

## TRIAZENIDO COMPLEXES $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{R}-\text{N}-\text{N}-\text{N}-\text{R}')$ WITH $\text{M} = \text{Mo}$ OR $\text{W}$ AND $\text{R} = \text{Aryl}$ OR $\text{Alkyl}$

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### Summary

The preparation, structure and some properties of compounds  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{R}-\text{N}-\text{N}-\text{N}-\text{R}')$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{R} = \text{aryl}$  and  $\text{R}' = \text{aryl}$  or  $\text{alkyl}$ ) are reported. Temperature dependent  $^{13}\text{C}$  NMR spectra show that for  $\text{R} \neq \text{R}' = \text{aryl}$  the complexes are fluxional, but not when one of the R groups is an alkyl group. The fluxional mechanism involves an interchange of the two CO groups via Berry type pseudorotations.

Mass spectrometric measurements show the formation of nitrene type species  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_n\text{M}=\text{NR}]^+$  with  $n = 0, 1, 2$ .

### Introduction

Our investigations into the chemistry of metal complexes containing pseudo-allylic and pseudo-allenic groups [1] has led us into the field of metal-triazenido complexes [2]. It is known that the triazenido group, which is formally analogous to both the allylic and the carboxylate groups, may act as a monodentate [3], a chelate [4], or as a bridging group [5], while we have recently shown [2] that the triazenido group can also use its bridging ability to stabilize  $\text{Rh}^{\text{I}}$  (or  $\text{Ir}^{\text{I}}$ )-to- $\text{Cu}^{\text{I}}$  (or  $\text{Ag}^{\text{I}}$ ) donor bonds (Fig. 1)\*.

We have now prepared complexes  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{R}-\text{N}-\text{N}-\text{N}-\text{R}')$  in which the azenido group acts as a chelate [6]. During the course of our investigations, King and Nainan [7] reported the preparation and a tentative structural assignment of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\text{C}_6\text{H}_5-\text{N}-\text{N}-\text{N}-\text{C}_6\text{H}_5)$ , which they prepared from the sodiumtriazenido salt.

We describe below the preparation of an extensive series of complexes of Mo and W, prepared by a different method, and also physical-chemical and chemical properties such as the fluxional behaviour and mass spectrometry.

\* In Fig. 1 the resonance structures have not been included.

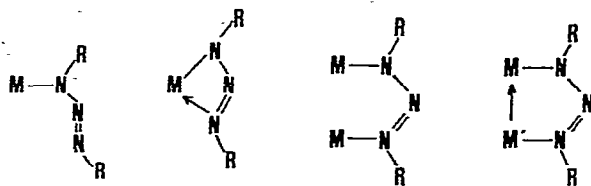


Fig. 1. Bonding modes for triazenido groups.

## Experimental

The symmetric and asymmetric triazenes [8], the silver triazenido salts [9] and the complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$  and  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{M}(\text{CO})_3\text{Cl}$  [10] ( $\text{M} = \text{Mo}, \text{W}$ ) were prepared by published methods.

All reactions were carried out under an inert atmosphere.

### Preparation of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\text{DpTT})$ (I, see Table 1)

A solution of 10 mmol  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$  and 10 mmol of the silver salt of di-*p*-tolyltriazene [ $\text{Ag}(\text{DpTT})$ ] in 50 ml toluene was stirred for 18 h at  $90^\circ\text{C}$  until the evolution of carbon monoxide ceased. After cooling and dilution with 75 ml hexane the solution was filtered through a 2 cm layer of  $\text{Al}_2\text{O}_3$ . The filtrate was evaporated under vacuum. The remaining solid was recrystallized from  $\text{CHCl}_3$ /hexane or  $\text{CH}_2\text{Cl}_2$ /pentane. The yield was about 50%.

The complexes II and III (see Table 1) were prepared similarly in yields of 50%.

### Preparation of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}(\text{DpTT})$ (IV)

The preparation was as described for compound I, but with a reaction temperature of  $110^\circ\text{C}$ . The complexes V and VI are prepared analogously in yields of 50%.

