8 ($CHCl_3$ adduct); found, 686. [k] Me_2SO adduct. [l] Incomplete combustion. [m] YCo(Salphen) PPh_3, 20 min in $CHCl_3$ with 3 equiv of py. Y = triaziole $H(C_2H_5O_2C)C_2N_3^-$.

Table V. Reaction Conditions and Physical Properties of the Alkyne Complexes Formed by Reaction of Terminal Alkynes with Cobalt Azido Chelate Complexes[a]

complex	react conditions	pptng solvent	% yield	recrystn solvent	color	elemental anal. % C calcd	% C found	% H calcd	% H found	% N calcd	% N found
6a	1 h, RT, CH_2Cl_2	pet. ether	32	$CHCl_3$/pet. ether	light red brown	45.61	44.99	4.79	4.53	16.63	15.89
6b	7 min, RT, CH_2Cl_2	pet. ether	54		dark red brown						
6c	3 min, RT, $CHCl_3$	pet. ether	39		dark brown	50.50	51.70	5.24	4.92	13.86	14.13
7a	1 day, 65 °C, $CHCl_3$	pet. ether	44	$CHCl_3$/pet. ether	brick red	46.24	45.13	4.29	4.56	13.49	12.87
7b	1 day, 100 °C, Me_2SO	CH_2Cl_2/ pet. ether	64	$CHCl_3$/pet. ether	dark red	63.15	61.57	4.48	4.55	6.90	6.23
8a	1 day, RT, CH_2Cl_2	ether	26	CH_2Cl_2/ether/PPh_3	red brown						

[a] RT = room temperature. pet. ether = petroleum ether.

Table VI. Reaction Conditions and Physical Properties of the Products from the Reaction of Cobalt Azido Chelate Complexes with Nitriles[c]

complex	react conditions	% yield	pptng solvent	dec pt, °C	color	elemental anal. %C calcd	found	%H calcd	found	%N calcd	found
9a	1 h, RT,[b] CH_2Cl_2	21	pet. ether	224	dark red brown	62.18	60.97	3.78	4.11	10.88	10.38
10a	2 days, RT, CH_2Cl_2	64	pet. ether with Ph_3P	199	light brown powder	51.51	52.13[a]	4.11	4.70	18.02	16.21
10b	2 days, RT, CH_2Cl_2	52	ether with Ph_3P	213	dark brown powder	64.94	63.98	3.74	4.55	10.82	10.78
11a	30 days, RT, $CHCl_3$	69	ether with Ph_3P		red brown	59.08	59.18	5.77	4.10	15.57	15.24

[a] CH_2Cl_2 adduct; see Table III for sturctures. [b] RT = room temperature. [c] Recrystallization solvent was CH_2Cl_2/petroleum ether.

All solvents were dried when necessary by standards procedures and stored over Linde 4-Å molecular sieves. Melting points were determined on a Meltemp apparatus and are uncorrected. Elemental analyses were performed by Institut für Anorganische Chemie, München, and by Chemalytics, Inc. Tempe, AZ. Molecular weights have been determined with a Mechrolab osmometer. Infrared spectra were recorded on Perkin-Elmer 599 and 325 spectrometers as Nujol mulls between NaCl plates or as KBr disks. The ^1H NMR spectra were recorded on $CDCl_3$ solutions relative to internal Me_4Si on Varian A 60 and Perkin-Elmer R24-B NMR spectrometers. The azide complexes were prepared as previously[22] described.

B. Syntheses and Reactions. (1) Reactions with Alkynes. To a solution of the azide complex in a suitable solvent was added 2 molar equiv of the alkyne, and the solution was stirred magnetically at room temperature. When the azide stretching frequency could no longer be observed in the infrared spectrum of 1 aliquot taken from these solutions, a precipitating solvent was added, and the precipitate was recrystallized from a suitable solvent. The reaction conditions are given in Table IV.

The following complexes were obtained in a similar manner from reaction of 1.36 g (2m mol) of $PPh_3Co(Salphen)N_3$ with 10 mmol of alkyne in 50 mL of $CHCl_3$ upon addition of petroleum ether.

3a. From 1,4-dichlorobutyne after 65 days at room temperature was obtained 1.2 (65%) of $(ClCH_2)_2(C_2N_3)Co(Salphen)PPh_3{\cdot}CHCl_3$. Anal. Calcd for $C_{43}H_{34}Cl_5CoN_5O_2P$: C, 56.14; H, 3.73; N, 7.61. Found: C, 55.48; H, 4.02; N, 7.45.

