Journal of Organometallic Chemistry, 369 (1989) 55–68
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09862

Chromium, tungsten, iron, and ruthenium complexes of the 4-membered ring diazene 3,4-diazatricyclo[4.2.1.0^{2,5}]non-3-ene

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(Received September 16th, 1988)

Abstract

The 4-membered ring diazene 3,4-diazatricyclo[4.2.1.0^{2,5}]non-3-ene (dtn) reacts with Cr and W carbonyls to give the complexes $M(CO)_5(dtn)$ (Ia,b), $[M(CO)_5]_2(dtn)$ (IIa,b), $M(CO)_4(dtn)_2$ (IIIa,b), $[M(CO)_4]_2(dtn)_2$ (IVa,b), and $[M(CO)_3]_2(dtn)_3$ (Va,b) where a = Cr and b = W. ^1H and ^{13}C NMR provide evidence that compounds III–V each exist in the predicted two isomeric forms and full assignment of the resonances is made for all but the Va ^{13}C spectrum. $Fe_2(CO)_9$ reacts with dtn to give $Fe(CO)_4(dtn)$ (Ic) and $Fe_3(CO)_9(dtn)$ (VIIIc). It is argued that steric effects from the hydrocarbon portion, notably C(9), of dtn prevents formation of the normally stable diiron complexes $Fe_2(CO)_6(dtn)$ (VIc) and $Fe_2(CO)_7(dtn)$ (VIIc). $Ru_3(CO)_{12}$ and dtn react to form only $Ru_3CO)_9(dtn)$ (VIIId). Variable temperature ^{13}C NMR studies reveal CO scrambling in VIIIc and VIIId at room temperature, which ceases at low temperature. Results for the dtn complexes are compared with results for another 4-membered ring diazene ligand as well as with results for 3-, 5-, and 6-membered ring diazenes.

Introduction

The reactions of cyclic *cis* diazene (azo) compounds with metal carbonyl systems have provided a large variety of complexes [1–10]. Studies with three-, four-, five-, and six-membered diazene rings reveal that the types of complexes formed depend strongly on the ring size. The differences in complex types and their stability have been attributed both to geometric effects arising from the orientation of the σ-bonding nitrogen lone pairs and to the donor strength of the lone pairs as indicated by the character of the highest occupied molecular orbital [1,6,7]. The cyclic structure of the ligand usually is retained in these complexes, but ring opening has been observed in some instances with the three-membered rings [9,10]. Complexes characterized which retain the diazene ring can be represented by structures I–VIII, where M represents a metal carbonyl group.

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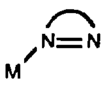

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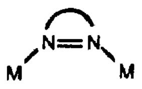

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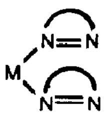
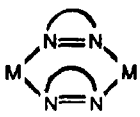


III



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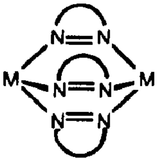

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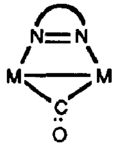
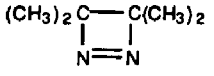


VI

VII

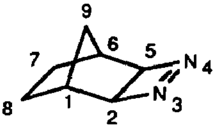
VIII

The four-membered ring system was the last to be investigated with only studies on 3,3,4,4-tetramethyl-1,2-diazetine (tmd) having been reported [6,7]. This is not surprising given the difficulty of synthesizing such compounds in quantity. However,



3,3,4,4-tetramethyl-1,2-diazetine

(tmd)



3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-3-ene

(dtn)

it is unfortunate since the four-membered rings appear to be at the transition point between the very different reactivity exhibited by the small three-membered rings compared to the larger five- and six-membered rings. Herein we report on the reactions of 3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-3-ene (dtn) with Cr, W, Fe, and Ru carbonyls which show some significant differences from reactions with tmd. In particular, our results extend the range of complexes formed with Cr for a four-membered diazene ring, provide the first evidence for isomers in complexes of types III–V for any size diazene ring, and show major differences from tmd in the types of Fe complexes formed.

Results

Cr and W complexes

Complexes of types I–V are readily synthesized for both Cr and W by the methods summarized in eqs. 1–3.

$$M(CO)_5(THF) + dtn \xrightarrow[\text{r.t.}]{\text{THF}} \underset{\text{(I)}}{M(CO)_5(dtn)} + \underset{\text{(II)}}{[M(CO)_5]_2(dtn)} \tag{1}$$

$$M(CO)_4(C_7H_8) + dtn \xrightarrow[\text{r.t.}]{\text{hexane or benzene}} \underset{\text{(III)}}{M(CO)_4(dtn)_2} + \underset{\text{(IV)}}{[M(CO)_4]_2(dtn)_2} \tag{2}$$

$$M(CO)_3(RCN)_3 + dtn \xrightarrow[\Delta]{hexane} \underset{(V)}{[M(CO)_3]_2(dtn)_3} \qquad (3)$$

For I–V: a: M = Cr; R = CH_3
b: M = W; R = CH_3CH_2

In reaction 1 equimolar amounts of reactants or excess dtn gives I as the dominant product, while II dominates with a 2/1 or greater molar ratio of $M(CO)_5(THF)$ to dtn. Pure I can be obtained from the less volatile II by sublimation, while II is obtained pure by crystallization from the more soluble I. Both compounds are also stable to chromatography, but do not separate cleanly because of their similar elution characteristics.