TABLE I

THE INVESTIGATED COMPOUNDS AND THEIR ANALYTICAL DATA

Compounds <sup>a, b</sup>	Analysis found (calcd.) (%)			Mol. wt. <sup>c</sup> found (calcd.)
	C	H	N	
I $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo-DpTT}$	57.29 (57.14)	4.45 (4.35)	9.48 (9.52)	445 (441.4)
II $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo-pTFT}$	46.71 (46.90)	2.65 (2.68)	7.16 (7.46)	
III $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo-DFT}$	40.29 (40.31)	2.01 (1.62)	6.12 (6.13)	
IV $(\text{C}_5\text{H}_5)(\text{CO})_2\text{W-DpTT}$	46.84 (47.65)	3.53 (3.63)	7.90 (7.94)	
V $(\text{C}_5\text{H}_5)(\text{CO})_2\text{W-pTFT}$	40.56 (40.55)	2.41 (2.30)	6.53 (6.45)	
VI $(\text{C}_5\text{H}_5)(\text{CO})_2\text{W-DFT}$	35.82 (35.72)	1.66 (1.44)	5.54 (5.44)	
VII $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo-iPr-Clt}$	46.52 (46.45)	3.78 (3.91)	10.15 (10.15)	
VIII $(\text{C}_5\text{H}_5)(\text{CO})_2\text{W-iPr-Clt}$	37.95 (38.30)	3.23 (3.22)	7.65 (8.37)	
IX $(\text{CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Mo-pTFT}$	48.00 (47.84)	2.97 (2.97)		
X $(\text{CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{W-pTFT}$	41.71 (41.52)	2.52 (2.58)		

<sup>a</sup> DpTT = *p*-tolyl-N-N-N-*p*-tolyl; pTFT = *p*-tolyl-N-N-N-3,5-( $\text{CF}_3$ ) $_2\text{C}_6\text{H}_3$ ; DFT = 3,5-( $\text{CF}_3$ ) $_2\text{C}_6\text{H}_3$ -N-N-N-3,5-( $\text{CF}_3$ ) $_2\text{C}_6\text{H}_3$ ; i-Pr-Clt = iso-propyl-N-N-N-4-ClC $_6\text{H}_4$ .

<sup>c</sup> Vapour-osmometric in  $\text{CHCl}_3$ .

<sup>b</sup> All compounds are red.

*Preparation of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\text{iPr-Clt})$  (VII)*

A solution of 5 mmol  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{MoCl}$  and 5 mmol  $[\text{Ag}(\text{iPr-Clt})]$  ( $\text{iPr-Clt} = \text{i-C}_3\text{H}_7\text{-N-N-N-4-ClC}_6\text{H}_4$ ) in 50 ml benzene was stirred for 4 h at  $80^\circ\text{C}$  until the evolution of CO ceased. After cooling and filtration through a layer (2 cm) of  $\text{Al}_2\text{O}_3$ , the complex was isolated as described above. The yield was about 40%. Compounds VIII, IX and X were prepared similarly with yields of 40%.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian HA 100 and a Varian CFT 20 spectrometer respectively. The IR spectra were measured with a Beckman 18A and 4250, while the mass spectra were recorded on a Varian Mat 711.

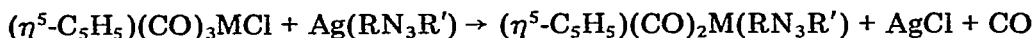
C and H analyses were carried out in this Laboratory. The N analysis in the Organic Chemistry Laboratory of TNO (Utrecht).

Compounds, analyses and colours are listed in Table 1.

## Results

### Structural characterization

The reaction of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{MCl}$  ( $\text{M} = \text{Mo}, \text{W}$ ) with the triazenido silver derivatives gave the red crystalline compounds  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{RN}_3\text{R}')$  according to:



A crystal structure determination [6] of III showed that the triazenido group is bonded as a chelate (Fig. 2). The molecule has a square pyramidal shape, with the cyclopentadienyl ring in the apex and the two CO groups in a *cis* position. The Mo atom and the three nitrogen atoms are coplanar while the N—N bond distances lie between single and double bond values, which is consistent with a  $\sigma, \sigma$ -attached delocalized chelate system, which is therefore analogous to chelating carboxylate groups and not to a  $\eta^3$ -allyl group.