4a. From propargyl alcohol after 80 days at room temperature was obtained 1.0 (50%) of $H(HOCH_2)(C_2N_3)Co(Salphen)PPh_3{\cdot}CHCl_3$. Anal. Calcd for $C_{42}H_{34}Cl_3CoN_5O_3P$: C, 59.13; H, 4.03; N, 8.21. Found: C, 59.88; H, 4.72; N, 7.96.

5a. From propargyl bromide after 80 days at room temperature was obtained 0.9 g (47%) of $H(BrCH_2)(C_2N_3)Co(Salphen)PPh_3{\cdot}CHCl_3$.

(2) Substitution Reactions with Terminal Alkynes. To a solution containing the azide complex in a suitable solvent was added 2 molar equiv of the alkyne, and the solution was stirred magnetically until the azide stretching frequency was no longer observable in the infrared spectrum of 1 aliquot of the reaction solution. The reaction conditions and physical properties of the products are given in Table V.

(3) Liberation of Coordinated Triazolate. (a) Concentrated HCl. To a solution containing 0.74 g (1 mmol) of $(CH_3CO_2)_2(C_2N_3)Co(DH)_2PPh_3$ in 50 mL of acetone was added 5mL of concentrated HCl, and the solution was stirred vigorously for 2 days at room temperature. The resultant brown needles of $PPh_3Co(DH)_2Cl$ (mp 220 °C)[64] were removed by filtration, washed with absolute ethanol and petroleum ether, and air-dried. Reduction of the acetone filtrate on a rotary evaporator produced a green oil. The green oil was extracted with hot petroleum ether from which 33 mg (18%) of thin yellow crystals of 4,5-bis(methoxycarbonyl)-1,2,3-triazole, mp 129–130 °C (lit.[34,65] 133–134.5 °C) separated. Similarly, reaction of the triazolate complex with HBr produced the bromide complex $PPh_3Co(DH)_2Br$ and the triazole.

(b) Acetyl Chloride. Similarly, 0.74 g (1 mmol) of $(CH_3CO_2)_2(C_2N_3)Co(DH)_2PPh_3$ was stirred with 1 mL of freshly distilled acetyl chloride for 10 min at room temperature under moisture-free conditions to produce a green oil. The oil was pumped on under high vacuum to remove the acetyl chloride and extracted with 15 mL of absolute diethyl ether, leaving behind green needles of $(Ph_3PO)_2CoCl_2$. To the filtrate was added petroleum ether, and after cooling, a mixture of the acetyltriazole and dimethylglyoxime diacetate precipitated. The mixture was separated by fractional crystallization from diethyl ether/petroleum ether in which the dioxime diacetate is the more soluble. In this way, 48 mg (21%) of $C_8H_9N_3O_5$(ν(C=O) 1790 cm^{-1}) was isolated. Hydrolysis of this acetyltriazole in warm moist petroleum ether afforded 25 mg (14%) of 4,5-bis(methoxycarbonyl)-1,2,3-triazole (mp 130–130.5 °C).

(4) Cycloaddition Reactions with Alkenes. Electron-poor alkenes such as diethyl fumarate, diethyl maleate, maleic anhydride, benzoquinone, and cyclopentadiene dimer were reacted with a variety of azido cobalt chelate complexes $LCo(chelate)N_3$ with the intent of preparing triazoline complexes. In each case the intended triazoline is thermally unstable. In only one case could an analyzable well-characterizeable product be isolated: that being the product of reacton of diethyl maleate and $NH_3Co(DH)_2N_3$.

A solution containing 1.74 g (5 mmol) of $NH_3Co(DH)_2N_3$ and 1.72 g (10 mmol) of diethyl maleate in 70 mL of Me_2SO was heated at 65 °C for 28 days. To a petroleum ether extract of the Me_2SO solution was added 140 mL of $CHCl_3$ producing a black oil. Dissolution of the oil in acetone followed by addition of petroleum ether afforded a light brown precipitate which was filtered, washed with petroleum ether, and dried for 3 h under high vacuum. There was obtained 0.66 g (25%) of $(EtO_2C)_2(H_2C_2N_3)Co(DH)_2NH_3CHCl_3$. Anal. Calcd for $C_{17}H_{28}Cl_3CoN_8O_8$: C, 32.01; H, 4.43; N, 17.57. Found: C, 32.25; H, 5.52; N, 18.02.