In reaction 2 a $M(CO)_4$(norbornadiene) to dtn molar ratio of 1/2 or less provides mostly III and a 1/1 ratio or higher gives predominantly IV. Only IIIb is stable to chromatography and can be separated from the mixture, including unreacted $M(CO)_4$(norbornadiene), by that means. The solubility of III and insolubility of IV in saturated hydrocarbon solvents offers another means of separating these compounds.

If reactions 1 and 2 are carried out at higher temperatures, V eventually results. However, the best procedure to obtain V is to reflux a 2/3 molar mixture of dtn and $M(CO)_3(RCN)_3$ in hexane as in reaction 3, followed by crystallization.

Physical and analytical data on the compounds are presented in Table 1. Many of the compounds gradually lose color on heating without melting, probably due to dtn decomposition, which also occurs for uncoordinated dtn [11]. Compounds have the same color in solution as in the solid except for V, which is a rich burgundy in polar solvents such as CH_2Cl_2. All of the compounds are stable as solids except Ia, which decomposes slowly even at $-25°$C under nitrogen.

Spectroscopic data are presented in Tables 2–4. The infrared spectra in the carbonyl stretching region (Table 2) are consistent with the assigned structures and generally similar to compounds of analogous types previously reported [1,3,4,7,8]. The best resolved and therefore most useful proton NMR signals (Table 3) are those due to the hydrogen atoms of the bridgehead positions 2,5 and 1,6. Their proximity to the coordinated nitrogen atom(s) also makes them the most sensitive to coordination effects. These protons generally appear as singlets or have very small additional splitting due to dihedral angles with neighboring protons that lead to coupling constants close to zero. A common feature in the ^{13}C NMR spectra (Table 4) is the significant downfield shift of the carbon atom adjacent to a coordinated nitrogen. Otherwise the shift differences within a given type of carbon, e.g. C(7,8) are not large and we have not attempted to assign them to individual atoms.

In the type I compounds coordination at only one nitrogen atom breaks the symmetry of the dtn molecule and separate resonances are observed for the 1,2,5, and 6 protons. Individual resonances for each carbon atom in dtn also are seen in the ^{13}C spectrum.

In the dtn bridged type II compounds dtn is in a symmetric environment, giving only one resonance each for the 2,5 and 1,6 proton sets. The ^{13}C spectrum also shows the four resonances expected for a symmetrically coordinated dtn and only two carbonyl carbon resonances for the equivalent $M(CO)_5$ groups.

The compounds of types III–V are each capable of existing in two isomeric forms since one of the dtn carbons bridges is two carbons long (C(7,8)), while the other

Table 1

Physical and analytical data

Compound	Color	M.p. [a] (°C)	Elemental analysis (Found (Calc.)(%))		
			C	H	N
Ia	gold	51–53	45.96	3.23	8.87
			(45.87)	(3.21)	(8.91)
Ib	yellow	73–75	31.73	2.68	6.08
			(32.31)	(2.26)	(6.28)
IIa	dark red	~115	40.08	2.05	5.45
			(40.33)	(1.99)	(5.53)
IIb	dark red	~150	26.61	1.35	3.59
			(26.52)	(1.31)	(3.64)
IIIa	red-brown	78–80	53.01	4.99	13.70
			(52.94)	(4.94)	(13.72)
IIIb	red-orange	85–86	40.03	3.76	10.30
			(40.02)	(3.73)	(10.37)
IVa	dark red	~195	46.06	3.60	9.71
			(46.16)	(3.52)	(9.79)
IVb	dark red	~210	31.76	2.49	6.60
			(31.60)	(2.41)	(6.70)
Va	red-brown	~155	50.90	4.78	13.13
			(50.79)	(4.74)	(13.16)
Vb	deep violet	~200	36.05	3.43	9.25
			(35.94)	(3.35)	(9.31)
VIIIc	green	~90	34.83	2.79	4.93
			(35.47)	(1.86)	(5.17)
VIIId	group	~90	27.71	1.59	4.03
			(28.36)	(1.49)	(4.13)

[a] Where only a single temperature is given the compound gradually loses color without melting, and the temperature is an estimate of onset of color loss.