The structure in the solid state persists in solution, as indicated by two carbonyl bands of about equal intensity in the infrared spectra. Furthermore  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show that the triazenido group is symmetrically bonded in the symmetrically substituted azenido metal compounds i.e. for compounds I, III, IV and VI (see Tables 2—4).

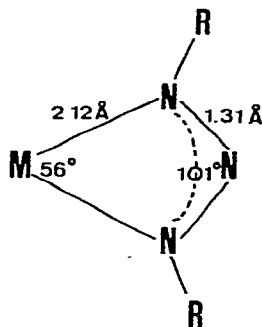


Fig. 2. Relevant part of the molecule III.

TABLE 2

IR SPECTROSCOPIC DATA (cm<sup>-1</sup>)<sup>a, b</sup>

	$\nu(\text{CO})$	$\nu(\text{triazenido})$
I	1963, 1879	1607, 1284
II	1981, 1892	1612, 1281
III	1983, 1903	1613, 1280
IV	1952, 1858	1609, 1285
V	1966, 1872	1615, 1280
VI	1969, 1886	1613, 1280
VII	1966, 1889	1589, not assigned
VIII	1955, 1867	1589, not assigned
IX	1974, 1884	1613, 1278
X	1953, 1882	1611, 1275

<sup>a</sup> Compounds I–VI, X in nujol, compounds VII–IX as KBr disc's. <sup>b</sup> No significant differences were observed in CH<sub>2</sub>Cl<sub>2</sub> solutions.

It should be noted that these chelating triazenido complexes, confirm with an empirical IR criterion [3,11] for distinguishing between monodentate, chelating and bridging ligands, in that they have IR bands at 1280–1300 and ~1600 cm<sup>-1</sup>.

#### Fluxional behaviour

In the case of the asymmetrically substituted triazenido complexes the <sup>13</sup>C NMR spectra showed only one <sup>13</sup>CO signal even at -80°C for the aryl substituted groups i.e. compounds II, V, IX and X, but two <sup>13</sup>CO signals for the complexes VII and VIII, which have one alkyl substituent. As accidental degeneracy for four complexes can be safely excluded in view of the fairly large chemical shift differences normally found in <sup>13</sup>C NMR \*, we have to assume fluxional behaviour for the complexes II, V, IX and X, as the process is intramolecular (see Discussion). A similar fluxional behaviour might also occur for the symmetrically substituted compounds, but this can not be detected by NMR.

TABLE 3

<sup>1</sup>H NMR SPECTROSCOPIC DATA (in ppm relative to TMS)<sup>a</sup>

	$\delta(\text{C}_5\text{H}_5)$	$\delta(\text{R}_1)$	$\delta(\text{R}_2)$
I	5.68	7.05, 2.30	
II	5.74	7.14, 2.34	7.52
III	5.79	7.61, 7.64	
IV	5.81	7.07, 2.31	
V	5.87	7.16, 2.36	7.55
VI	5.92	7.66	
VII	5.56	1.20d, 1.16d, 3.84m	7.05m, 6.72m
VIII	5.71	1.18d, 1.11d, 3.77m	7.13m, 6.81m
IX	5.64m <sup>b</sup> , 5.32m <sup>b</sup> , 1.86	7.11, 2.34	7.49
X	5.76m <sup>b</sup> , 5.49m <sup>b</sup> , 1.92	7.12, 2.34	7.50

<sup>a</sup> All spectra were run in CDCl<sub>3</sub>, d = doublet, m = multiplet. <sup>b</sup> Complicated multiplets, with different line-width in 100 MHz, resp. 60 MHz spectra.

\* For example, compare the <sup>13</sup>C(CO) chemical shifts of I with II and those of IV with VI (Table 4).