(5) Cycloaddition Reactions with Nitriles. An excess of an electron-poor nitrile was reacted with azido cobalt chelate complexes in a suitable solvent, isolated and recrystallized as described in Table VI.

(6) Reactions with Heterocumulenes. The azido cobalt chelate complexes reacted with a variety of heterocumulenes such as isocyanates, thiocyanates, and isothiocyanates to produce five-membered heterocycles by 1,3-dipolar cycloadditions that were usually not isolable because of the decomposition of the five-membered ring (see, for example, ref 60). From the reaction of $CH_3SC{\equiv}N$ with $PPh_3Co(DH)_2N_3$, there was obtained the cyano complex $CH_3SCNCo(DH)_2CN$ as follows: A solution containing 2.97 g (5.0 mmol) of $PPh_3Co(DH)_2N_3$ and 0.7 g (10 mmol) of CH_3SCN in 50 mL of $CHCl_3$ was refluxed for 51 days at which time the azide stretching frequency had disappeared. Addition of petroleum ether to the solution precipitated a yellow solid which was filtered, washed with petroleum ether, and air-dried; 66% $CH_3SCNCo(DH)_2CN$. Anal. Calcd for $C_{11}H_{17}CoN_6O_4S$: C, 34.02; H, 4.42; N, 21.65. Found: C, 33.58; H, 5.48; N, 19.90 (see reaction 8).

(7) Other Reactions. (a) Isocyanate complexes were prepared by metathesis of the corresponding chloro complex with NaNCO in $CHCl_3/CH_3OH$ or by heating a solution of the azide complex at 50 °C in $CHCl_3$ or THF under 40 atm of CO. In each case the isocyanate complex was recrystallized from $CHCl_3$. Anal. Calcd for $C_{27}H_{29}CoN_5O_5P$ (**12a**, $PPh_3Co(DH)_2NCO$, dark brown): C, 54.64; H, 4.93; N, 11.80. Found: C, 52.95, 52.68; H, 4.94, 4.79; N, 12.09, 11.21. Anal. Calcd for $C_{14}H_{19}CoN_6O_5$ (**12b**, $pyCo(DH_2)NCO$, beige powder): C, 40.95; H, 4.66; N, 20.48. Found: C, 41.32, 41.06; H, 4.36, 5.33; N, 19.25, 18.47.

(b) Reactions with CS_2. A suspension of $PPh_3Co(DH)_2N_3$ or $pyCo(BAE)N_3$ in 100 mL of CS_2 was stirred for 22 h. During this time no evolution of N_2 occurred, the azide stretching frequency was still present, and upon removal of the CS_2 on a rotary evaporator the complexes were recovered unchanged.

(c) Reactions with Acids. Treatment of the azide complexes with HCl liberated HN_3 and produced the chloride complexes as follows: HCl gas was bubbled through an acetone solution containing either 0.59 g (1 mmol) of $PPh_3Co(DH)_2N_3$ or $pyCo(DH)_2N_3$ to produce

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(64) G. N. Schrauzer, *Inorg. Synth.*, **11**, 61 (1968).

(65) V. G. Ostroverkhov and E. A. Shilov, *Chem. Abstr.*, **52**, 7828 (1958).

0.25 g (43%) (mp 208 °C) of dark brown crystals of $PPh_3Co(DH)_2Cl$ or 0.25 g (57%) (mp 248 °C) of light brown crystals of $pyCo(DH)_2Cl$.

Anal. Calcd for $PPh_3Co(DH)_2Cl$ ($C_{26}H_{29}ClCoN_4O_4P$): C, 53.19; H, 4.98; N, 9.95. Found: C, 53.27; H, 5.45; N, 9.24. Molecular weight for $PPh_3Co(DH)_2Cl$: calcd, 587.0; found ($CHCl_3$), 625.0.

Anal. Calcd for $pyCo(DH)_2Cl$ ($C_{13}H_{19}ClCoN_5O_4$): C, 38.68; H, 4.74; N, 17.35. Found: C, 38.64; H, 4.57; N, 16.93.

If these same complexes are left in contact with concentrated aqueous HCl for a long time, $CoCl_2{\cdot}6H_2O$ precipitates.