Table 2

Infrared carbonyl stretching frequencies [a]

Compound	ν(CO) (cm^{-1}) [b]
Ia	2072m, 1994m, 1951vs, 1935s
Ib	2078m, 1988m, 1947vs, 1934s
Ic	2060m, 1985s, 1967s, 1949s
IIa	2081w, 2055m, 2000mw, 1944w,sh, 1970s, 1950vs, 1934m
IIb	2087w, 2056m, 1995mw, 1989w,sh, 1966s, 1948vs, 1929m
IIIa	2020m, 1916s, 1885m
IIIb	2021m, 1909s, 1885m
IVa [c]	2036w, 1999s, 1949vs, 1924vs, 1882s
IVb [c]	2040w, 1998vs, 1946vs, 1920vs, 1880s
Va [c]	1902vs, 1858m
Vb [c]	1899vs, 1854m
VIIIc	2075m, 2050w, 2039w, 2025vs, 2018vs, 1995vs, 1986m, 1974w
VIIId	2082m, 2054w, 2041vs, 2038vs, 2020w, 2006m, 1996m, 1989m, 1985m

[a] Hexane solvent unless otherwise noted. [b] Abbreviations: m, medium; s, strong; w, weak; v, very; sh, shoulder. [c] CH_2Cl_2 solvent.

Table 3

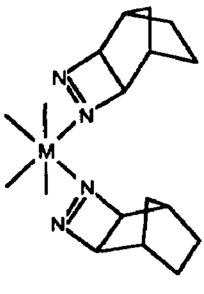
^{1}H NMR shifts in $CDCl_3$ vs. TMS

Compound	H(1), H(6)	H(2), H(5)	H(7), H(8) [a]	H(9), H(9′) [b]
dtn	2.42m	4.40d ($J \sim 0.6$)	1.60m, 0.93dm	1.22m
Ia	2.53d, 2.49m	4.56qt, 4.33qt	1.65dm, 0.98qt	1.28ABqt
Ib	2.58m, 2.53m	4.70qt, 4.34qt	1.67dm, 1.02dm	1.31ABqt
IIa	2.76s	4.53s	1.73d, 1.1m	1.50m, 1.1m
IIb	2.76s	4.55s	1.76d, 1.2m	1.55m, 1.2m
IIIa	2.65s, 2.47s	4.64m, 4.30qt	1.63m, 0.98d	1.32s
IIIb	2.60s, 2.53s	4.71qt, 4.26qt	1.64dm, 1.00d	1.33s
IVa	2.67s	4.46s	1.67d, 1.05d	1.47d, 1.28d
IVb	2.64s	4.29s, 4.26s [c]	1.66d, 1.07d	1.41ABqt
Va-1	2.68s	4.42s		
			{1.60d, 1.34m, 1.0m} [d]	
Va-2	2.73s, 2.63s	4.46s, 4.34s, 4.32s		
Vb-1	2.69s	4.31s		
			{1.84d, 1.65m, 1.48d, 1.0m} [d]	
Vb-2	2.75s, 2.61s	4.35s, 4.24s4.22s		
VIIIc	2.81s	4.50s	1.76d, 1.08d	2.72d, 1.86d
	2.83s [e]	4.54s [e]	1.76d, 1.09d [e]	2.71d, 1.88d [e]
	2.77s [f]	4.50s [f]	1.65d, 1.00d [f]	2.50d, 1.81d [f]
VIIId	2.70s	4.58s	1.69m, 1.06d	2.53d, 1.70dm
	2.71s [g]	4.60s [g]	1.66d, 1.06d [g]	2.43d, 1.69d [g]

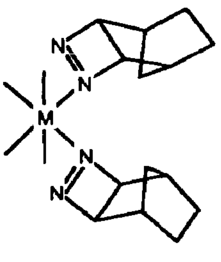
[a] Coupling constants for doublets are ~ 8 Hz. [b] Coupling constant for doublets or AB quartets fall in the range of 10–13 Hz. [c] Each signal corresponds to a different isomer.[d] These signals could not be assigned to individual isomers. [e] In CD_2Cl_2. [f] In CD_2Cl_2 at −90 °C. [g] At −55 °C.

bridge has only one carbon (C(9)). No evidence for these isomers was noted in the synthesis and purification process. However, there is clear NMR evidence for both isomers in each compound type.

The ^{1}H NMR spectra of the type III compounds are similar to those for type I. The carbon spectra also are similar to I except that in IIIa one of the C(2,5) resonances and one of the C(1,6) resonances are split into doublets while in IIIb one of the C(2,5) resonances and both of the C(1,6) resonances are doublets. We attribute these splittings to small differences in the two bridgehead carbon atoms adjacent to the coordinated nitrogen atom in the isomers III-1 and III-2, which are present in equal amounts. Apparently the more remote 7, 8, and 9 carbon atoms do not differ enough to give separate signals in the isomers. The two dtn ligands within an isomer may or may not be equivalent, depending on their relative conformations. Since there is only one signal for each isomer, free rotation about the M–N bond