TABLE 4  
 $^{13}\text{C}$  NMR SPECTROSCOPIC DATA (in ppm relative to TMS)<sup>a</sup>

	$\delta(\text{CO})$	$\delta(\text{C}_5\text{H}_5)$	$\delta(\text{aryl})^c$	$\delta(\text{substituents})$
I	237.7	95.3	R <sub>1</sub> : 147.2, 115.2, 129.1, 133.5	20.8
II	239.9	95.3	R <sub>1</sub> : 146.5, 116.0, 129.3, 135.5	20.8
			R <sub>2</sub> : 150.3, 114.4, 132.0, 116.3	not assigned
III	242.1	95.5	R <sub>2</sub> : 149.7, 115.6, 132.5, 118.0	123.1
IV	245.7	93.7	R <sub>1</sub> : 146.7, 115.4, 129.0, 133.8	20.7
V	242.8	93.9	R <sub>1</sub> : 146.1, 115.3, 129.3, 135.8	20.9
			R <sub>2</sub> : 149.9, 114.8, 132.0, 115.3	123.2
VI	240.3	93.8	R <sub>2</sub> : 149.3, 115.5, 132.4, 118.2	123.0
VII	257.0	94.7	R <sub>3</sub> : 148.3, 115.0, 128.3, 126.9	
	254.1		R <sub>4</sub> : 59.8, 23.0, 22.6	
VIII	248.2	93.3	R <sub>3</sub> : 147.8, 115.3, 128.4, 127.5	
	245.5		R <sub>4</sub> : 60.1, 23.4, 22.8	
IX <sup>b</sup>	255.5	96.2, 89.6 <sup>e</sup>	R <sub>1</sub> : not assigned	20.2, not assigned
		95.5, 88.7	R <sub>2</sub> : not assigned	12.0 <sup>d</sup>
X	243.6	96.0, 88.8 <sup>e</sup>	R <sub>1</sub> : 145.6, 116.4, 129.3, 135.8	20.8, not assigned
		95.0, 87.9	R <sub>2</sub> : 149.4, 114.9, 132.1, 116.3	13.6 <sup>d</sup>

<sup>a</sup> All spectra were in  $\text{CDCl}_3$  unless otherwise noted. <sup>b</sup> In toluene- $d_8$ . <sup>c</sup> The order is: azenido-C, *ortho*-C, *meta*-C, *para*-C; R<sub>1</sub> = *p*-tolyl; R<sub>2</sub> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> ( $J(\text{F}-\text{CF}_3) \simeq 273$  Hz,  $J(\text{F}-\text{C}_{3,5}) \simeq 33$  Hz,  $J(\text{F}-\text{C}_4) \simeq J(\text{F}-\text{C}_{2,6}) \simeq 3$  Hz); R<sub>3</sub> = 4-ClC<sub>6</sub>H<sub>4</sub>; R<sub>4</sub> = *iso*-propyl). <sup>d</sup> Methyl-C resonance of the methylcyclopentadienyl ring. <sup>e</sup> Methylcyclopentadienyl ring carbons; CH<sub>3</sub>-C is not observed.

### Chemical properties

Solutions of all the compounds decompose slowly in presence of air, but the solids seem air-stable, when kept in the cold.

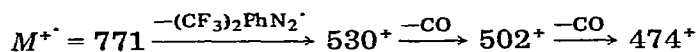
The chemical properties of compounds I–VI have been studied more extensively: oxidation with I<sub>2</sub> in most cases gives intractable products. In one case (V), a precipitate, obtained in quantitative yield, had two carbonyl bands shifted to higher frequency, but unfortunately it was too insoluble for a satisfactory characterization.

The compounds are not attacked by phosphines in boiling toluene, or by hydrochloric or acetic acid in ether at room temperature. Lewis acids (AlCl<sub>3</sub> and BF<sub>3</sub> · etherate) cause complete decomposition with gas evolution, and a dark mass is obtained, which has no carbonyl IR frequencies or cyclopentadienyl NMR resonances.

In an inert atmosphere the solids and their solutions in naphthalene are stable up to 200°C.