Treatment of 0.53 g (1 mmol) of $PPh_3Co(DH)_2N_3$ or 0.41 g (1 mmol) of $pyCo(DH)_2N_3$ in 50 mL of acetone with 5 mL of 70% $HClO_4$ produces upon addition of ether $[PPh_3Co(DH)_2]^+ClO_4^-$ or $[pyCo(DH)_2]^+ClO_4^-$. Addition of $NaBPh_4$ in ethanol to the $[PPh_3Co(DH)_2]^+ClO_4$ solution precipitates $[PPh_3Co(DH)_2]^+BPh_4^-$ as follows. Anal. Calcd for $C_{26}H_{29}ClCoN_4O_8P$ (0.51 g, 79%; $[PPh_3Co(DH)_2]^+ClO_4^-$: C, 47.97; H, 4.50; N, 8.61. Found: C, 46.88; H, 4.78; N, 7.97. Anal. Calcd for $C_{13}H_{19}ClCoN_5O_8$ (0.33 g, 72%; $[pyCo(DH_2)]^+ClO_4^-$): C, 34.41; H, 4.23; N, 12.35. Found: C, 34.07; H, 5.01; N, 11.94. Anal. Calcd for $C_{50}H_{49}BCoN_4O_4$ (0.54 g, 88%; $[PPh_3Co(DH)_2]^+BPh_4^-$): C, 71.51; H, 5.89; N, 6.67. Found: C, 69.24; H, 5.04; N, 7.19.

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Registry No. **1a**, 80462-11-9; **1b**, 80462-10-8; **1c**, 80462-09-5; **1d**, 80462-08-4; **1e**, 80462-07-3; **1f**, 80462-06-2; **1g**, 80462-05-1; **1h**, 80462-04-0; **1i**, 80462-03-9; **1j**, 80462-02-8; **1k**, 80462-01-7; **1l**, 80462-00-6; **1m**, 80461-98-9; **1n**, 80461-97-8; **1o**, 80462-40-4; **1p**, 80462-38-0; **1q**, 80462-37-9; **2a**, 80462-36-8; **2b**, 80462-35-7; **2c**, 80462-34-6; **2d**, 80462-33-5; **2e**, 80462-31-3; **2f**, 80462-30-2; **3a**, 80462-39-1; **4a**, 80462-29-9; **5a**, 80462-28-8; **6a**, 80462-27-7; **6b**, 80462-26-6; **6c**, 80462-25-5; **7a**, 80462-24-4; **7b**, 80462-23-3; **8a**, 80462-22-2; **9a**, 80462-21-1; **10a**, 80471-14-3; **10b**, 80462-20-0; **11a**, 80462-19-7; **12a**, 77172-84-0; **12b**, 30786-24-4; 1,4-dichlorobutyne-2, 821-10-3; propargyl alcohol, 107-19-7; propargyl bromide, 106-96-7; 4,5-bis(methoxycarbonyl)-1,2,3-triazole, 707-94-8; diethyl maleate, 141-05-9; $C_8H_9N_3O_5$, 80461-78-5; $(EtO_2C)_2(H_2C_2N_3)Co(DH)_2NH_3$, 80462-18-6; $CH_3SCNCO(DH)_2CN$, 80462-53-9; $PPh_3Co(DH)_2Cl$, 23295-34-3; $pyCo(DH)_2Cl$, 23295-32-1; $[PPh_3Co(DH)_2]^+ClO_4^-$, 80462-52-8; $[pyCo(DH)_2]^+ClO_4^-$, 80513-21-9; $[PPh_3Co(DH)_2]^+BPh_4^-$, 80462-51-7; $PPh_3Co(DH)_2N_3$, 69879-86-3; $MePPh_2Co(DH)_2N_3$, 80462-49-3; $Me_2PPhCo(DH)_2N_3$, 80462-48-2; $PBu_3Co(DH)_2N_3$, 51194-39-9; $P(Bzl)_3Co(DH)_2N_3$, 80462-47-1; $P(OCH_3)_3Co(DH)_2N_3$, 61024-83-7; $P(OPh)_3Co(DH)_2N_3$, 70106-13-7; $PhNH_2Co(DH)_2N_3$, 66496-40-0; $pyCo(DH)_2N_3$, 56589-86-7; $NH_3Co(DH)_2N_3$, 66496-39-7; 1-MeImCo$(DH)_2N_3$, 80462-46-0; $AsPh_4[Co(DH)_2(N_3)_2]$, 43128-64-9; $PBu_3Co(DPH)_2N_3$, 80462-45-9; $[Co[(DO)(DOH)pn](N_3)_2]$, 69879-56-7; $PPh_3Co(Salen)N_3$, 70106-20-6; $PPh_3Co(Salphen)N_3$, 62858-89-3; *cis*-$PPh_3Co(acac)_2N_3$, 70100-51-5; $pyCo(Salphen)N_3$, 69907-81-9; $CH_3CO_2C{\equiv}CCO_2CH_3$, 762-42-5; $HC{\equiv}CCO_2Et$, 623-47-2; $HC{\equiv}CC(O)H$, 624-67-9; $HC{\equiv}CCH(O_2CCH_3)_2$, 67088-67-9; $NCCF_3$, 353-85-5; $NCCO_2C_2H_5$, 623-49-4; $NCCH_2CN$, 109-77-3.