III-1



III-2

Table 4

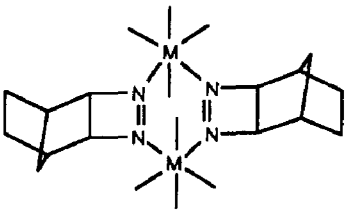
^{13}C NMR spectral data

Compound	C(2), C(5)	C(1), C(6)	C(7), C(8)	C(9)	CO [a]
dtn	83.83	32.054	23.94	29.90	
Ia	92.41, 83.89	33.86, 33.84	24.28, 23.30	30.01	220.88(t), 213.92(c)
Ib	93.18, 83.85	33.99, 34.05	24.38, 23.09	30.14	202.82(t), 196.86(c)
IIa	92.47	36.60	24.04	29.69	221.39(t), 213.42(c)
IIb	92.76	36.92	24.06	30.01	202.93(t), 196.13(c)
IIIa [b]	90.75 [c], 90.87 [c] 82.75	33.99 [c], 34.05 [c] 33.90	24.48br, 23.43	30.16	226.93(t), 214.69(c)
IIIb [b]	91.85 [c], 91.94 [c] 83.36	34.14 [c], 34.10 [c] 33.95 [c], 33.91 [c]	24.55, 23.18	30.16	212.18(t), 201.39(c)
IVa-1	89.99	36.28	23.92	30.05	226.89(t) {217.41(c), 216.41(c), 215.78(c)} [d]
IVa-2	89.88	36.19	23.92	30.17	226.89(t)
IVb-1	91.14	36.37	23.71	30.29	212.10(t) {203.19(c), 202.72(c), 202.37(c)} [d]
IVb-2	91.11	36.32	23.71	30.37	212.04(t)
Va [b]	88.60, 88.52 88.20, 88.19	35.76, 35.71 35.09br	23.64, 23.54	30.43, 30.34 30.11, 30.01	231.64, 230.21, 229.81, 229.74
Vb-1	89.85	35.98	23.24	30.25	217.54
Vb-2	90.17, 89.94 89.65	35.24	23.33	30.68, 30.52	217.92, 217.73, 217.29
VIIIc	89.52 89.01 [e]	40.05 39.59 [e]	23.54 22.78 [e]	33.58 33.02 [e]	210.73 (215.42, 211.44, 210.93, 200.40) [e]
VIIId	87.15 86.97 [f]	40.59 40.59 [f]	23.45 23.42 [f]	33.65 33.73 [f]	195.70 (203.76, 196.04, 194.43, 187.42) [f]

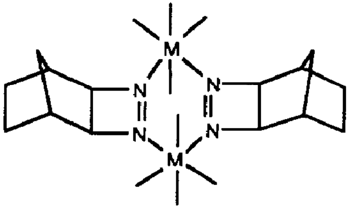
[a] t, a CO *trans* to dtn; c, a CO *cis* to dtn. [b] Signals originate from two isomers which cannot be individually assigned. [c] One of a pair of equally intense doublets. [d] Resonances cannot be assigned to an individual isomer. [e] At −90 °C in CD_2Cl_2. [f] At −55 °C.

must render the dtn ligands within a given isomer equivalent on average. Because the isomers are present in about equal amounts we are unable to use intensity patterns to assign a set of resonances to a particular isomer. The carbonyl groups in the two isomers for a given metal are apparently very similar, since only two signals due to the CO carbons are observed for the isomeric mixture.

In the two possible isomers of type IV one has both dtn ligands with the CH_2 bridge oriented in the same sense around the M–M axis (IV-1), while the other has them oriented opposite to one another (IV-2). Within each isomer the dtn ligands are equivalent and symmetric. Only the W compound IVb gives evidence of an



IV-1

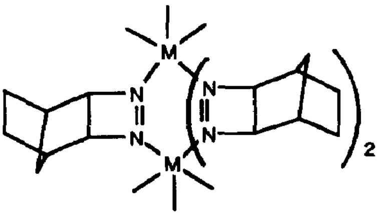


IV-2

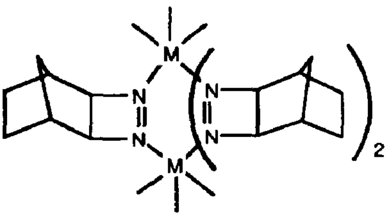
isomeric mixture in the ^{1}H spectrum with the two closely spaced and equally intense signals for the 2,5 protons. However, in the ^{13}C spectrum both IVa and IVb have two resonances for C(2,5), for C(1,6), and for C(9). The grouping of the dtn signals for a given isomer is based on the fact that one signal in each pair is more intense than the other. However, the assignment of a specific isomer is based on analysis of the resonances due to the carbonyl groups.

In isomer IV-1 the carbonyls *trans* to dtn are all equivalent as are the *cis* carbonyls. Thus, two ^{13}C resonances are expected for the COs. In isomer IV-2 the *trans* carbonyls are again all equivalent, but the *cis* carbonyls fall into two groups, so that three ^{13}C signals are expected. The spectrum of IVb exhibits the five carbonyl resonances expected of the isomeric mixture, but IVa has only four resonances due, we believe, to coincidence of the *trans* signals. Even in IVb the *trans* signals are barely resolved. If IV-1 and IV-2 were present in equal amounts, the intensity of the two *trans* CO resonances should be the same *and* the *cis* CO resonance due to IV-1 should be twice the intensity of the two *cis* CO resonances due to IV-2. Since the three *cis* resonances are of comparable intensity in both IVa and IVb, it appears that the IV-1 isomer is present in roughly half the abundance of the IV-2 isomer, and the more intense dtn signals must be due to IV-2. However, because the CO resonances are of comparable intensity, it is not possible to say which one belongs to IV-1 and which two belong to IV-2.