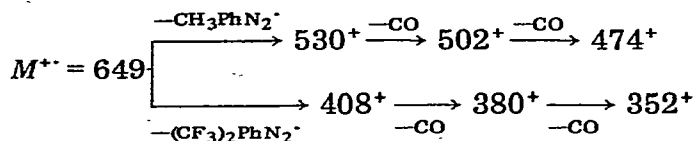
### Mass spectrometric data

From the mass spectra it is deduced, that all compounds are monomeric, since the molecular ions appear at the proper values. The spectra are not fully interpreted, but sets of three fragments occur with a very high intensity. This suggests the following main reaction path, as demonstrated for ( $\eta^5\text{-C}_5\text{H}_5$ )(CO)<sub>2</sub>-W(DFT) (VI):



The other symmetrical compounds show similar patterns with the proper values.

When the compound is asymmetrical, two sets are observed, for example:  
 $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}(\text{pTFT})$  (V):



## Discussion

The triazenido complexes are part of the series of compounds *cis*-( $\eta^5\text{-C}_5\text{H}_5$ )- $\text{M}(\text{CO})_2(\text{L-L})$  in which L-L is  $\pi$ -allyl ( $\eta^3\text{-C}_3\text{H}_5$ ) [12], 2-azaallyl ( $\text{>C-N-C<}$ ) [13], amidino ( $\text{-N-C-N-}$ ) [14], or triazenido ( $\text{-N-N-N-}$ ).

The resemblance between the triazenido and the amidino compounds is especially noteworthy, since in each case the bidentate group is linked to the metal via a  $\sigma, \sigma$ -bonding mode and not via a  $\pi$ -allyl mode. The carbonyl stretching frequencies are shifted to characteristically low values, while the trends in the stretching frequencies are as expected when the aryl substituents in the triazenido group are changed. However, there are no correlations between  $\nu(\text{CO})$  and the  $^{13}\text{C}$  NMR carbonyl-C resonance such as are found for many Group VI  $\text{M}(\text{CO})_5\text{L}$  [15] series.

The mechanism of the fluxional behaviour of several of the reported compounds is of interest. Some of these (VII-X) were prepared to elucidate the mechanism.

Several mechanisms are possible in principle: (A) an intermolecular exchange of CO; (B) an intermolecular exchange of the azenido ligand; (C) a reversible conversion of the two ends of the azenido group via a monodentate intermediate (Fig. 3), which is the opposite of that proposed by Robinson and Uttley [16] for some triazenido complexes of Pt. (D) An inverted Berry type of pseudorota-

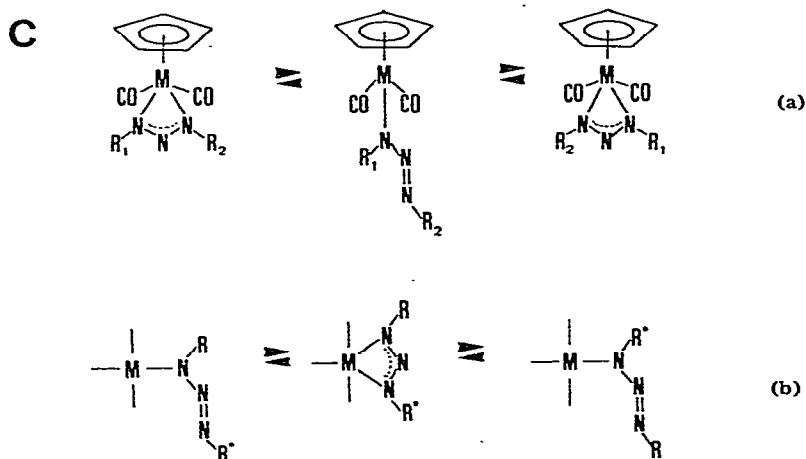


Fig. 3. (a). Possible exchange mechanism for Mo, W compounds. (b). Proposed [16] exchange mechanism for Pt compounds.