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Electron Transfer. 51. Reactions of Riboflavin Radicals with Metal-Center Oxidants[1]

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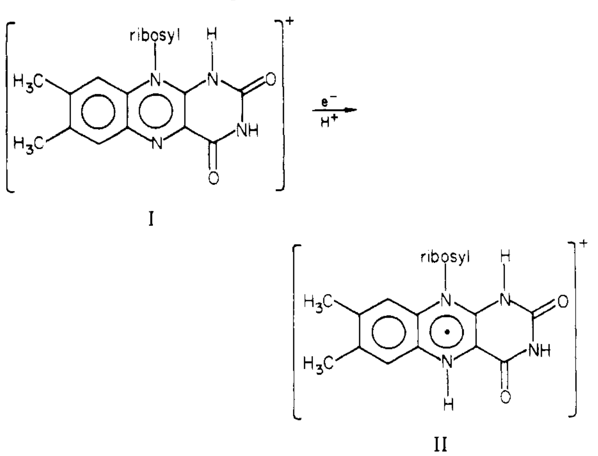
Riboflavin undergoes successive one-electron reductions by Eu^{2+} or V^{2+} in aqueous $HClO_4$, giving first the radical ion, II, and then the dehydro compound, III. Specific rates (21 °C, 0.12 M $HClO_4$) for the two V^{2+} reductions are 8.0×10^4 and 3.6×10^4 M^{-1} s^{-1}, both far above the substitution-controlled upper limit for inner-sphere V(II) reactions. Calculated formal potentials for the two reductions in 1 M H^+ are 0.220 and 0.150 V. Rates of reactions of the radical cation Rb· with Hg^{2+}, $(NH_3)_5CoBr^{2+}$, and the *N*,*N*-dimethylnicotinamide derivative of $(NH_3)_5Co^{III}$ (IV) are inversely proportional to $[H^+]$ (in the range of 0.7–1.3 M H^+), indicating that the flavin radical cation is undergoing partial deprotonation to the active reducing species. Reactivity patterns for reductions of $(NH_3)_5Co^{III}$ complexes by the radical are devoid of those substituent effects that characterize inner-sphere reductions by transition-metal centers but resemble instead the pattern for reductions by the outer-sphere reagent $Ru(NH_3)_6^{2+}$. This similarity, in conjunction with the characterization of the oxidation product as riboflavin (with the ring system apparently unaltered), indicates that reductions by Rb· of these complexes follow outer-sphere paths. Specific rates of reaction of Rb· (25 °C, 1.3 M $HClO_4$) with the oxidizing metal centers Fe^{3+}, Tl^{3+}, Cu^{2+}, Hg^{2+}, VO^{2+}, and UO_2^{2+} are not related simply to oxidation potential, ionic charge, electronic structure, self-exchange rates, or the accessibility of an oxidation state lying one unit below.

Among the oxidation coenzymes, flavin derivatives rank second to none in importance and diversity of role.[2] Much of their versatility reflects the ease with which the isoalloxazine unit, a general feature of the class, can participate in both one- and two-electron transactions, leading to the ability to mediate between electron-transfer processes and the even-electron processes characterizing metabolic conversions.

The impetus for the present work, which deals principally with the reactions of protonated riboflavin (I) and its reduced radical cation or semiquinone derivative (II) with metal-centered electron-transfer species, was the expectation that flavins, because of their dual redox functionality, might catalyze re-



I

II

(1)

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[2] See, for example: (a) Walsh, C. *Annu. Rev. Biochem.* **1978**, *47*, 881. (b) Metzler, D. E. "Biochemistry"; Academic Press: New York, 1977; p 476. (c) Hemmerich, P. *Adv. Chem. Ser.* **1977**, *No. 162*, 312. (d) Mayhew, S. G.; Ludwig, M. L. *Enzymes, 3rd Ed.* **1975**, *12*, 47. (e) Hemmerich, P.; Veeger, C.; Wood, H. C. S. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 671.

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