In the two possible isomers of type V one has all three dtn ligands with the CH_2 bridge arranged in the same sense around the M–M axis (V-1), while the other isomer has one dtn opposed to the sense of the other two (V-2). In V-1 all three dtn ligands are equivalent, while in V-2 each dtn is unique. Likewise, all of the carbonyl groups are equivalent in V-1, but they fall into three groups of two each in V-2. The ^{1}H spectra of Va and Vb each show four signals due to the 2,5 protons, consistent with the presence of both isomers. The intensity pattern for these protons was the same for different preparations of Va, but the resonance at 4.31 ppm varied for different preparations of Vb. Accordingly, we assign the 4.31 ppm feature to the Vb-1 isomer and the three equally intense resonances at 4.35, 4.24, and 4.22 ppm to the Vb-2 isomer. The resonances due to the 1,6 protons are broader and only three in number. The intensity of the 2.69 ppm resonance correlates with the 4.31 ppm resonance and therefore also is assigned to the Vb-1 isomer. The 2.61 and 2.75 ppm signals are then assigned to the Vb-2 isomer with the 2.61 ppm signal being due to two of the dtn ligands because of the 2/1 intensity ratio. The assignment of the Va isomers is made by analogy. On statistical grounds alone the ratio of V-1/V-2 would be 1/3 which is what is found for the Cr case. Some preparations of Vb also gave this distribution, but most had a greater abundance of Vb-1.



V - 1



V - 2

The ^{13}C spectra of Va and Vb also show clearly the effect of an isomeric mixture.

In this case separate signals for the bridging carbons of dtn also are seen with four resonances for the C(9) but only two for the C(7,8) set. Intensity pattern variations of the dtn resonances for different preparations permit assigning the Vb isomers with confidence, but the data do not allow us to do so for Va. Both Va and Vb exhibit the four signals expected in the carbonyl region. The assignment of the 217.54 ppm resonance to Vb-1 is based on its higher intensity, leaving the other three resonances of equal intensity for Vb-2. However, the four carbonyl resonances in the Va spectrum are all of comparable intensity, so it is not possible to associate them with a specific isomer.

Fe and Ru compounds

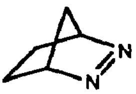
The reaction of dtn with $Fe_2(CO)_9$ provides two products in low yields, $Fe(CO)_4(dtn)$ (Ic: $M = Fe(CO)_4$) and $Fe_3(CO)_9(dtn)$ (VIIIc: $M = Fe(CO)_3$ (eqn. 4).

$$Fe_2(CO)_9 + dtn \xrightarrow[0\text{–}25\,°C]{\text{hexane or THF}} \underset{(Ic)}{Fe(CO)_4(dtn)} + \underset{(VIIIc)}{Fe_3(CO)_9(dtn)} \qquad (4)$$

At 0 °C in THF or at ≤ 10 °C in hexane Ic is virtually the only product, while at room temperature VIIIc is the dominant product. Infrared monitoring of these reactions gave no evidence for other products and only two bands were observed during chromatography, even at -10 °C. VIIIc also is obtained from photolysis of dtn and $Fe(CO)_5$, but only decomposition materials are obtained from refluxing dtn and $Fe_3(CO)_{12}$ in hexane.

Attempts to obtain Ic analytically pure were unsuccessful due to its low stability. However, its identity is clear based on its infrared spectrum in the carbonyl stretching region (Table 2), which resembles that of other $Fe(CO)_4$(diazene) complexes [1,6]. In solution it gradually decomposes to materials that include $Fe(CO)_5$ and VIIIc based on infrared spectral monitoring.

The reason for an irregularly high hydrogen analysis for VIIIc is unclear. However, its color, the ν(CO) spectrum (Table 2), and the proton and carbon NMR spectral patterns (Tables 3 and 4) are all similar to those of $Fe_3(CO)_9$(2,3-diazabicyclo[2.2.1]hept-2-ene) [9] whose structure has been confirmed by X-ray crystallography [12]. Spectroscopic data (Tables 2–4) for $Ru_3(CO)_9(dtn)$ (VIIId), which is obtained in low yield by refluxing a 1/1 mixture of dtn and $Ru_3(CO)_{12}$ in hexane, also are similar to the DBH analog [9]. The equivalence of the 2 and 5 protons and of the 1 and 6 protons in the ^1H NMR and the presence of only four resonances for dtn in the ^{13}C spectrum support a symmetrically coordinated in both VIIIc and VIIId. These features do not change significantly with temperature. In contrast the signals due to the carbonyl groups change significantly with temperature. At room temperature both compounds show only a single CO related resonance, but at a sufficiently low temperature four signals are observed. At -55 °C VIIId shows peaks at 203.76, 196.04, 194.43, and 187.42 ppm in the intensity ratio of 2/3/2/2.