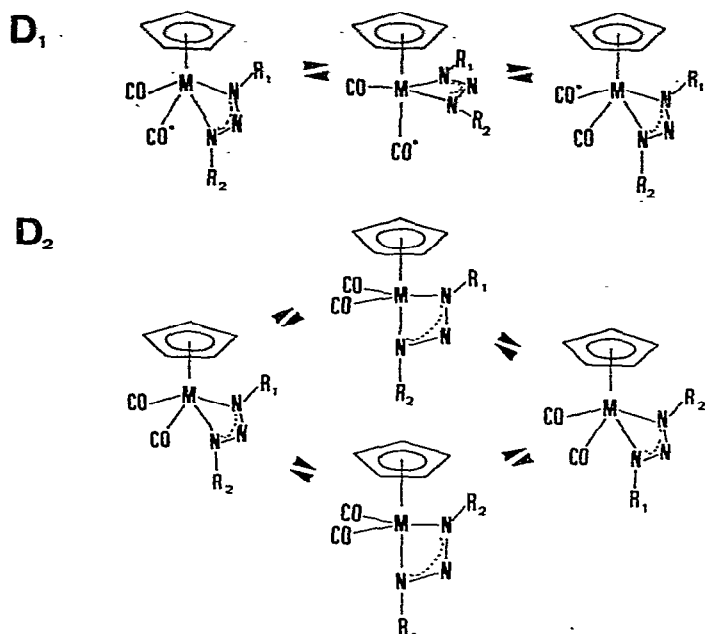


Fig. 4. Pseudo-rotational exchange routes.

tion which involves an interconversion of a square pyramidal type of molecule via a trigonal bipyramidal intermediate.

One may imagine a route  $D_1$  in which the carbonyl groups interchange their positions while the azenido group remains rigid relative to the cyclopentadienyl group. In the other route  $D_2$  the substituents on the azenido group interchange their position relative to the cyclopentadienyl group (Fig. 4).

Although satellites due to the  $^{183}W$  isotope are not observed, intermolecular CO exchange is excluded as mixtures of IV, V and VI, and of V and X gave separate CO signals without any detectable broadening. This also excludes intermolecular exchange of triazenido groups via, for example, a binuclear intermediate with bridging azenido groups. Also free triazene does not show the exchange with the coordinated ligand which has been observed for other compounds [2].

The results on the methylcyclopentadienyl compounds made it possible to

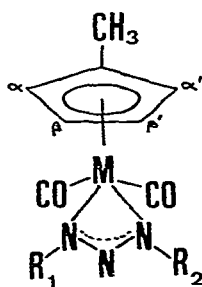
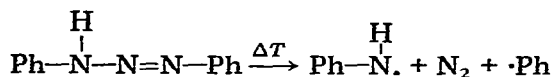


Fig. 5.

distinguish between mechanisms *C*, *D*<sub>1</sub> and *D*<sub>2</sub>. In the complexes IX and X (Fig. 5) the <sup>13</sup>C NMR spectra showed that, while the <sup>13</sup>CO signals have completely collapsed, the <sup>13</sup>C signals of the α and α' C atoms are separate and sharp, as are also the β and β' signals. This shows conclusively that the triazenido group remains rigid relative to the methylcyclopentadienyl group, while the CO groups interchange their positions. This excludes mechanisms *C* and *D*<sub>2</sub> and supports mechanism *D*<sub>1</sub>. These results are in contrast with those for (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>M(X)(PR<sub>3</sub>) complexes \* [17], and steric factors may well account for this.

Since the N—metal—N valency angle is small (56° for III), the CO groups are less hindered with internal rotation. However electronic factors will undoubtedly be important too, and could be the reason, that alkyl-substituted triazenido complexes VII and VIII, do not show the fluxional behaviour.

Finally it is of interest that the azenido group is more stable when complexed to a metal than to a proton, as the free triazenes are readily decomposed to radicals [18]:



In respect with this it is interesting that in the mass spectrometer metal—nitrene fragments occur in large abundance. Although the mass spectra are rather complicated, the fragments [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>*n*</sub>M=N-φ]<sup>+</sup> (*n* = 0, 1, 2) have been demonstrated beyond doubt. Attempts to form metal—nitrene species by reactions of azenido complexes have not yet been successful.

### Acknowledgements

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\* These compounds are not strictly comparable, since the fluxional process here involves *cis*—*trans* isomerization. Nevertheless the proposed intermediates are similar and have both carbonyl groups at equatorial positions.