2,3-diazabicyclo[2.2.1]hept-2-ene

(DBH)

VIIIc requires a lower temperature to develop fully a similar pattern and at −90 °C has signals at 215.42, 211.44, 210.93, and 200.40 ppm in the intensity ratio of 2/2/3/2. A careful study of the more stable VIIId revealed that with increasing temperature the 196.04 ppm signal is unaffected except for a slight upfield shift, while the other three signals broaden and diminish in intensity until at about 0 °C they are no longer visible. Attempts to obtain spectra of either VIIIc or VIIId much above room temperature were complicated by decomposition. At 55 °C the ^{13}C spectrum of VIIId did show a single carbonyl resonance at 195.60 ppm, but it was relatively weak and the sample developed much solid decomposition material.

These NMR data are similar to those for the analogous DBH complexes [9] and suggest that VIIIc and VIIId have the structure previously determined for $Fe_3(CO)_9(DBH)$ [12]. In this structure the four-membered ring would be positioned perpendicular to the triangular $M_3(CO)_9$ base with the N–N bond parallel to one of the M–M bonds. The metal centers are then divided into two equivalent $M(CO)_3$ and one unique $M'(CO)_3$ unit. This places the dtn in a symmetrical position. The carbonyl ^{13}C NMR data are then interpreted as for the DBH complexes [9]. At low temperature the two $M(CO)_3$ groups are static and divide into three sets of two COs, each set giving rise to one of the NMR signals of relative intensity two. The three COs on the unique $M'(CO)_3$ either are undergoing rapid mutual exchange, even at low temperature, or have accidentally coincidental shifts and give rise to the signal of relative intensity three. With increasing temperature the COs on the two $M(CO)_3$ groups undergo mutual exchange, but not with the $M'(CO)_3$ group. Eventually these six carbonyls should provide a single sharp resonance, but decomposition appears to set in before this attained.

Discussion

Cr and W compounds

Dtn readily forms the complete set of compound types I–V with both Cr and W carbonyls. This observation confirms the conclusions based on the tmd compounds concerning the coordination properties of 4-membered diazene rings compared with the smaller 3-membered rings and the larger 5- and 6-membered rings [7]. The decreased stability of the IV and V dtn compounds to chromatography contrasts with the stability of the analogous DBH compounds [8] and is another indication that multiply bridged compounds become less favored with decreasing diazene ring size. A notable difference from tmd is the isolation of the Cr compounds of types II and IV with dtn. Failure to obtain II for tmd was attributed to interaction of the two $Cr(CO)_5$ groups due to a short Cr–N bond [7]. This explanation seems untenable in light of the dtn results. Since tmd and dtn have virtually electronic structures associated with the 4-membered ring [13,14], the electronic and steric properties of the "lone pair" orbitals for coordination should be identical. Also, molecular models do not indicate any notable differences in steric effects due to the rest of the tmd or dtn molecule in II and IV. Consequently, the lack of type II and IV Cr complexes for tmd is puzzling.

Compounds III–V of dtn are the first cases for which isomers have been observed. The analogous DBH complexes can give rise to the same types of isomers, but none were observed using only low field ^1H NMR [8]. The greater success of ^{13}C NMR in detecting the dtn isomers suggests the DBH complexes might be profitably reexamined with this probe.

Fe and Ru compounds

Thermal reactions of cyclic diazenes with $Fe_2(CO)_9$ have been proposed to proceed through the sequence of complexes [1,2]:

I → II → VI → VII → VIII

This sequence has been well-established for 5-membered rings. However, 3-membered rings do not produce VI or VII because the separation of the metal centers is too large to permit M–M bond formation. Instead II reacts further to give products in which N–N bond cleavage has occurred [15]. The 4-membered tmd ring appears to follow the same sequence as the 5-membered rings with I detected as an unstable initial product and VI and VII isolated as the final products; however, the last member VIII was not detected [6]. By contrast dtn gives unstable Ic as the initial product and VIIIc as the final product. No trace of VI or VII, usually the most stable Fe complex in the sequence, was found. Since tmd and dtn are electronically identical [13,14], we believe these product differences are due to the adverse steric effect of the larger hydrocarbon framework of dtn.

The absence of compounds of types VI and VII in the dtn/Fe system are most likely a consequence of steric effects. The crystal structure of the type VII complex of DBH shows that the N–N and Fe–Fe alignments are perpendicular to one another but with what was the N–N π bond aligned parallel to the Fe–Fe axis [16]. One of the CO groups on each Fe is oriented toward the diazene in the direction of the hydrocarbon portion of the diazene ligand. In the case of DBH the carbon framework is sufficiently distant that interaction with this CO group is not severe. In the case of tmd the CH_3 groups in such a structure would point upward and out from this CO group. However, in the case of dtn the C(9) carbon bridge must point downward and directly at one of these CO groups. This interaction apparently is great enough so that the complex is too unstable to be detected. Except for the addition of a bridging CO, the same considerations must apply to VI, although no crystal structures of type VI complexes have been reported. The low yield of VIIIc is likely due to the interruption of the normal mechanistic pathway through VI and VII. We note that 3-membered diazene rings also provide type VIII complexes only in low yield [15].

As noted before, in $Fe_3(CO)_9(DBH)$ the N–N bond is parallel to one of the Fe–Fe bonds of the triangular $Fe_3(CO)_9$ base [12]. If dtn is substituted for DBH, the C(9) group of dtn must point down toward this base. However, if the C(9) group is oriented away from the unique $Fe(CO)_3$ unit, it will point toward the middle of an Fe–Fe bond where steric effects will be lower. The large low-field shift of one of the C(9) hydrogen atoms is consistent with this structural prediction.

A comparable series of complexes to those of Fe has not been observed for Ru. But, the yield of the dtn type VIII compound is much lower than that of the DBH compound by the same synthetic method. This may reflect the different steric interactions of these two ligands with the $Ru_3(CO)_9$ framework.

Experimental

All reactions were carried out under a dry and oxygen-free atmosphere of nitrogen, using standard Schlenk techniques. Solvents were distilled under nitrogen; hexane from CaH_2, CH_2Cl_2 from P_4O_{10}, and tetrahydrofuran (THF) from sodium benzophenone ketyl. Usually chromatography was done on a 2 × 30-cm column of alumina or Florisil slurry-packed with petroleum ether. Photolyses were done at room temperature in a Pyrex vessel using a 450 watt Hanovia medium pressure mercury lamp and a solution volume of 100 ml.

Microanalyses were performed by Atlantic Microlab. Inc., Atlanta, Ga. Infrared spectra were recorded on Perkin–Elmer Model 621 or 580B spectrometers. Melting points were taken on a Kofler hot-stage microscope and are uncorrected. Proton and carbon NMR spectra were obtained on an IBM/Bruker NR200 instrument at 200 and 50 MHz, respectively. Because of low solubility and long accumulation times for obtaining ^{13}C spectra, T_1 measurements were not feasible. However, in cases where peak intensities were important for isomer assignment spectra were recorded again using a 20s delay between pulses. In all cases these spectra were identical to those obtained using the normal 2.5s pulse delay.

Dtn was synthesized by the general procedure outlined by Lemal [11]. However, the saponification of the ester was done with potassium t-butoxide [17] and the final diazene product was freed from its cuprous chloride complex as described by Adam [18] and purified by sublimation to a −78°C probe under static vacuum. The compounds $C_7H_8M(CO)_4$ (C_7H_8 = norbornadiene; M = Cr [19], W [20]. *fac*-$(CH_3CN)_3Cr(CO)_3$ [21], *fac*-$(CH_3CH_2CN)_3W(CO)_3$ [22], and $Fe_2(CO)_9$ [19] were prepared by published procedures. Commercial $M(CO)_6$ (M = Cr, W) was sublimed before use. Photolysis of $M(CO)_6$ in THF to give $M(CO)_5(THF)$ was continued until infrared spectroscopy showed the conversion to be complete. All other reagents were used as obtained from commercial sources.

$M(CO)_5(dtn)$ (M = Cr, W) (Ia, Ib)

To 0.41 mmol of $M(CO)_5(THF)$ in 100 ml of THF was added 0.41 mmol of dtn, and the solution stirred for 2 h at room temperature during which time the initially yellow solution turned orange. After removal of solvent the solid residue was chromatographed on a Florisil column. Elution with pure petroleum ether or up to 15% CH_2Cl_2 provided the yellow band of Ia, which normally was not fully separated from the earlier pink to red band of IIa. Following solvent removal, the Ia was sublimed at 40°C onto a −78°C probe. Yield: M = Cr (Ia), 54 mg (0.17 mmol, 46%); M = W (Ib), 111 mg (0.25 mmol, 62%).

$[M(CO)_5]_2(dtn)$ (M = Cr, W) (IIa, IIb)

To 1.03 mmol of $Cr(CO)_5(THF)$ in 100 ml of THF was added 0.42 mmol of dtn, and the solution was stirred for 3 h during which the color changed from yellow to red. After solvent removal the solid was crystallized from hexane at −78°C, washed twice with cold hexane, and dried under vacuum to give 118 mg (0.25 mmol, 55%) of red IIa. For the W analog 1.31 mmol of $W(CO)_5(THF)$ was stirred with 0.51 mmol of dtn for 1 h at ambient. Following solvent removal, the solid was chromatographed on a 2.5 × 50-cm alumina column. The major band of the magenta product eluted first with 15% CH_2Cl_2 in petroleum ether and was followed by smaller amounts of IIIb and IVb. Removal of solvent gave 145 mg (0.19 mmol, 37%) of pure IIb.

$M(CO)_4(dtn)_2$. M = Cr (IIIa). A mixture of 218 mg (0.85 mmol) of $Cr(CO)_4(C_7H_8)$ and 206 mg (1.69 mmol) of dtn in 50 ml of hexane was stirred for 24 h at room temperature. The solution was filtered, and the solid was washed

repeatedly with hexane until the filtrate was only lightly colored. The red-brown filtrate and washings were combined and cooled to −78 °C. After several hours the liquid was removed, the solid was washed twice with −78 °C hexane, and the solid was dried under vacuum. Finally, the solid was heated to 40 °C for 2 h, and the $Cr(CO)_6$ present sublimed to a −78 °C probe. The yield was 91 mg (0.22 mmol, 26%) of pure red-brown IIIa.

M = W (IIIb). A mixture of 196 mg (0.50 mmol) of $W(CO)_4(C_7H_8)$ and 121 mg (0.99 mmol) of dtn in 35 ml of benzene was stirred at room temperature for 7 h. After solvent removal the solid was chromatographed on Florisil to give three bands on elution with a CH_2Cl_2/petroleum ether mixture: (1) 1/4 mixture, yellow Ib, (2) 1/3 mixture, brown IIb, and (3) 2/3 mixture, red-brown IIIb. Solvent removal from band 3 and crystallization from hexane gave 100 mg (0.19 mmol, 38%) of pure IIIb.

$[M(CO)_4]_2(dtn)_2$ (M = Cr, W) (IVa, IVb). A mixture of $M(CO)_4(C_7H_8)$ and dtn was stirred at room temperature in hexane for 24 h. The solution was filtered, and the solid was washed with hexane until the filtrate was only lightly colored. The solid was dissolved in CH_2Cl_2 and filtered through Celite, and hexane was added to increase the volume several-fold. The solvent volume was reduced to about 30 ml, the liquid was removed by cannula, and the solid was washed with hexane and dried under vacuum. A mixture of 1.63 mmol of $Cr(CO)_4(C_7H_8)$ and 0.42 mmol of dtn gave 0.11 mmol (50%) of IVa, while 1.02 mmol of $W(CO)_4(C_7H_8)$ and 1.02 mmol of dtn gave 0.19 mmol (40%) of IVb.

$[M(CO)_3]_2L_3$ (M = Cr, W) (Va, Vb)

A mixture of dtn and *fac*-$(CH_3CN)_3Cr(CO)_3$ or *fac*-$(CH_3CH_2CN)_3W(CO)_3$ in a 3/2 ratio in 30 ml of hexane was refluxed for 15–20 h. After solvent removal the product was isolated as described for IV except that all operations were done at 0 °C. For M = Cr 0.55 mmol of dtn gave 58 mg (0.091 mmol, 49%) of Va and for M = W 0.42 mmol of dtn gave 22 mg (0.024 mmol, 16%) of Vb after two recrystallizations.

Reactions of $Fe_2(CO)_9$ with dtn

$Fe_2(CO)_9$ and dtn were added to hexane or THF at 0, 10 °C, or room temperature and stirred until the solid $Fe_2(CO)_9$ had all disappeared. The ratio of $Fe_2(CO)_9$ to dtn ranged from 2/1 to 6/1. After removal of solvent the remaining solid was chromatographed on Florisil, giving either a yellow band of Ic, a green band of VIIIc, or both on elution with CH_2Cl_2/petroleum ether mixtures. When both were present, the yellow band preceded the green band, which was eluted with a 25–35% CH_2Cl_2 solvent content. Purification of Ic by chromatography on Florisil at −10 °C or by recrystallization from hexane at temperatures never exceeding 0 °C failed to give an analytically pure product.

VIIIc was crystallized from hexane at −78 °C after filtration through Celite. Yields were low, ranging from none at 0 °C in THF or $\leq$ 10 °C in hexane to 8% in THF at room temperature.

Photolysis of $Fe(CO)_5$ with dtn

A mixture of 0.50 ml (3.64 mmol) of $Fe(CO)_5$ and 53 mg (0.43 mmol) of dtn was photolyzed for 1 h, producing a dark solution. Solvent removal and chromatography of the residual solid on Florisil gave a very small amount of a yellow band followed closely by an overlapping green band on elution with petroleum ether. A 10–30% CH_2Cl_2/petroleum ether mixture was used once the green band had begun to emerge. The solvent was removed, and the solid was recrystallized as described above, giving 42 mg (0.077 mmol, 18%) of dark green crystals of VIIIc.

Reaction of $Fe_3(CO)_{12}$ with dtn

A mixture of 208 mg (0.41 mmol) of $Fe_3(CO)_{12}$ and 50 mg (0.41 mmol) of dtn in 30 ml of hexane was refluxed for 6 h. Work up revealed no hexane or CH_2Cl_2 soluble materials.

$Ru_3(CO)_9(dtn)$ (VIIId)

A solution of 258 mg (0.41 mmol) of $Ru_3(CO)_{12}$ and 49 mg (0.41 mmol) of dtn in 30 ml of hexane was refluxed for 6 h. The cooled solution was chromatographed on a 2.5 × 40-cm Florisil column. After elution of a yellow band of unreacted $Ru_3(CO)_{12}$ with petroleum ether, the orange band of product was eluted with 20% CH_2Cl_2 in petroleum ether. Removal of solvent left an orange solid which was crystallized from hexane at −78 °C after filtration through Celite. Yield: 29.4 mg (0.043 mmol, 11%) of VIIId.

Acknowledgement

We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Oberlin College Research and Development Committee for partial financial support, and Oberlin College for a sabbatical leave during which some of this work was conducted. Purchase of the NMR spectrometer was made possible by grants from the Booth Ferris Foundation and the National Science Foundation Chemical Instrumentation Program (CHE-8508737).

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